

Summary Chapter 2: Wave diffraction and the reciprocal lattice.

In chapter 2 we discussed crystal diffraction and introduced the reciprocal lattice. Since crystals have a translation symmetry as discussed in chapter 1, crystals act like three dimensional gratings that will diffract waves whose wavelength are smaller than twice the lattice constant. Different types of waves are used for diffraction experiments, i.e. X-ray photons, electrons, and neutrons. X-ray photons and electrons diffract of the periodic charge density of crystals, while neutrons interact with the spins of the atoms. Note that one cannot use visible light for diffraction experiment to learn more of the various plane spacings in the crystal as visible light has a wavelength that is much larger than the lattice spacings. Visible light however can be used to measure film thicknesses in thin film and multilayers provided that their wavelength is smaller than twice the thickness to be measured. This latter effect is not addressed in chapter 2 of Kittel but is used in the optical characterization equipment of the department, i.e. the ellipsometers and the nanospec.

We discussed the diffraction of waves by a crystal structure by first considering the diffraction of the top atom layer. This top atom layer will strongly reflect the incident wave if the angle of incidence is equal to the angle of reflection. Note that that first plane does not completely reflect the wave and will only reflect maybe 10^{-3} to 10^{-5} of the incident wave, the rest is transmitted into the material and partly reflected by deeper planes. Only for the directions for which all those reflected waves are in phase with each other a diffracted intensity is to be expected. This direction can be calculated from the following diffraction condition:

$$2d \sin(\theta) = n\lambda \quad [1]$$

Where n is an integer, θ is the angle of incidence, and d is the spacing between the atom planes parallel to the surface of the sample. So by measuring the angles for which for example X-rays with a certain wavelength λ strongly reflect of a sample, one can determine the lattice spacings. Notice that the position of the diffraction peaks only depends on the lattice spacings and not on the basis of the crystal. Also note that strained samples that have a slightly different lattice spacing will show a slightly shifted diffraction pattern where the position of all peaks is slightly shifted. The intensity of the diffraction peaks depends on various factors including the crystal size and the basis, i.e. the atoms and their position within the unit cell.

Kittel shows two different X-ray patterns, i.e. the 2θ scan of single crystal (Fig. 3 on page 26) and the 2θ scan of a powder sample (Fig. 4 on page 26). Note that the latter contains peaks of all kind of planes that all have different normal vectors. The 2θ scan of the single crystal only contains peaks of planes that are normal to a specific crystal direction.

X-ray photons and electrons mainly scatter from the electron number density function, $n(\mathbf{r})$. The electron number density is a scalar field with a periodicity equal to the lattice, i.e.

$$n(\vec{r} + \vec{T}) = n(\vec{r}) \quad [2]$$

Where \mathbf{T} is a linear combination of an integral multiple of the lattice translation vectors introduced in chapter 1, i.e.

$$\vec{T} = u_1 \vec{a}_1 + u_2 \vec{a}_2 + u_3 \vec{a}_3 \quad \text{with } u_1, u_2, \text{ and } u_3, \text{ integers.} \quad [3]$$

Since $n(\mathbf{r})$ is periodic in all three directions, $n(\mathbf{r})$ can be described by a Fourier series. The amplitudes of its Fourier components is often referred to as its spectra. Rather than writing $n(\mathbf{r})$ as a sum of cosines and sines, we write $n(\mathbf{r})$ as a sum of complex exponential functions, i.e.

$$n(\vec{r}) = \sum_{\vec{G}} n_{\vec{G}} e^{i\vec{G} \cdot \vec{r}} \quad [4]$$

Note that because $n(\mathbf{r})$ is a real function that $n_{\vec{G}}$ should be equal to $n_{-\vec{G}}^*$. In your homework you proved this for a 1D lattice. The Fourier coefficients form themselves a periodic function that is often referred to as the spectrum in engineering or the reciprocal lattice in solid state physics. The magnitude of $n_{\vec{G}}$ can be considered to be the strength of the spatial frequency component \mathbf{G} in the electron number density function. So if the x-dependence of $n(\mathbf{r})$ consists of sinusoidal function with a periodicity equal to the lattice parameter in the x-direction one expect $n_{\vec{G}}$ to have a large magnitude for $(2\pi/a, 0, 0)$ and $(-2\pi/a, 0, 0)$ but zero for lattice points farther away from the origin in the reciprocal space. If $n(\mathbf{r})$ is an array of delta functions one expects all spatial frequency components to be present and $n_{\vec{G}}$ to be non-zero for reciprocal lattice points farther away from the origin. Notice that Kittel not really discusses the magnitude of the $n_{\vec{G}}$ components, but emphasizes their position in reciprocal space. The $n_{\vec{G}}$ s can be calculated from:

$$n_{\vec{G}} = \frac{1}{V_{c \text{ cell}}} \int n(\vec{r}) e^{-i\vec{G} \cdot \vec{r}} dV \quad [5]$$

