Characterization of Construction Materials
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Lecture 16
X Ray diffraction Diffractogram

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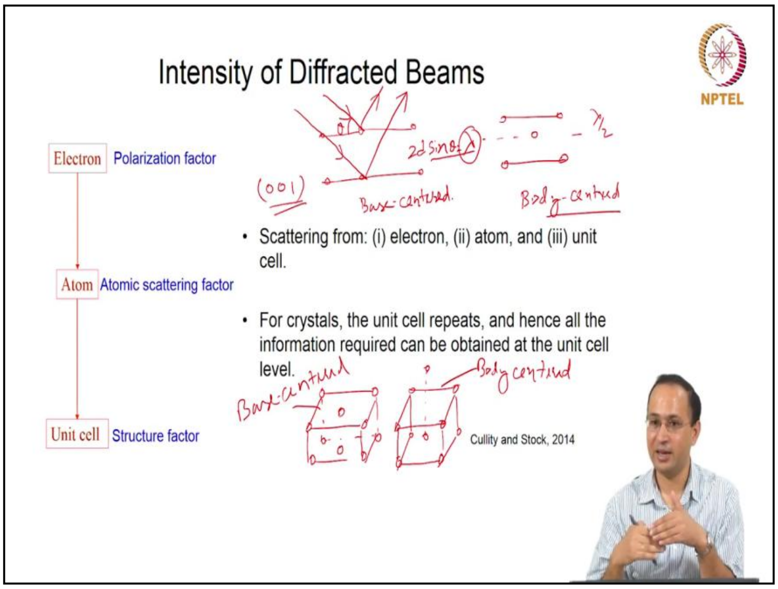

Intensity of Diffracted Beams

- Scattering from: (i) electron, (ii) atom, and (iii) unit cell.
- For crystals, the unit cell repeats, and hence all the information required can be obtained at the unit cell level.

Cullity and Stock, 2014

Hello everyone, today we will continue our discussion on x-ray diffraction. So, let us recap what we have learned so far. So, we know how x-rays are produced. And we know that x-rays are used to study crystals and we studied about various crystal systems in the last lecture. So, also we saw how x-rays interact with crystals; in the sense that, for diffraction, Bragg's law is to be satisfied. When the Bragg's condition is satisfied then you get diffraction.

So we saw what that condition is. You have to have $2d\sin\theta = n\lambda$. So, that is the condition for diffraction. So, we know how x-rays interact with atoms in unit cell. So, the next question is, we know now that when the Bragg's condition is satisfied you get diffraction. The second question comes what are the things that are dependent on the arrangement of atoms in the unit cell.

We are now talking about intensity of diffracted beams. Intensity of diffracted beam will depend on the atomic arrangement in unit cell. It will not be same for all. So, just to appreciate that point let us take one example (Figure 1).

So one is the case of body-centered unit cell and one is base-centered (orthorhombic unit cells). We are talking about, let us say, (001) plane.

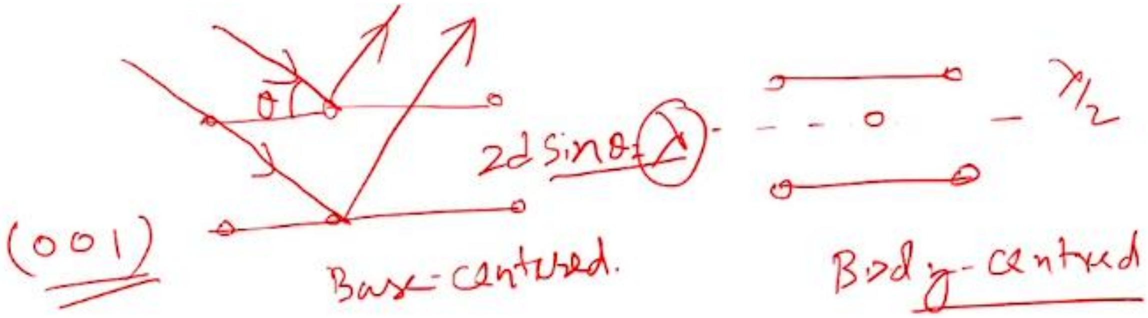

Figure 1 Base-centred (Left) and Body-centred (Right)

So, if you have diffraction for this base-centered orthorhombic unit cell. So, you will get the condition $2d\sin\theta = \lambda$ (Refer θ in Figure 1). Another representation of base-centered and body centered unit cells is given in Figure 2 for better understanding.

