Chemical Crystallography
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Basics, Symmetry and Equivalent Points in Crystallography
Lecture - 01
Introduction to X-Ray Crystallography

Good morning students. Welcome to this course of Chemical Crystallography. I am Dr. Angshuman Roy Choudhury; I am an assistant professor at Indian Institution of Science Education and Research at in the Department of Chemical Sciences. In this presentation, you can see my e-mail address and the webpage for further details. In this course, I will be having two tutors, two of my PhD students Anamika Avni, and Labhini Singla. So, they will help you in corrections and answering questions in this course.

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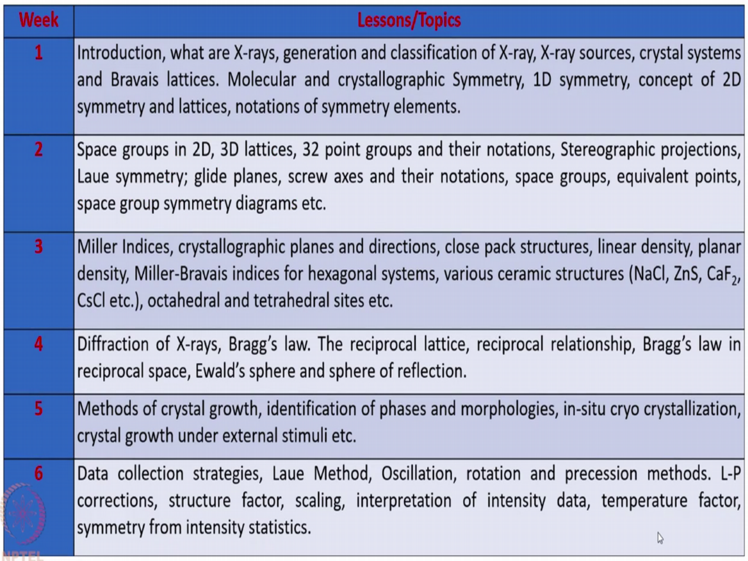

Week	Lessons/Topics
1	Introduction, what are X-rays, generation and classification of X-ray, X-ray sources, crystal systems and Bravais lattices. Molecular and crystallographic Symmetry, 1D symmetry, concept of 2D symmetry and lattices, notations of symmetry elements.
2	Space groups in 2D, 3D lattices, 32 point groups and their notations, Stereographic projections, Laue symmetry; glide planes, screw axes and their notations, space groups, equivalent points, space group symmetry diagrams etc.
3	Miller Indices, crystallographic planes and directions, close pack structures, linear density, planar density, Miller-Bravais indices for hexagonal systems, various ceramic structures (NaCl, ZnS, CaF_2, CsCl etc.), octahedral and tetrahedral sites etc.
4	Diffraction of X-rays, Bragg's law. The reciprocal lattice, reciprocal relationship, Bragg's law in reciprocal space, Ewald's sphere and sphere of reflection.
5	Methods of crystal growth, identification of phases and morphologies, in-situ cryo crystallization, crystal growth under external stimuli etc.
6	Data collection strategies, Laue Method, Oscillation, rotation and precession methods. L-P corrections, structure factor, scaling, interpretation of intensity data, temperature factor, symmetry from intensity statistics.

As you might have seen in the introductory video and also in the material that has been uploaded in the link, this will be a 12 week course in which we have to discuss about a large number of topics in X-ray crystallography. So, in above in the first week, we will talk about introduction, what are X-rays generation and classification of X-rays, crystal systems, Bravais lattices, 2D and 3D lattices, 1D symmetry etcetera.

Then we will talk about space groups in two-dimensional and three-dimensional lattices, 32 point groups and their representation, stereographic projections; glides plane crew as screw axes, space groups, equivalent points in three dimension. Then we will discuss about the crystallographic planes, directions, miller indices for simple systems, and Miller-Bravais indices for hexagonal systems. Then we will learn about various ceramic structures like sodium chloride, zinc sulfide, calcium chloride etcetera.

