Lecture 12

Determination of crystal structure by X-ray diffraction

The typical interatomic distances in a solid are on the order of an angstrom ($\sim 10^{-10}$ m). Then, an em wave that will be used as a probe to view the microscopic structure of a solid must ~~be~~ have a wavelength at least this short, which will correspond to an energy of the order –

$$\frac{hc}{\lambda} = \frac{hc}{10^{-10}} \approx 12.3 \times 10^{3}\ eV$$

Energies like this (and wavelength) are characteristic of X-rays. In this section we will describe how the diffraction of X-ray scattered by a rigid, periodic array of atoms/ions reveals the location of the atoms/ions within that structure. There are two equivalent ways to ~~se~~ view the scattering of X-ray by a perfectly periodic structure – by Bragg and by von Laue. We will describe both of them and finally discuss about an equivalance between these two.

Bragg formulation of X-ray diffraction by a crystal

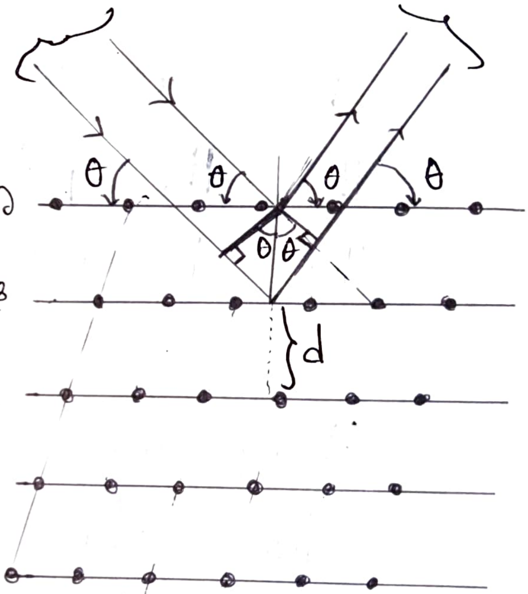
Bragg diffraction was first proposed by Lawrence Bragg and his father William Henry Bragg in 1913, after their discovery that crystalline solids produced surprising patterns of reflected X-rays in contrast to those produced by liquids. They found that, these crystals, at specific wavelengths and incident angles produced intense peaks of reflected radiation. These peaks are now known as Bragg peaks. Lawrence Bragg and his father W.H. Bragg were awarded the ~~Noble~~ Nobel prize in Physics in 1915 for their work in determining the crystal structure. They are the only father-son duo to jointly win the Nobel prize.

W.L. Bragg accounted for the intense peaks by regarding a crystal lattice made out of parallel planes of ions/atoms spaced a distance d apart. This is what we described in the last lecture. The condition for sharp peak in intensity of the scattered radiation were–

(i) The X-rays should be specularly reflected from

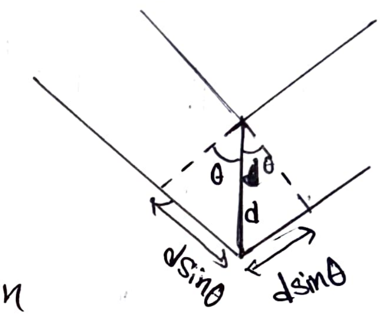
~~from a~~ by the ions/atoms in any one plane. By specular reflection we mean that the angle of incidence is equal to the angle of reflection. It is as if the planes of atoms/ions are ~~acting~~ acting as partially reflective mirror planes.

(ii). The reflected rays from successive planes should interfere constructively.



Consider the figure here, that shows specularly reflected rays from ~~the~~ a particular family of planes in a crystal lattice separed by a distance d. The angle of incidence and reflection both are θ. Note that, in X-ray crystallography, the angle of incidence is conventionally measured from the plane of reflection rather than the normal to the plane of reflection, as in classical optics. Also note that, the angle of incidence θ is just half the angle of deflection of the beam (2θ).

Now, the two reflected waves from consecutive planes will arrive at a point infinitely far from the lattice planes and will constructively interfere given that the path difference between these two rays are integer multiple of wavelengths, say λ.