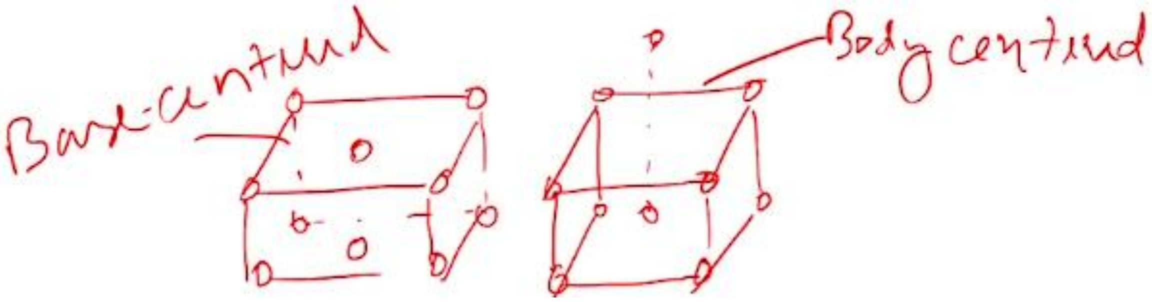

Figure 2 Base--centered and body-centered orthorhombic unit cells

So, same thing we are considering here in Figure 1, now we are considering the diffraction. Suppose you have Bragg's condition satisfied for this base-centered, where the arrangement is like this we are taking the 2 layers (in Figure 1). Now you know that there is a difference of λ. Now for body-centered the difference has to be $\left(\frac{\lambda}{2}\right)$, but then the waves will be out of phase.

We know that when it is a whole number integer multiple of lambda, then only Bragg's condition is satisfied. So, the point is, suppose we are talking about is (001) plane, (001) reflection will be absent in body-centered, just because you have an atom, there is another layer between these two. So, (001) is present in base-centered, (001) reflection is absent in body-centered. So, the idea is just the way atoms are arranged in unit cell affects the diffraction.

So, that is why we are going to talk about the intensity of diffracted beams. What are the factors which influence intensity of deflected beams? So, now we are talking about the interaction between X-rays and unit cell. So, before we go to unit cell, we know that, X-rays will interact with electrons; we have to consider X-rays interaction with atoms. And finally overall picture will be X-rays interaction with unit cell because we are talking about the crystals where you have unit cells arranged in periodic manner.

So, obviously when we consider the interaction of X-ray with electron, we need to consider the polarization factor. We are not going in detail; you can refer to this book just to get more information, Cullity and Stock (2014), in the interest of time. Similarly, when the X rays interact with atom, the intensity is influenced by atomic scattering vector small (f).

And now you have atoms arranged in this unit cell, so this is also a unit cell where you have atoms arranged. We are talking about the interaction of x-rays with unit cell, and that is influenced by ‘structure factor’ and that is what we will focus on here, because that gives you overall picture. So, for crystals the unit cell repeats and hence all information required can be obtained at the unit cell level, if you know this interaction we can then calculate the intensity.

But now you are convinced that it is the atomic arrangement within unit cell that affects the intensity. So suppose you have a (001) reflection for one unit cell, it will not hold for another atomic arrangement.

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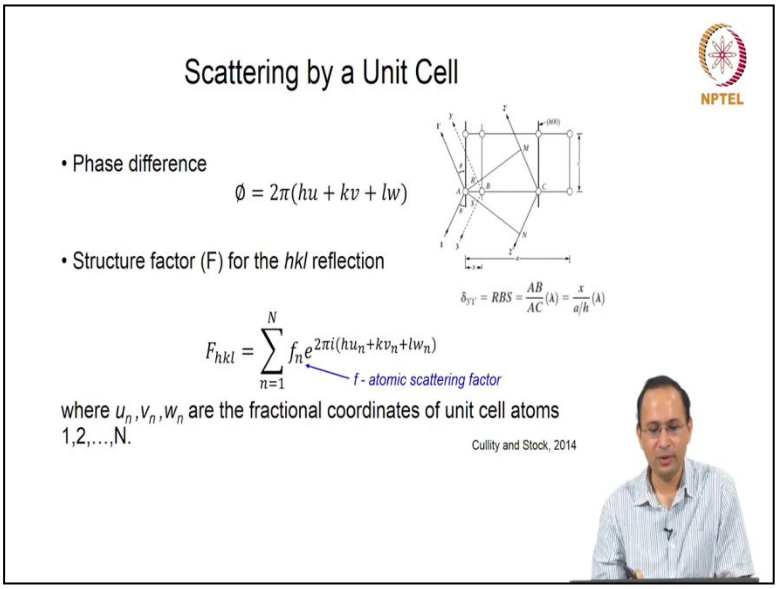