And then we will move to the Bragg's law of Bragg's law for X-ray diffraction. The reciprocal lattice, reciprocal relationship of Bragg's law in reciprocal space, Ewald's sphere and sphere of reflection; Then we will move to the second part of this course, where we will discuss about the methods of crystal growth, different ways to modify crystal structures, and crystal growth under external stimuli. Then we will talk about the data collection strategies, Laue method, oscillation method, rotation and all that. And then we will discuss about the modern day data collection procedures.

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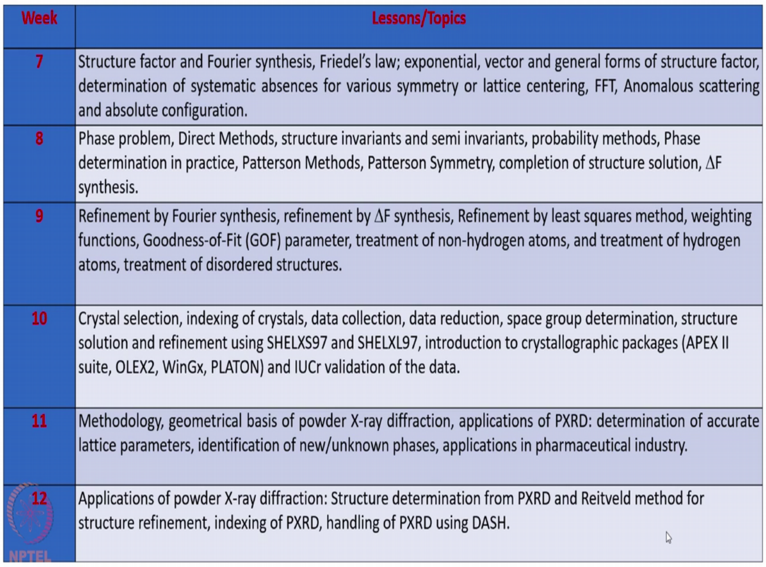

Week	Lessons/Topics
7	Structure factor and Fourier synthesis, Friedel's law; exponential, vector and general forms of structure factor, determination of systematic absences for various symmetry or lattice centering, FFT, Anomalous scattering and absolute configuration.
8	Phase problem, Direct Methods, structure invariants and semi invariants, probability methods, Phase determination in practice, Patterson Methods, Patterson Symmetry, completion of structure solution, ΔF synthesis.
9	Refinement by Fourier synthesis, refinement by ΔF synthesis, Refinement by least squares method, weighting functions, Goodness-of-Fit (GOF) parameter, treatment of non-hydrogen atoms, and treatment of hydrogen atoms, treatment of disordered structures.
10	Crystal selection, indexing of crystals, data collection, data reduction, space group determination, structure solution and refinement using SHELXS97 and SHELXL97, introduction to crystallographic packages (APEX II suite, OLEX2, WinGx, PLATON) and IUCr validation of the data.
11	Methodology, geometrical basis of powder X-ray diffraction, applications of PXRD: determination of accurate lattice parameters, identification of new/unknown phases, applications in pharmaceutical industry.
12	Applications of powder X-ray diffraction: Structure determination from PXRD and Reitveld method for structure refinement, indexing of PXRD, handling of PXRD using DASH.

Then we will talk about the structure factor, Fourier synthesis, Friedel's law, and things like that to give you an input about how to go about understanding the structure solution from a given data. Then we will introduce you to the phase problem, we will talk about direct methods, Patterson methods, and Patterson symmetry, and completion of structure using delta F synthesis. So, then we will discuss about refinement of the determined structures, refinement by least squares method, the weighting scheme, Goodness-of-fit parameter, the all factors weight weighting ask factors and all that.

Then we will talk about latest software in which all these are incorporated. So, we will start from crystal selection how to choose a good crystal, indexing of crystals using a diffractometer, data collection, data reduction, in practice using the relevant software packages, and what is the validation of this particular data that we have collected; and based on that we should know how to prepare a crystal data for publication.

Then we will move towards the end of this course to the methodology and geometrical basis of powder X-ray diffraction, applications of PXRD, determination of accurate lattice parameters using powder diffraction, and different applications of powder X-ray diffraction methodologies, and its application in pharmaceutical industry. Application of powder diffraction, structure determination from X-ray diffraction data and Reitveld analysis also will be touched upon towards the end of this course.