Now, the geometry suggests that the path difference between these two rays should be $= d\sin\theta + d\sin\theta$

$$= 2d\sin\theta$$

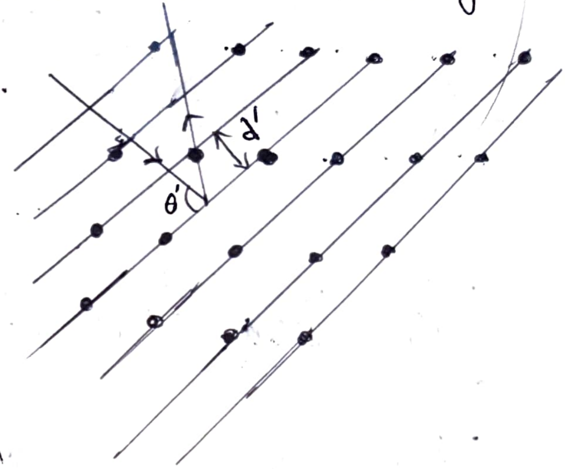
Hence, we arrive at the celebrated Bragg condition for the intense peaks given by,

$$\boxed{2d\sin\theta = n\lambda}$$

The integer n is known as the order of the corresponding reflection.

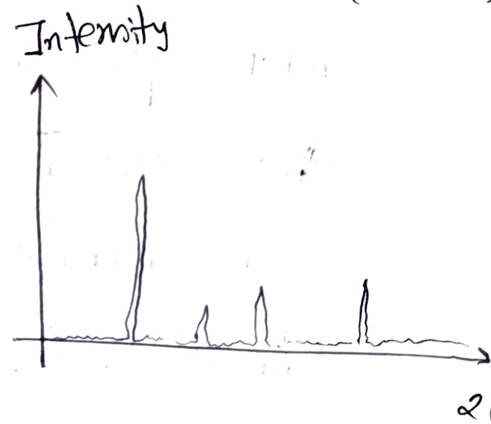
Note that, there are many different ways of sectioning the crystal into planes, each of which will itself produce further reflections.

For example, the same crystal shown in the last page could be described as consisting of a different family of planes.



The incident ray is the same one as in the first example. However, both the direction ~~and~~ of the reflected ray and the wavelength is different here. The wavelength which will now produce the intense peak for this plane will be found from the Bragg condition $2d' \sin\theta' = n\lambda'$.

In X-ray crystallography people uses X-ray sources and detectors to look for ~~f~~ peaks in the intensity of the scattered light from the family of planes in a crystal and plots the intensity as a function of 2θ (convention).



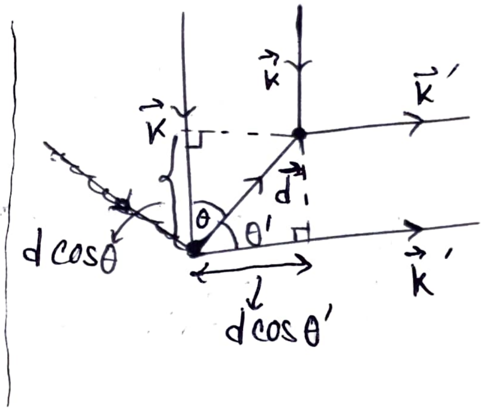
A typical X-ray diffraction plot is shown here. Then, finding the location of the peaks they calculate the interplanar spacing d. Along with some other information, this gives insights about the structure of the crystal. The different peaks corresponds to various ~~maxima~~ constructive interferences coming from various family of planes.

Von-Laue formulation of X-ray diffraction by a crystal

There is an equivalent, but more intuitive approach to study the X-ray diffraction by a crystal. Bragg diffraction was very simple (although works) and had some preassumptions (like specular reflection). The Von-Laue approach differs from the Bragg approach in that, no particular sectioning of the ~~pla~~ crystal into lattice planes is singled out, and no ad-hoc assumption of specular reflection is imposed. Instead, one considers the crystal as made of identical microscopic objects (sets of ions or atoms) placed at the site $\vec{R}$ of a Bravais lattice, each of which can radiate the incident radiation in all the directions. Sharp peaks will be observed only in directions and at wavelengths for which the rays scattered from all lattice points interfere constructively.

To find the condition for constructive interference, consider first just two scatterers, separated by a displacement vector $\vec{d}$. Let an X-ray be incident from very far away, along in a direction $\hat{n}$, with the wavelength λ and wave-vector $\vec{k} = \frac{2\pi}{\lambda}\hat{n}$. A scattered ray will be observed in the direction $\hat{n}'$ with wavelength λ and wave-vector $\vec{k}' = \frac{2\pi}{\lambda}\hat{n}'$. (we are considering that the incident and scattered rays have same λ, meaning their energies are same. So no energy is lost in the scattering process and so the scattering is elastic. Although to a good approximation the bulk of the scattered radiation is elastic, the small component of inelastic scattering also provides some insights, which is a different topic). But the ray will be observed in the $\hat{n}$ direction only if the scattered rays interfere constructively, that is, the path difference between them is integer multiple of wavelength λ.