Scattering by a Unit Cell

- Phase difference

$$\emptyset = 2\pi(hu + kv + lw)$$

- Structure factor (F) for the *hkl* reflection

$$F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

f - atomic scattering factor

where u_n, v_n, w_n are the fractional coordinates of unit cell atoms 1,2,…,N.

$$\delta_{3'1'} = RBS = \frac{AB}{AC}(\lambda) = \frac{x}{a/h}(\lambda)$$

Cullity and Stock, 2014

So, how do we study this? Little bit of background - scattering by a unit cell; that is what we will look in this lecture. So, in the interest of time I am not going in detail how to derive this expression (Refer equations in slide), again you can go through any standard textbook, you can also refer to Cullity and Stock. Basically what you see here is, we are talking about a unit cell, these are nothing but atoms arranged in unit cell.

And we are looking at the interaction of this unit cell with X-rays. X-rays you see here (in Figure in slide), these are incident X-rays and then diffracted beams. We are interested in what are the things which influence the intensity. So, the phase difference, ϕ can be expressed as:

$$\emptyset = 2\pi(hu + kv + lw)$$

Now h k l are the planes that you are considering. So, whenever we talk about the diffraction, the first thing that comes to mind is the planes. We now know that, based on the planes you will get different θ values.

So, suppose you are considering a type of plane, obviously it will be denoted as h k l, as studied in Miller indices. And u v w are the fractional coordinates of unit cell atoms. Suppose you have a unit cell now, it will have atoms, so what are the fractional coordinates? Suppose you consider in this case, atoms located at B, so the fractional coordinate will be x/a, that is

$$u = \frac{x}{a}$$

So A is your unit cell parameter and fractional coordinate will be its location, so x is AB, $x/a = u$. Similarly if there are 'n' atoms you can write it for all 'n', in the x, y and z directions. We would not go in detail, but just making you understand what this means. So, first we have to consider the phase difference, because that will influence your intensity. We know that phase difference is the key.

Phase difference obviously depends on the path difference. How did you get the phase difference? First you have to calculate the path difference and from path difference you get the phase difference, because that will tell you about the interaction between 2 rays. So, without going too much in detail, we can now say that the interaction between X-rays and unit cell depends on the structure factor and that can be written in this form.

$$F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}$$

So, you see that it depends on number of atoms, so if you have n number of atoms you have to add it. And what is important, you see ‘f’ comes into picture. ‘f’ is nothing but atomic scattering factor, this is the interaction between X-rays and one atom. Obviously unit cell has lot of atoms, and so this factor comes into picture.

And you need to know atomic scattering factor and also you need to know the planes, obviously when you are talking about the diffraction you have to know the plane. So, you already know that – hkl; and you also know where the atoms are located, i.e., you know the fractional coordinates. So, you know everything and in this way we can calculate the structure factor.

We will do a small exercise so that you know how to calculate this structure factor.

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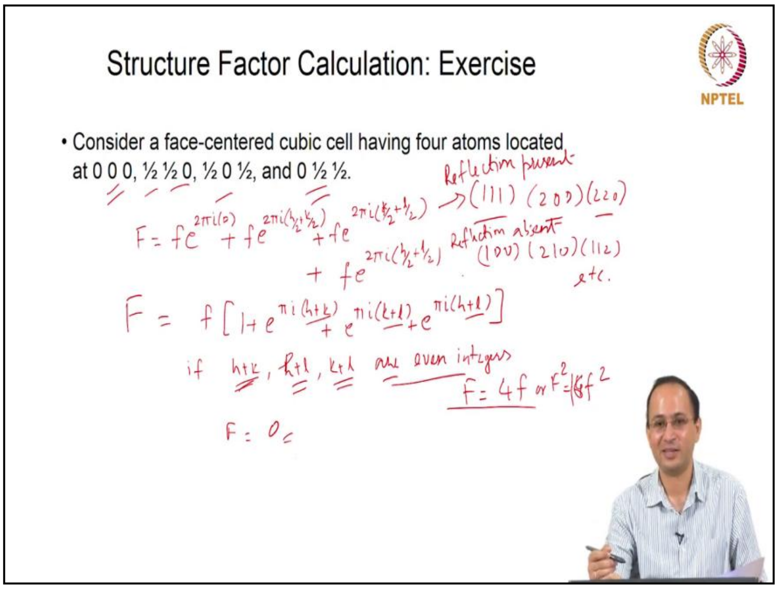

Structure Factor Calculation: Exercise

- Consider a face-centered cubic cell having four atoms located at 0 0 0, ½ ½ 0, ½ 0 ½, and 0 ½ ½.