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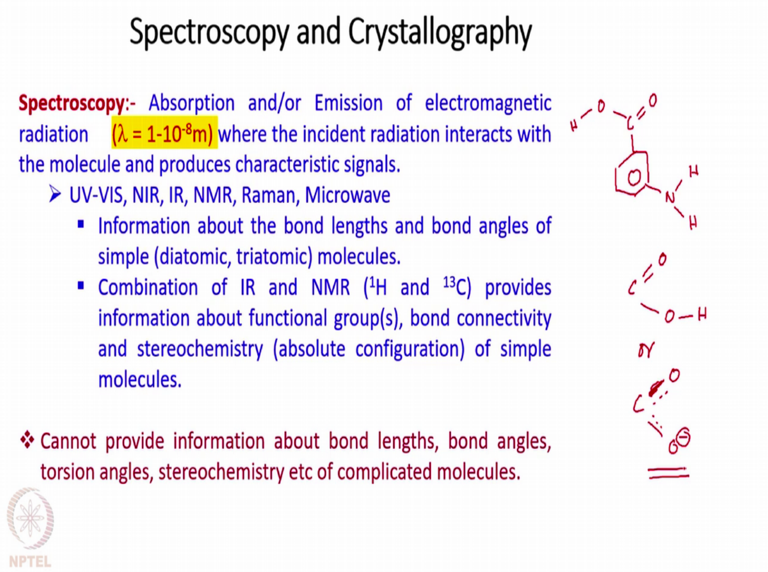

Spectroscopy and Crystallography

Spectroscopy:- Absorption and/or Emission of electromagnetic radiation ($\lambda = 1\text{-}10^{-8}$m) where the incident radiation interacts with the molecule and produces characteristic signals.

- UV-VIS, NIR, IR, NMR, Raman, Microwave
  - Information about the bond lengths and bond angles of simple (diatomic, triatomic) molecules.
  - Combination of IR and NMR (^{1}H and ^{13}C) provides information about functional group(s), bond connectivity and stereochemistry (absolute configuration) of simple molecules.

❖ Cannot provide information about bond lengths, bond angles, torsion angles, stereochemistry etc of complicated molecules.

So, to start with we should have is idea, why it should we need, why do we need to study X-ray crystallography at all. If you many of us has studied spectroscopy in the past, and as we know the spectroscopy is a method of absorption and or emission of electromagnetic radiation of a large range of wavelengths starting from 1 to 10 to the power minus 8 meter, where the incident radiation interacts with the molecule and produces characteristic signals. The common well known examples are different spectroscopic techniques or UV visible spectrophotometry near IR spectrophotometry, IR spectrum, NMR, Raman, Microwave all these.

All these different spectroscopies are used to get the bond lengths and bond angles of very simple molecules like diatomic, and triatomic molecules. But, if I want to determine the bond length of a difficult molecule such as a one which I am drawing here on the screen, all the bond lengths and bond angles may not be possible to be determined using a spectroscopic technique. If you want to determine whether it is a C double bond; O, H or it is a C double C C O and O minus, whereas both the bonds are partially single or partially double, so 1.5 bond. We would not be able to determine using spectroscopic techniques. So, in these cases, we would like to have a concrete information from structural data.

Combination of IR and NMR spectrum provides information about the functional groups that are present in the compound, it gives the bond connectivity and sometimes we can derive the absolute configuration that is the stereochemistry of very simple molecules. But in case, the molecule has multiple chiral centers, it becomes difficult to establish the absolute configuration of all those chiral centers that are present in the molecule.

So, in a nutshell, it cannot provide the spectroscopic methods cannot provide information about bond lengths, bond angles, torsion angles, stereochemistry etcetera of any complicated molecule. And most of these spectroscopic methods are done in solution state. So, the information that we obtain are in solution. And in case of crystal structures, we get to know the structure of a material in their solid state, and it gives us information about the accurate bond lengths, bond angles, and torsion angles.