From the figure, path difference is just $= d\cos\theta + d\cos\theta'$



$$= \vec{d}\cdot(-\hat{k}) + \vec{d}\cdot\hat{k}'$$

$$= \vec{d}\cdot(-\hat{n}) + \vec{d}\cdot\hat{n}' = \vec{d}\cdot(\hat{n}-\hat{n}')$$

So, the condition for constructive interference is then,

$$\vec{d}\cdot(\hat{n}-\hat{n}') = m\lambda \quad \text{with } m\in\mathbb{Z}$$

Multiplying both sides with $\frac{2\pi}{\lambda}$ yields a condition on the incident and scattered wave-vectors:

$$\vec{d}\cdot(\vec{k}-\vec{k}') = 2\pi m \quad \text{—— ①}$$

Now, we consider not just two scatterers, but an array of scatterers which are at the site of the Bravais lattice. Since the lattice sites are displaced from one another by the lattice vectors $\vec{R}$, the condition that all lattice vectors interfere constructively is that, the condition ① hold simultaneously for all values of $\vec{d}$ that are Bravais lattice vectors.

$$\therefore \vec{R}\cdot(\vec{k}-\vec{k}') = 2\pi m \;; \quad \text{for } m\in\mathbb{Z} \text{ and for all Bravais lattice vectors } \vec{R}.$$

We can also write the condition as –

$$e^{+i(\vec{k}'-\vec{k})\cdot\vec{R}} = 1 \quad \text{for all Bravais lattice vectors } \vec{R}$$

Now, if you compare the condition with the definition of a reciprocal lattice given by $\{e^{i\vec{G}\cdot\vec{R}} = 1$, where $\vec{G}$ is the reciprocal lattice vector, then we see that the Laue condition of constructive interference is that, the change in the wave-vector, $\Delta\vec{k} = \vec{k}' - \vec{k}$, is a vector of the reciprocal lattice.

$$\boxed{\therefore \Delta\vec{K} = \vec{G}}$$

It is sometimes convenient to have an alternative formulation of Laue condition, stated entirely in terms of the incident wave-vector $\vec{k}$. First note that, since reciprocal lattice is a Bravais lattice, if $\vec{k}'-\vec{k}$ is a Bravais lattice vector, so is $\vec{k}-\vec{k}'$. Defining the latter vector as $\vec{G}$, that is, $\vec{G} = \vec{k}-\vec{k}'$, the condition that $\vec{k}$ and $\vec{k}'$ has the same magnitude is given by-

magnitude of $\vec{k}$ and $\vec{k}'$

$$\vec{k}' = \vec{k} - \vec{G} \Rightarrow k = |\vec{k} - \vec{G}|$$

Squaring both sides yields the condition -

$$k^2 = (\vec{k}-\vec{G})\cdot(\vec{k}-\vec{G}) \qquad \Big| \quad A^2 = \vec{A}\cdot\vec{A}$$

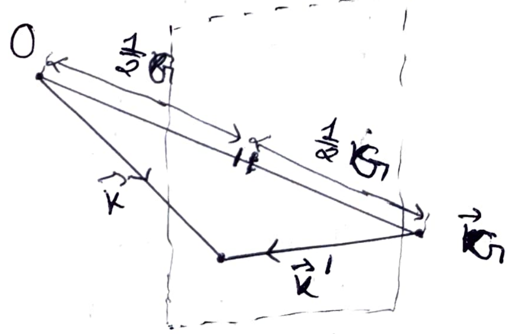
$$\Rightarrow k^2 = \vec{k}\cdot\vec{k} - \vec{G}\cdot\vec{k} - \vec{k}\cdot\vec{G} + \vec{G}\cdot\vec{G}$$

$$\Rightarrow k^2 = k^2 - 2\vec{G}\cdot\vec{k} + G^2 \quad \Rightarrow \quad 2\vec{G}\cdot\vec{k} = G^2$$

$$\boxed{\therefore \vec{k}\cdot\hat{G} = \frac{1}{2}G}$$

So, the component of the incident wave-vector $\vec{k}$ in the direction of reciprocal lattice vector $\vec{G}$ must be half of the magnitude of $\vec{G}$.