$F = fe^{2\pi i(0)} + fe^{2\pi i(h/2+k/2)} + fe^{2\pi i(k/2+l/2)} + fe^{2\pi i(h/2+l/2)}$

Reflection present $\rightarrow$ (111) (200) (220)

Reflection absent (100) (210) (112) etc.

$F = f[1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)}]$

if $h+k$, $h+l$, $k+l$ are even integers $F = 4f$ or $F^2 = 16f^2$

$F = 0$

Now just so that you get some hands-on experience in this calculation, let us consider the calculation of structure factor of a face-centered cubic cell, all of you know what it looks like. So, you have atoms in the corners and also in each face (Figure 3)

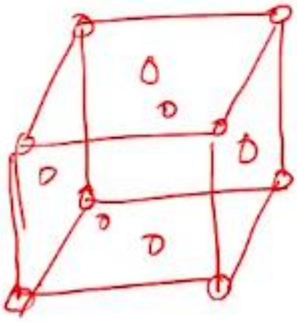

Figure 3 Face-centered cubic cell

Now so we are considering a face-centered cubic cell having 4 atoms, located at 0 0 0 (origin) $\frac{1}{2}\,\frac{1}{2}\,0$, $\frac{1}{2}\;0\;\frac{1}{2}$ and $0\;\frac{1}{2}\,\frac{1}{2}$, so you are considering the faces. So, this unit cell has how many atoms? Face-centered cubic cell has 4 atoms $\left(8 * \frac{1}{8} + \; 6 * \frac{1}{2}\right)$. So, this is the description. So, now you know the location of the atoms.

So we have now a condition where you can relate this structure factor as

$$F = fe^{2\pi i\,(0)} + fe^{2\pi i\,(\frac{h}{2}+\frac{k}{2})} + fe^{2\pi i\,(\frac{k}{2}+\frac{l}{2})} + fe^{2\pi i\,(\frac{h}{2}+\frac{l}{2})}$$

Which is then simplified to

$$F = f\left(1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(h+l)}\right)$$

(h + k), (h +l), (k+l) are even integers, what has happened to structure factor?

$$F = 4f \text{ (or) } F^2 = 16f^2$$

That means if you are considering 2 of the indices are odd and 1 even, or 2 even and 1 odd. So, you will get f = 0 in that case because (1 - 1 + 1 – 1), you can try that combination. So, basically what is it telling again? It is telling you the reflection may occur for such planes, such as (1 1 1) plane (2 0 0), and (2 2 0), you will get reflections, it will be diffraction, because you are meeting this condition (h + k) (h + l) (k + l) are even integers, i.e., for these planes you are meeting the first condition. You will have reflection present for these planes, because it meets the condition.

Now the reflection absent planes – (1 0 0), (2 1 0), (1 1 2), etc., we are not considering all the planes, that is the point. For these planes (1 0 0), (2 1 0), (1 1 2), you do not satisfy the first condition, you satisfy the second one, where you have 2 of the indices are odd and 1 even or 2 even 1 odd, so you have 0. So, this exercise tells you that, there would not be any reflection from these planes. So, just based on the arrangement of atoms in unit cell you can tell whether you will get diffraction or not. You may have to do more exercise, but this just gives you a flavour as to how to do this simple calculation.

But at least now you are convinced that it is the atomic arrangement within unit cell that influences your intensity. Even if the unit cell is of the same size but the atomic arrangement is different, that will affect your diffraction pattern. You may not see some planes which you would see in former case.

