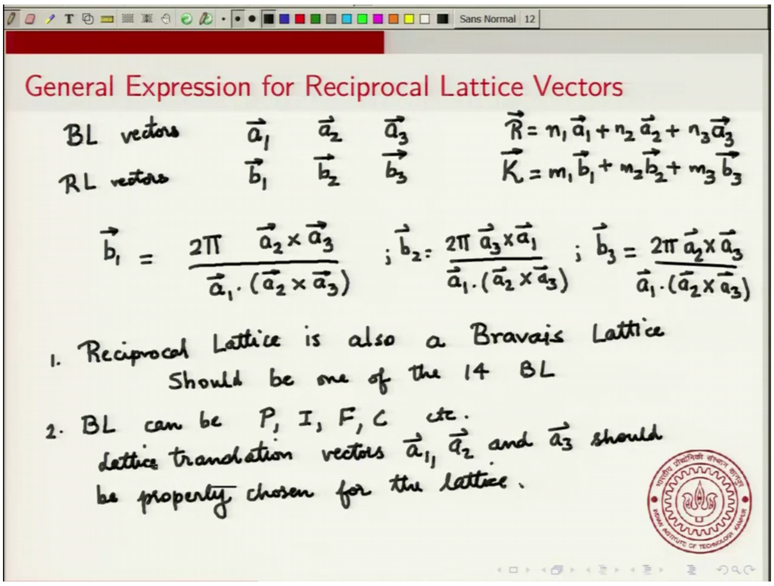
Solid State Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture - 39
Reciprocal Lattice, XRD instrumentation

Now, I will start the 4th lecture of week 8 of this course. And in this lecture, I will talk a little bit more about the Reciprocal Lattice that I just briefly introduced in the last lecture and then, I will get into the instrumental details of the x-ray diffractometer. So, we have already learnt about the Bragg scattering law which which tells you the condition for constructive interference of x-ray scattering of some sample. Now, now we want to put this into place in an instrument, put this to use in the form of an instrument and that is what we will do when we see the x-ray diffractometer, ok.

So, week 8 lecture 4 we are going to talk about Reciprocal Lattice and XRD Instrumentation. XRD stands for X-ray Diffractometer or X-ray Diffraction.

(Refer Slide Time: 01:15)



General Expression for Reciprocal Lattice Vectors

BL vectors $\vec{a}_1$ $\vec{a}_2$ $\vec{a}_3$ $\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

RL vectors $\vec{b}_1$ $\vec{b}_2$ $\vec{b}_3$ $\vec{K} = m_1\vec{b}_1 + m_2\vec{b}_2 + m_3\vec{b}_3$

$$\vec{b}_1 = \frac{2\pi \quad \vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \; ; \vec{b}_2 = \frac{2\pi\, \vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \; ; \vec{b}_3 = \frac{2\pi\, \vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

1. Reciprocal Lattice is also a Bravais Lattice
   Should be one of the 14 BL
2. BL can be P, I, F, C etc.
   Lattice translation vectors $\vec{a}_1$, $\vec{a}_2$ and $\vec{a}_3$ should be properly chosen for the lattice.

So, now we have talked about reciprocal lattice vectors in the context of a cubic or orthorhombic structures, but we can write a general expression for reciprocal lattice vectors. So, so suppose the Bravais Lattice vectors Bravais Lattice vectors and the basis, ok. So, the basis for this bravais lattice vectors are a 1 a 2 a 3 ok, then that means any bravais lattice vector R is a is a linear combination n 1 a 1. So, that is any bravo lattice translation vectors.

So, this is where we start off with. We start off with a 1 a 2 and a 3 as a as the primitive translation vectors for the bravais lattice n. Now, for the reciprocal lattice vectors we will denote them by b 1. So, the notation is b 1 b 2 b 3 and basically this arbitrary reciprocal lattice vector K can be written as a linear combination of b 1 b 2 and b 3, ok. So, these are like so this b 1 b 2 and b 3 are like the like a 1 and a 2 a 3 for the real lattice, for the bravais lattice and these are for the reciprocal lattice.

Now, the question is what is the relation between how can how can b 1 b 2 and b 3 be expressed in terms of a 1 a 2 a 3. So, so you can write a general expression for an arbitrary lattice and that is the following. So, b 1 is a vector that is perpendicular to it is actually perpendicular to the plane of a 2 and a 3, and this is written in the following way. So, 2 pi and you know iin the case of the cubic lattice, you just had b 1 was proportional to a 1, ok.