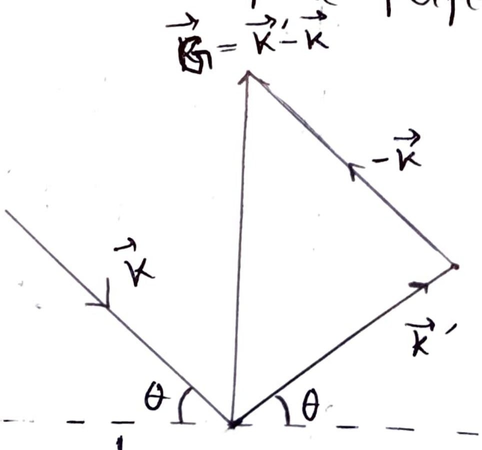
Thus, an incident wave-vector $\vec{k}$ will satisfy the Laue condition if and only if the tip of the vector lies in a plane, that is the perpendicular bisector of a line joining the origin of ~~k-sp~~ G-space to a reciprocal lattice point $\vec{G}$. This is so,



because the sum of $\vec{k}$ and $-\vec{k}'$ is $\vec{G}$, and for $\vec{k}$ and $\vec{k}'$ having the same magnitude, the tip of $\vec{k}$ has to be equidistant from both the origin and the $\vec{G}$. So, it must lie in a plane bisectiong the line joining the origin to $\vec{G}$. Such planes are known as Bragg planes.

Equivalance of Bragg and Von-Laue formulations

Say, the incident and scattered wave vectors $\vec{k}$ and $\vec{k}'$ satisfies the Laue condition, that is $\vec{G} = \vec{k}' - \vec{k}$ is a reciprocal lattice vector. Since $\vec{k}'$ and $\vec{k}$ has the same magnitudes, it follows that $\vec{k}'$ and $\vec{k}$ makes the same angle θ with the plane perpendicular to $\vec{G}$. This is evident from the figure here. The plane of the paper contains the incident and reflected wave-vector $\vec{k}$ and $\vec{k}'$ and their difference $\vec{G}$. Since $\vec{k}$ and $\vec{k}'$ has the same magnitude, $\vec{G}$ basically bisects the angle between $\vec{k}$ and $\vec{k}'$. Therefore, the scattering can be viewed as a Bragg reflection, with Bragg angle θ,



~~Plane of the page~~

Intersection of the plane perpendicular to $\vec{G}$ with the page from the family of direct lattice planes perpendicular to the reciprocal lattice vector $\vec{G}$ (recall the theorem we proved in the last lecture). The angle θ is between the incident ray ~~and~~ with the perpendicular plane to $\vec{G}$ and also between the reflected/scattered ray with the perpendicular plane to $\vec{G}$.

To show that this reflection satisfies Bragg condition, note that the vector $\vec{G}$ is an integer multiple of the shortest reciprocal lattice vector ~~par~~ $\vec{G}_0$ parallel to $\vec{G}$ (again, from the theorem and the fact that reciprocal lattice is a Bravais lattice). According to the theorem, the magnitude of $\vec{G}_0$ is just $\frac{2\pi}{d}$, where d is the distance between successive planes in the family of planes perpendicular to $\vec{G}_0$ or $\vec{G}$.

$$\therefore\ G = \frac{2\pi n}{d}$$

On the other hand, from the figure in the last page,

$$G = 2k\sin\theta$$

$$\therefore\ 2k\sin\theta = \frac{2\pi n}{d}$$

$$\therefore\ k\sin\theta = \frac{n\pi}{d}$$

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

and angle between $\vec{k}'$ and $\vec{k}$ is $(90^\circ - 2\theta)$. You can then find that $G = 2k\sin\theta$.

Now, since $K = \frac{2\pi}{\lambda}$, the condition is again,

$$\boxed{2d \sin\theta = n\lambda}$$

Thus, a Laue diffraction peak corresponding to a change in wave-vector given by the reciprocal lattice vector $\vec{G}$ corresponds to a Bragg reflection from the family of direct lattice planes perpendicular to $\vec{G}$. The order, n, of the Bragg reflection is just the length of $\vec{G}$ divided by the length of the shortest reciprocal lattice vector parallel to $\vec{G}$.

Since reciprocal lattice associated with a given Bravais lattice is far more easily visualized than the set of all possible planes into which the Bravais lattice can be resolved, the Laue condition for diffraction peaks is far more simple to work with than Bragg condition. We will proceed further using the Laue condition.