The reciprocal lattice points are defined by the reciprocal space translation vectors, \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 :

$$\vec{G} = v_1 \vec{b}_1 + v_2 \vec{b}_2 + v_3 \vec{b}_3 \quad \text{with } v_1, v_2, \text{ and } v_3 \text{ integers.} \quad [6]$$

\mathbf{b}_1 defines the periodicity of the lattice perpendicular to the \mathbf{a}_2 and \mathbf{a}_3 lattice translation vectors, \mathbf{b}_2 defines the periodicity of the lattice perpendicular to the \mathbf{a}_1 and \mathbf{a}_3 lattice translation vectors, and \mathbf{b}_3 defines the periodicity of the lattice perpendicular to the \mathbf{a}_1 and \mathbf{a}_2 . lattice translation vectors

If we calculate \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 can be calculated from \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 via:

$$\begin{aligned} \vec{b}_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} \\ \vec{b}_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_2 \cdot \vec{a}_3 \times \vec{a}_1} \\ \vec{b}_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_3 \cdot \vec{a}_1 \times \vec{a}_2} \end{aligned} \quad [7]$$

The corresponding electron number density given by expression [4] will have the correct periodicity given by equation [2].

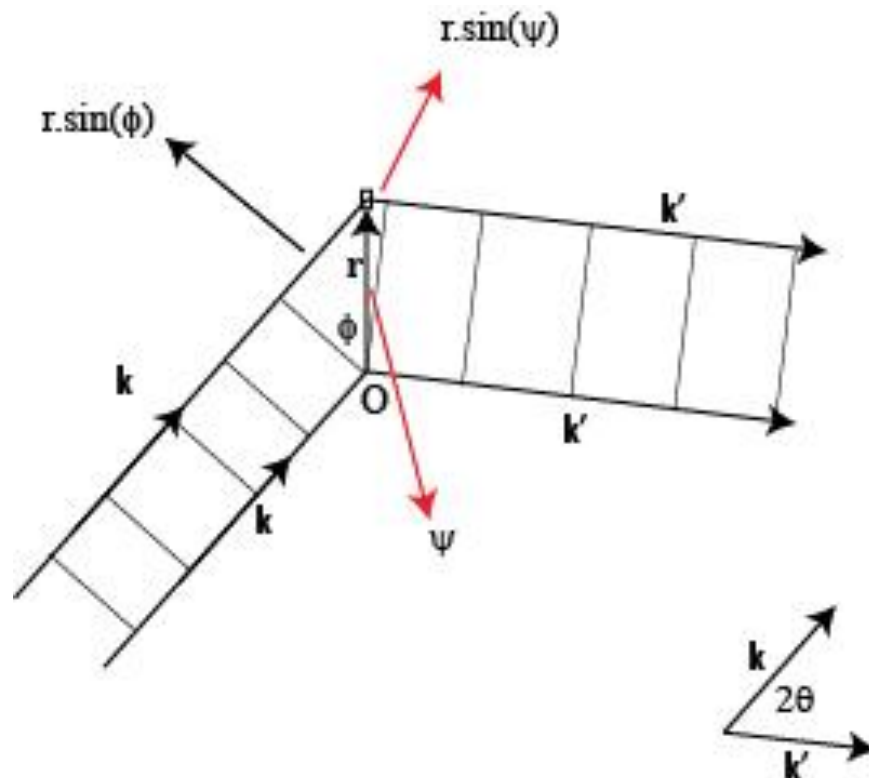
Note that \mathbf{b}_1 is perpendicular to \mathbf{a}_2 and \mathbf{a}_3 , etc, so:

$$\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij} \quad [8]$$

Kittel concludes with the fact that a crystal structure has two lattices associated with it, the crystal lattice and the reciprocal lattice. The crystal lattice tells us the translation symmetry of the atoms in real space, and the reciprocal lattice tells us the diffraction pattern of the crystal.

The explanation of the diffraction condition in Kittel is abstract, but I would like everybody to understand the physics of it.

I redrew Fig. 6 on page 30 below. The little cube is the volume segment of the crystal that we consider. It is a fraction of the unit cell. I have an incident plane wave indicated by \mathbf{k} , and a diffracted plane wave indicated by \mathbf{k}' . Both are wave vectors. Their directions indicate the direction of the incident and diffracted wave. Their magnitude is $2\pi/\lambda$. Since we only consider elastic scattering, both the \mathbf{k} and \mathbf{k}' vector have the same length. I redrew the \mathbf{k} and \mathbf{k}' vector on the lower right. The angle between them is of course the 2θ from the x-ray graphs of Fig. 17. So somewhere near the tail of the \mathbf{k} -vector is the X-ray source and somewhere near the head of the \mathbf{k}' vector is the X-ray detector. The location of the little cube is \mathbf{r} .