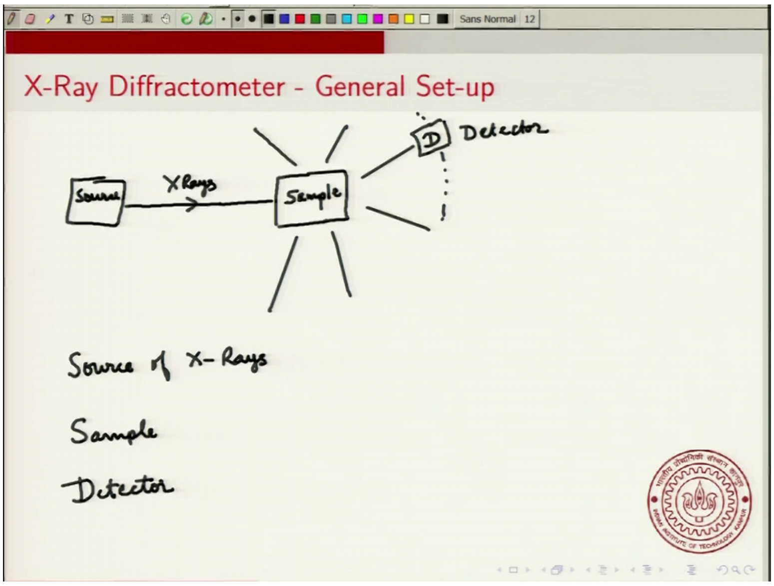
But in a more general case it is actually proportional to a 2 cross a 3 and a 2 cross a 3 is a vector that is perpendicular to both a 2 and a 3, ok. So, this is a vector that is perpendicular to both a 2 and a 3, ok. So, let me and there is a the denominator is the volume of the cell a 1 dot a 2 cross a 3. Similarly I can write b 2 as 2 pi a 3 cross a 1. You have to follow a cyclic order divided by a 1 dot a 2 cross a 3 and finally, we can write b 3 as 2 pi a 2 cross a 3 ok.

So, that is b 1 b 2 and b 3, ok. So, so this is the general expression and you can use this for any bravais lattice, ok. So, this can be used for any bravais lattice. Now, a few things about the reciprocal lattice, ok. So, the first thing is that reciprocal lattice is also a bravais lattice and I cannot emphasize this enough ok. I cannot emphasize this enough ok. It is a bravais, it should be one of the 14 bravais lattices, ok. So, it should be bravais lattice.

The second point is that the bravais lattice can be primitive body centered, face centered, C centered etcetera, ok. So, the reciprocal lattice can also be so; that means, reciprocal lattice can also be any of these. So, what is important is that the lattice translation vectors a 1 a 2 and a 3 should be properly chosen for the lattice ok. This is another important point which so for example if you have a face centered cubic lattice, then a 1 a 2 and a 3 will be different from a body centered cubic lattice or a simple cubic lattice, ok.

So, these are things to be kept in mind when you are dealing with reciprocal lattice vectors, ok. I want I mean we will we will keep looking at we will keep seeing the reciprocal lattice vectors as we go along ok, but I will as we go along both in x-ray diffraction and in band theory of solids,, so but I will stop discussing the concept of reciprocal lattice vectors for now and now I want to go to the Instrumental set up for the x-ray diffractometer.

(Refer Slide Time: 09:10)



X-Ray Diffractometer - General Set-up

Source of X-Rays

Sample

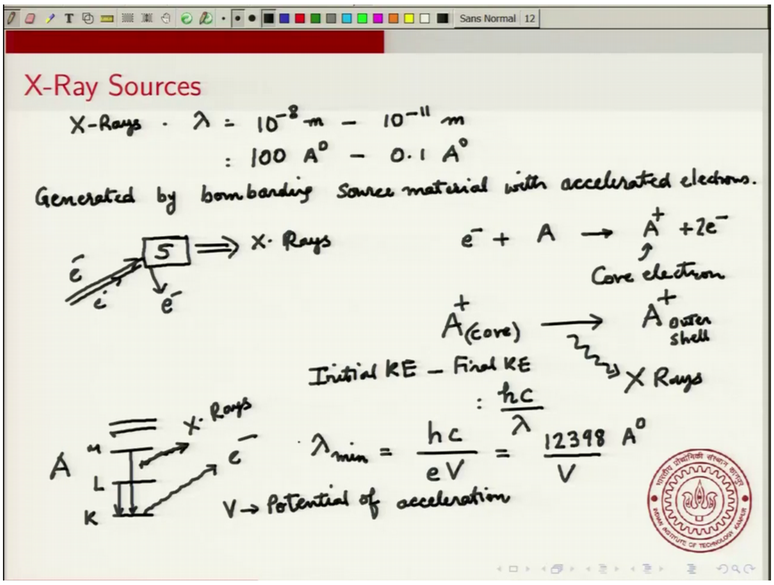
Detector

So, a typical x-ray disc diffractometer consists of a source of x-rays, ok. So, I will just I will just show it this way source and from the source there are these x-ray beams that are coming typically they are a series of parallel x-ray beams, and they typically fall on some sample and when they fall of the sample, they are scattered in all directions and basically there is a detector. This is a detector d detector and typically this detector can be rotated, so that you can look at you can pick up the scattering at different angles.