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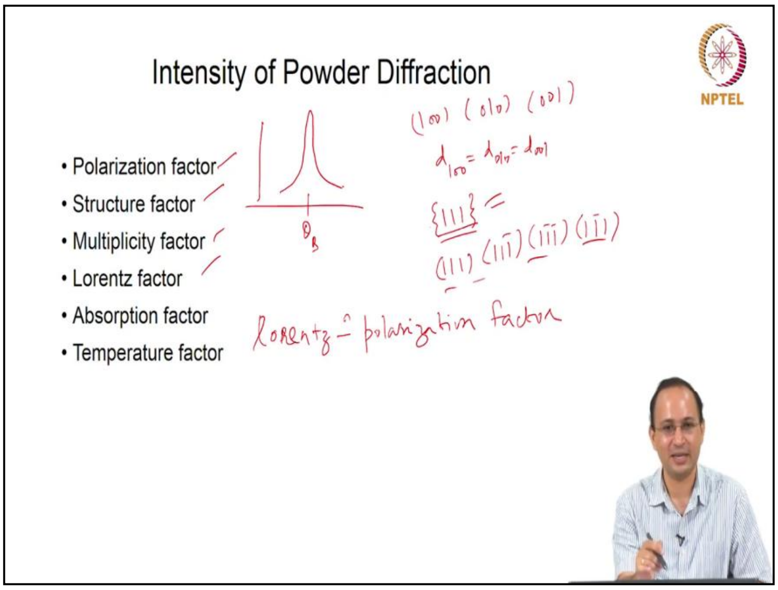

Intensity of Powder Diffraction

- Polarization factor
- Structure factor
- Multiplicity factor
- Lorentz factor
- Absorption factor
- Temperature factor

(100) (010) (001)

$d_{100} = d_{010} = d_{001}$

$\{111\} =$

$(111)\ (11\bar{1})\ (1\bar{1}\bar{1})\ (1\bar{1}1)$

Lorentz – polarization factor

So, so far we have considered structure factor, because that tells you the interaction between the X-rays and unit cell. There are other things which also influence the intensity. So, polarization factor, we have already talked about it a little. Polarization factor comes from the interaction between X-rays and electron. Structure factor is the interaction between X-rays and the unit cell.

Multiplicity factor, it is another thing to talk about. What is multiplicity factor? We would not go in detail, just want you to appreciate these terms, and why we are using these terms. You can refer to a textbook, any reference book on X-ray diffraction to know more. But so far you know what polarization factor is, it is just about the interaction between X-rays and electron and structure factor comes from the interaction between X-rays and unit cell.

It is easy to now visualize, consider (1 0 0) reflection from a cubic lattice. So, in the powder specimen, what will happen is, some of the crystals will be so oriented that (1 0 0) diffraction occurs. Suppose you have crystals oriented in (1 0 0) direction, you will have that diffraction. So, other crystals of different orientation may be in such position that (0 1 0) or (0 0 1) diffraction can occur.

$d_{100} = d_{010} = d_{001}$, the spacing is same, either you consider (1 0 0), (0 1 0), (0 0 1), if you draw these planes you see that spacing'd' is basically same. So, when we use this {111} that means it is the family of; so that will tell you $(1\ 1\ 1), (1\ 1\ \bar{1}), (1\ \bar{1}\ \bar{1})$ (this bar is for negative). If you refer to Miller indices chapter in any textbook, you will get more details.

We did not go in detail, but basically it tells you that there are like 4 sets. Simply because there are more planes, what happens is the probability that this family {1 1 1} will be correctly oriented for diffraction is $\frac{4}{3}$ times the probability of {1 0 0} since you have only 3 planes, and in the other you have 4 planes. So, now we can appreciate, if you consider different planes you can get this multiplicity factor. That is where this multiplicity factor comes in, because we are talking about the relative intensities. So it will depend on the plane, how it is oriented, what its hkl is. So, we would not go in detail but that is where it comes into picture.

There is another factor called the Lorentz factor. Usually what happens is the Lorentz factor is combined with polarization factor. Again where does this come from Lorentz factor? You have diffraction, so, θ_B, the Bragg's condition - you meet this and you get diffraction.

But even if your θ is slightly off from this θ_B, the diffraction will be there, it would not be 0. Suppose you are talking about the neighborhood of the θ_B, you know that at θ_B you have diffraction, but for a small $\pm\delta_\theta$, you'd get the diffraction. So, this is basically the origin of this. How do you consider that? So, it depends on θ (we will come to the expression later).

Now, absorption factor - so you are diffracting X-rays, but part of it will also get absorbed, so you need to consider that absorption. So, that is where this absorption factor comes in. And another factor is temperature factor, because depending on your temperature your unit cell dimensions may change. If you are doing experiments at suppose, 30 °C, 40 °C, so that will also affect the intensity of diffraction.