The incident and diffracted beam are plain waves. It is clear that the incident wave at the origin has another phase than the incident wave at the cube. For the cube the traveled length is longer, i.e. the wave needs to travel a longer length which will result in the incident plane wave having a different phase at the cube than at the origin:

$$r \sin(\phi) \rightarrow 2\pi \frac{r \sin(\phi)}{\lambda} \quad [9]$$

Note that $2\pi/\lambda$ is equal to the magnitude of \mathbf{k} and note that is equal to the magnitude of \mathbf{k}' . Furthermore note that the dot product of \mathbf{k} and \mathbf{r} is equal to:

$$\vec{k} \bullet \vec{r} = |\vec{k}| |\vec{r}| \cos(90 - \phi) = \frac{2\pi}{\lambda} r \sin(\phi) \quad [10]$$

Note that this is exactly equal to the phase difference given in equation (1) above. Similarly the diffracted waves from the origin and cube are out of phase as the diffracted wave from the cube has to travel a longer distance:

$$r \sin(\psi) \rightarrow 2\pi \frac{r \sin(\psi)}{\lambda} \quad [11]$$

The dot product of \mathbf{r} and \mathbf{k}' is given by:

$$\vec{k}' \bullet \vec{r} = |\vec{k}'| |\vec{r}| \cos(90 + \psi) = -|\vec{k}'| |\vec{r}| \cos(90 - \psi) = -\frac{2\pi}{\lambda} r \sin(\psi) \quad [12]$$

So equal to the phase difference between a wave coming from the cube and a wave coming from the origin. So the total phase difference for a ray diffracted from the origin and a ray diffracted from the cube is equal to:

$$\vec{k} \bullet \vec{r} - \vec{k}' \bullet \vec{r} \quad [13]$$

To find the scattering amplitude we will assume that the scattering is linear proportional to the local charge density $n(\mathbf{r})$. So summing up the contributions of all cubes gives:

$$F = \int dV n(\vec{r}) e^{i(\vec{k} \bullet \vec{r} - \vec{k}' \bullet \vec{r})} \quad [14]$$

Now substitute in the Fourier series we developed for $n(\mathbf{r})$:

$$F = \sum_{\vec{G}} \int dV n_{\vec{G}} e^{i(\vec{G} + \vec{k} - \vec{k}') \bullet \vec{r}} \quad [15]$$

Note that because of the phase factor which is different for each dV , normally the scattering amplitude will be zero. So only if the phase factor is constant, we expect a strong scattering amplitude. Note that each dV has its own \mathbf{r} , so the only constant phase factor occurs if $\mathbf{G} + \mathbf{k} - \mathbf{k}' = 0$ or if $\mathbf{G} + \mathbf{k} = \mathbf{k}'$. So notice that

only when $\mathbf{k}-\mathbf{k}'$ is equal to a reciprocal lattice vector we expect strong constructive interference of the scattered x-ray and thus a diffracted beam. So the diffraction pattern tells us the reciprocal lattice. Of course once we know the reciprocal lattice we can determine the normal crystal structure. Taking the magnitude square on both sides and using the fact that the magnitude of \mathbf{k} and \mathbf{k}' are the same we find the diffraction condition:

$$\Delta\vec{k} = \vec{G} \Leftrightarrow 2\vec{k} \bullet \vec{G} + G^2 = 0 \Leftrightarrow 2\vec{k} \bullet \vec{G} = G^2 \quad [16]$$

It might not be very clear but this last expression is equivalent to the diffraction condition given by equation [1].

$$2 \frac{2\pi}{\lambda} |\vec{G}| \sin(\theta) = |\vec{G}|^2 \quad \therefore 2 \frac{2\pi}{\lambda} \sin(\theta) = \frac{2\pi}{d(hkl)} \quad \therefore 2d(hkl)\sin(\theta) = \lambda \quad [17]$$

The first diffraction condition of equation [16] shows that the diffraction condition is fulfilled if the scattering vector, i.e. $\mathbf{k}-\mathbf{k}'$ is equal to a reciprocal lattice vector \mathbf{G} . This leads to the geometrical interpretation of Fig. 8 where the direction of \mathbf{k} is drawn on top of the reciprocal lattice so it ends on a reciprocal lattice point. Now a circle is drawn with the center at the tail of \mathbf{k} and the circle itself through the head of \mathbf{k} . For reciprocal lattice points on the circle the diffraction condition is fulfilled and the diffraction angle θ can be read from the figure.

Dividing the right equation of [16] by four on both sides gives another interpretation of the diffraction conditions:

$$\vec{k} \bullet \left(\frac{1}{2} \vec{G} \right) = \left(\frac{1}{2} G \right)^2 \quad [18]$$

So for any wave whose wave-vector ends on the perpendicular bisectors of the reciprocal lattice vectors will diffract constructively in the $\mathbf{k}-\mathbf{G}$ direction. Note that these wave-vectors are located at the planes that define the Wigner-Seitz primitive cell discussed in chapter 1.

Kittel discusses the reciprocal lattice vectors of the sc, the bcc, and the fcc crystal structures. The reciprocal lattice to the sc crystal structure is sc and has a lattice constant of $2\pi/a$. The reciprocal lattice of the bcc lattice is an fcc lattice and the reciprocal lattice of an fcc lattice is a bcc lattice.

Not included yet: structure factor and atomic form factor.