So, so this is the general setup of the x-ray diffractometer. So, we see that there are three main components. There is the source of x-rays. So, so these are x-rays source of x-rays ok, then there is the sample that you are using and in the sample there are different ways to prepare the sample, ok. So, the sample preparation will be one of the one of the topics that we look at and the last part is the detector, ok.

So, these are the this is a general setup of the x-ray diffractometer of any x-ray diffractometer. In fact, in fact this is typical for almost all spectroscopic instruments.

(Refer Slide Time: 11:16)



X-Ray Sources

X-Rays . $\lambda = 10^{-8}\,m - 10^{-11}\,m$

$: 100\,A^{\circ} - 0.1\,A^{\circ}$

Generated by bombarding Source material with accelerated electrons.

$e^- + A \rightarrow \overset{\uparrow}{A^+} + 2e^-$

Core electron

$A^+_{(core)} \longrightarrow A^+_{\text{outer shell}}$

X Rays

Initial KE – Final KE

$: \frac{hc}{\lambda}$

$\lambda_{min} = \frac{hc}{eV} = \frac{12398}{V}\,A^{\circ}$

V → Potential of acceleration

So, now, now let us look in detail about each of these. Let us look at the x-ray sources, ok. So, if you how can you how can you generate x-rays ok. Now, typically the way to I mean x-rays are x-rays have a wavelength have a wavelength that is typically of the order of 10 raise to minus 8 meter to 10 raise to minus 11 meters.

So, this typically this works out to about 100 angstroms. So, 2.1 angstros, ok. So, they are very short wavelength and very high energy beams, ok. So, how do you how do you generate x-rays ok? So, the typical way you will generate x-rays is actually to you have a, so to generate x-rays you have a you generated by bombarding source materials with accelerated electrons.

So, what do I mean is a following that you have a source material and you and you hit it with electrons and if you bombard it with very high energy electrons ok, then these electrons will collide with the atoms of the source and one of the things they do when they collide with the atoms of the source is that this electron so will collide with this atom to give to give an to ionize the atom, and emit another electron emit a second electrons, ok.

So, now if these electrons are very high energy ok, then this electron that is taken out from this atom A is from is a core electron. So, in other words this A plus is missing a core electron. That means, a core electron means not from the valence shell, but one of the inner shells. So, the electron in this atom A is the electron that is removed with a core electron electron removed.

And when this core electron is removed ok, then one of the higher shell electrons we will go and fill that vacancy and in the process it will generate x-ray radiation. So, that means this A plus with the core vacancy we will go to A plus with a outer shell vacancy where the way, so the electron from the outer shell will go to the core shell and during this process this will this will generate x-rays, ok.

In other words, if you if you look at the if you look at the energy levels of A, so if you take A ok, you have the very low line core shells. So, this is the K shell maybe the L shell and so on and then and then and you will have the valence electrons way up here and your valence electrons will be somewhere here. Now, now what is happening is that an electron is being is being when this electron bombards A, then the ionization is taking place due to an electron going out of here electron is ionized from this A shell.

And what will happen is one of these higher level shells will come down here, ok. One of the electrons from the L or M shell will come and when they when they land they will they will they will give x-rays. So, this is how x-rays are generated and so the electron beam hits the sample and x-rays are generated. So, we can do some fairly simple calculations to find out the wavelength of the x-rays. So, if we see the electrons the initial kinetic energy of the electrons, so the initial kinetic energy of the electrons is KE minus final KE.