So far, a crystal has been considered as a collection of atoms located at fixed points. We are considering they are fixed, but that is not the real picture. Actually what happens is the atoms undergo thermal vibration about their mean position, even at absolute zero temperature, there is this thermal vibration. And the amplitude of this vibration increases as the temperature increases.

So, that is where this factor comes in, it is important to consider the temperature. just so that you can appreciate, in aluminium at room temperature the average displacement of an atom from its mean position is about 0.17 Å, that happens just at room temperature for aluminium. So, 0.17 Å which is by no means negligible when we are talking about an order of spacing of 1Å, 0.17 Å is not insignificant, that is the point. So, you have to consider it. So we will not go in detail but just so that you appreciate where these factors come into picture.

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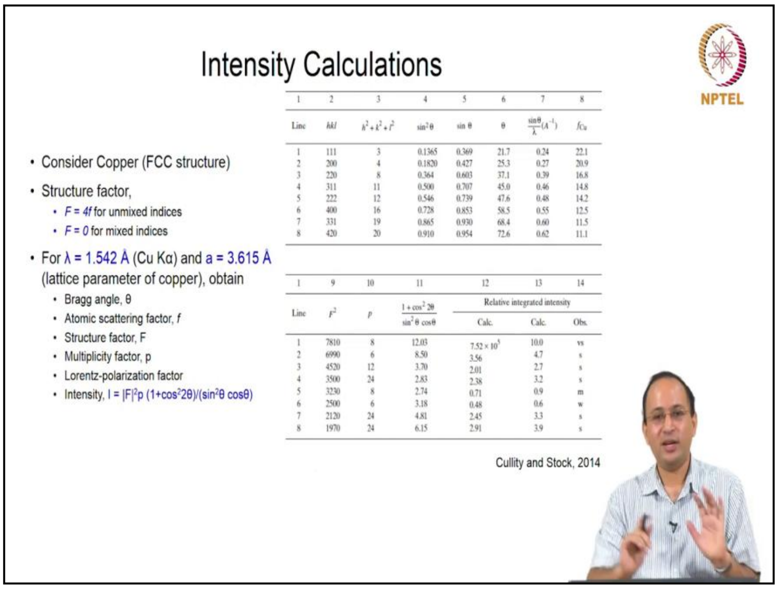

Intensity Calculations

- Consider Copper (FCC structure)
- Structure factor,
  - *F = 4f* for unmixed indices
  - *F = 0* for mixed indices
- For $\lambda = 1.542$ Å (Cu Kα) and $a = 3.615$ Å (lattice parameter of copper), obtain
  - Bragg angle, θ
  - Atomic scattering factor, *f*
  - Structure factor, F
  - Multiplicity factor, p
  - Lorentz-polarization factor
  - Intensity, $I = |F|^2 p\,(1+\cos^2 2\theta)/(\sin^2\theta \cos\theta)$

1	2	3	4	5	6	7	8
Line	*hkl*	$h^2+k^2+l^2$	$\sin^2\theta$	$\sin\theta$	θ	$\frac{\sin\theta}{\lambda}(Å^{-1})$	f_{Cu}
1	111	3	0.1365	0.369	21.7	0.24	22.1
2	200	4	0.1820	0.427	25.3	0.27	20.9
3	220	8	0.364	0.603	37.1	0.39	16.8
4	311	11	0.500	0.707	45.0	0.46	14.8
5	222	12	0.546	0.739	47.6	0.48	14.2
6	400	16	0.728	0.853	58.5	0.55	12.5
7	331	19	0.865	0.930	68.4	0.60	11.5
8	420	20	0.910	0.954	72.6	0.62	11.1

1	9	10	11	12	13	14
Line	F^2	*p*	$\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$	Relative integrated intensity		
				Calc.	Calc.	Obs.
1	7810	8	12.03	7.52×10^5	10.0	vs
2	6990	6	8.50	3.56	4.7	s
3	4520	12	3.70	2.01	2.7	s
4	3500	24	2.83	2.38	3.2	s
5	3230	8	2.74	0.71	0.9	m
6	2500	6	3.18	0.48	0.6	w
7	2120	24	4.81	2.45	3.3	s
8	1970	24	6.15	2.91	3.9	s

Cullity and Stock, 2014

Now the next question comes. We know which are the planes which will give you diffraction, and the planes in which it will be absent. Now the question is how we calculate the intensities. So, you know the location of θ, from Bragg’s condition you know where you will get the peak. Now the question that whether this peak will be more intense than the other one, that is the question we are trying to answer now.