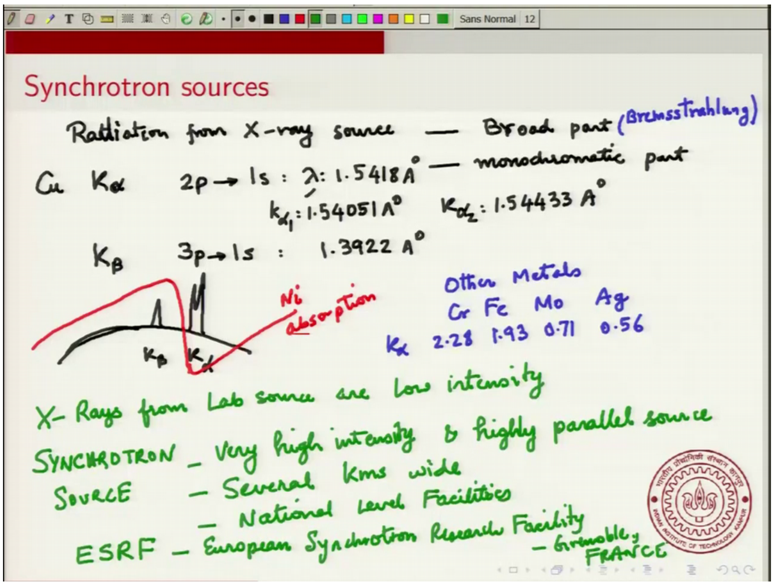
So, this difference between the initial kinetic energy of the electron and the final kinetic energy. So, this electron after it hits the sample, it goes with some final kinetic energy and so, this difference between the initial and final kinetic energy should be equal to the energy of the x-ray beam which is hc by lambda where lambda is the wavelength of the x-ray, ok. So, now now clearly this if this final kinetic energy is 0 ok, that means all the initial kinetic energy of the electron is transferred into the x-ray beam, then the wavelength will be the smallest or this or the kind of the energy of the x-ray will be the largest.

So, so we can immediately write that the minimum value of wavelength that will correspond to hc divided by the initial kinetic energy and the initial kinetic energy is we can write it as e times v where e is the electronic charge and v is the voltage through which its accelerated.

So, this kinetic energy this initial kinetic energy it depends on how much voltage it was accelerated by and then, we can show that it is equal to e times v and now we see that h is Plancks constant, c is the speed of light, e is the charge of an electron. These three are fundamental numbers. So, so we can write this lambda min in terms of v, we can and this number if you calculate it comes to 12398 angstroms divided by v.

So, basically the wavelength, the minimum wavelength can be calculated of the x-ray can be calculated using this expression. So, if these electrons are accelerated through some potential v ok, so v is the potential of acceleration of electrons, ok. So, v is the potential of acceleration and if they are accelerated through some potential v, then you can calculate this wavelength ok. So, this wavelength of the x-ray, x-ray beam can be calculated and typically this wavelength.

(Refer Slide Time: 20:40)



Synchrotron sources

Radiation from X-ray source — Broad part (Bremsstrahlung)

Cu K_α $2p \rightarrow 1s$: λ: 1.5418 Å — monochromatic part

K_{α_1}: 1.54051 Å K_{α_2}: 1.54433 Å

K_β $3p \rightarrow 1s$: 1.3922 Å

Other Metals

	Cr	Fe	Mo	Ag
K_α	2.28	1.93	0.71	0.56

X-Rays from Lab source are low intensity

SYNCHROTRON SOURCE – Very high intensity & highly parallel source

– Several kms wide

– National level Facilities

ESRF – European Synchrotron Research Facility – Grenoble, FRANCE

So, the wavelength the radiation that is obtained from an x-ray source this has two parts. So, one part is a broad part and other is a monochromatic part, ok. So, you have a broad part and a monochromatic part ok. The broad part is called the is referred to as the Bremsstrahlung. You do not have to remember this name, but it is still useful to know. So, the broad part is called the Bremsstrahlung and the monochromatic part is what we are interested in using for the x-rays for the x-ray diffraction.

So, the most common, the most common x-ray source is the copper K alpha the radiation and in this you have a 2 p2 1s transition. So, an electron from 2 p transitions to 1s of copper and the wavelength generated is 1.5418 angstroms OK. Copper k alpha this is the most, one of the most common sources ok. This is actually it is a double x; actually this appears as a double x two closely spaced peaks.

So, there is K alpha 1 which is 1.54051 angstroms and K alpha 2 which is 1.54433 angstroms, then there is K beta of copper which is which involves 3 p to 1s and this has a wavelength of 1.3922. So, this is much higher energy, ok. So, if you look at the if you look at the emission spectrum of copper ok, if you look at the emission spectrum of copper ok, then you will see that, that you have a broad part you have a broad part which is the Bremsstrahlung and then, on top of that you have the you have the few peaks.

So, this is the K beta and the K alpha which is a doublet and K alpha is much more intense than the K beta. Now, if you want only K alpha radiation ok, if you want only K alpha radiation, then you use a filter ok. So, you use a filter which will absorb lot of the radiation except for the K alpha radiation and one useful filter is Nickel. So, nickel has an absorption spectrum that looks this is the absorption spectrum of nickel. So, this is nickel absorption. So, it will absorb all the lights except those in the K alpha region. So, if you pass this x-ray through this nickel filter, then you will get only the K alpha radiation.

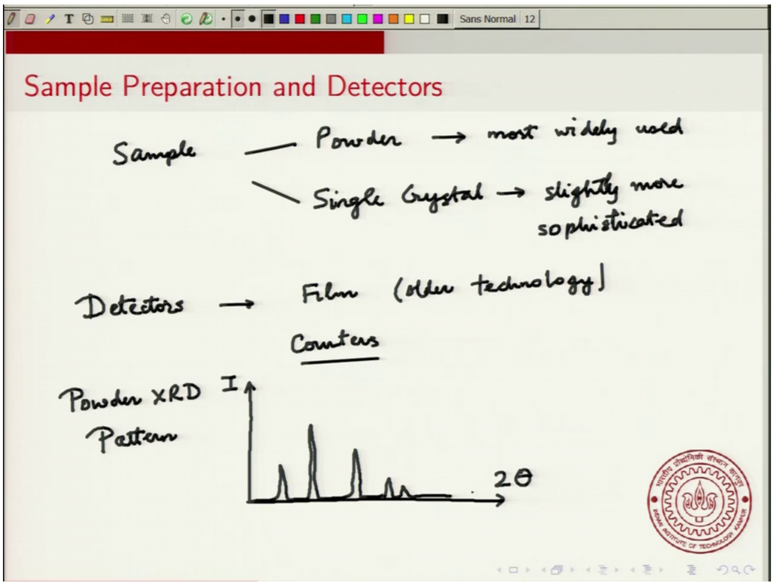
Now, there are other metals that can be used. It can be used for example you can use chromium iron of course, using copper, then you can see molybdenum, silver, and so, the K alpha for each of these. So, for chromium is about 2.28 angstroms ion is 1.93 molybdenum is 0.71 and silver is 0.56, ok.

So, as you go to heavier elements the wavelength will decrease, wavelength of K alpha will decrease because there and the energy will increase. So, this is a source of the x-ray radiation, but this x-rays that you generate using typical laboratory source are low intensity or low intensity and so one of the things you need to do is to, if you want a really high intensity source ok, then you can use what is called a synchrotron source. So, synchrotron source is a high intensity source. This is very high intensity and highly parallel, ok.

And you know synchrotron sources are usually several kilometers, wide several kilometers wide and usually these are national facilities. National level facilities in the sense that they will not be available in each in each institute or each college larger. There will be one for the whole nation or typically for a whole region. So, for example the Euro European synchrotron research facility ESRF, this is European Synchrotron Research Facility. This is in Grenoble France and it is used by researchers all over Europe .

It is used by researchers all over Europe and even from India; even from India people sometimes send samples to the Synchrotron Research Facility if they want a very accurate measurement and usually synchrotron sources have several instruments not just an x-ray, not just an x-ray diffractometer. So, the synchrotron radiation usually is used for several different instruments, but x-rays from synchrotron are extremely powerful in order to detect very minute quantities and very accurately.

(Refer Slide Time: 29:22)



Sample Preparation and Detectors

Sample — Powder → most widely used
— Single Crystal → slightly more sophisticated

Detectors → Film (older technology)
Counters

Powder XRD Pattern

Now, the next point I will just mention briefly here is the sample preparation and detectors. So, the sample can be either a powder or single crystals and the powder XRD is the most widely used and this is the one that is very widely used. It is the most in some sense it is the easiest instrument. Single crystal is more sophisticated ok, but still even single crystal x-ray diffraction is so fairly widely used.

So, slightly more sophisticated ok. Obviously, obviously the sample that you prepare your sample which you want to whose x-ray diffraction you want to do that sample in the first case you have to make it into a fine powder. In the second case, you need to have a single crystal grown of it and the last thing is about the detector the detectors can be either a film or a counter. So, film detectors are not I mean these are these are the older technology. Nowadays they usually have counters. So, you have some sort of counter, ok.

So, it could be some something that that either like a photomultiplier tube or some such feature that will count the that lab a counter that will tell you the intensity of the x-ray, x-ray diffraction pattern. So, so at the end of all this the resulting powder XRD pattern, sorry pattern and this is nowadays this is regularly seen in this format looks like this.

So, there is as a function of 2 theta. 2 theta; theta is a scattering angle. You have intensity as a function of your 2 theta and you typically have various peaks something like this. So, this is what an x-ray diffraction pattern typically looks like. So, with this I will conclude this lecture 4. This is a 4th lecture of week 8 and in the next lecture, we will review what we learnt in this week and do some practice problems.

Thank you.