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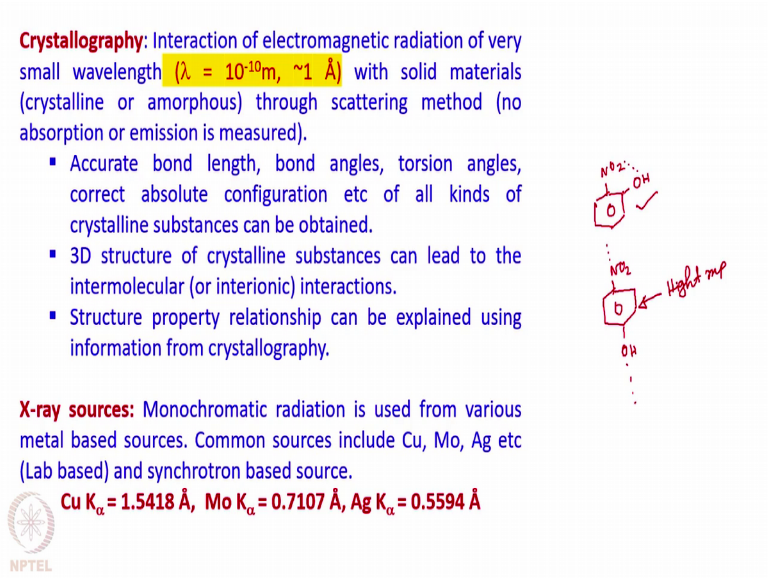

Crystallography: Interaction of electromagnetic radiation of very small wavelength (λ = 10^{-10}m, ~1 Å) with solid materials (crystalline or amorphous) through scattering method (no absorption or emission is measured).

- Accurate bond length, bond angles, torsion angles, correct absolute configuration etc of all kinds of crystalline substances can be obtained.
- 3D structure of crystalline substances can lead to the intermolecular (or interionic) interactions.
- Structure property relationship can be explained using information from crystallography.

X-ray sources: Monochromatic radiation is used from various metal based sources. Common sources include Cu, Mo, Ag etc (Lab based) and synchrotron based source.

Cu K_α = 1.5418 Å, Mo K_α = 0.7107 Å, Ag K_α = 0.5594 Å

So, what is crystallography, in crystallography in the interaction of electromagnetic radiation of very small wavelength, you can see the bond length the wavelength is in the order of 10 to the power minus 10 meter that is about 1 angstrom with solid crystalline materials or amorphous materials. Through a scattering method, and no absorption or emission takes place. So, this is not a spectroscopy, so one whenever we want to talk about X-ray diffraction, we should call it as a diffraction and not spectroscopy. X-ray spectroscopy, X-ray (Refer Time: 08:19) photoelectron spectroscopy is a different thing. Here we are talking about X-ray diffraction, which is a scattering method.

So, in this what we get is that accurate bond length, bond angles, torsion angles, correct absolute configurations of all kinds of substances that are solid and crystalline material. From this three-dimensional structure of crystalline substances, we can talk about the intermolecular interactions or interionic interactions. How one molecule is seeing another molecule in space? How one molecule is interacting with another molecule in the solid state? All these information can be derived from this structural study that we and the generally do. Based on the crystal structures that have been derived, one can explain lot of different a lot of different properties, which are related to their structure.

For example, melting point of compounds like this if you have a nitro phenol when it is ortho nitro phenol, and when it is a para nitro phenol, as we know. In case of ortho nitro phenol, we have hydrogen bonding intramolecular hydrogen bonding; whereas in para nitro phenol the hydrogen bonding is intermolecular, as a result this para nitro phenol has higher about melting points higher melting point compared to the ortho nitro phenol. So, this higher melting point is a physical property of this particular compound which can be explained, if we know the crystal structure of these two compounds.

So, for this purpose we need a particular source of type of X-ray source. What we need is a monochromatic radiation used from various metal based sources. Common sources include copper, molybdenum, silver, etcetera, these are lab based sources and synchrotron based sources. Here I have given some numbers, which are important, because we will be a referring to these wavelengths very often.

The K alpha radiation coming from copper is about 1.54 angstroms, when we talk about molybdenum K alpha it is 0.71, and when we use silver K alpha, the wavelength is 0.55 angstroms. These wavelengths are highly significant; and we will see towards the middle or end of the course that the choice of wavelength is very important for the experiment that we are going to do.

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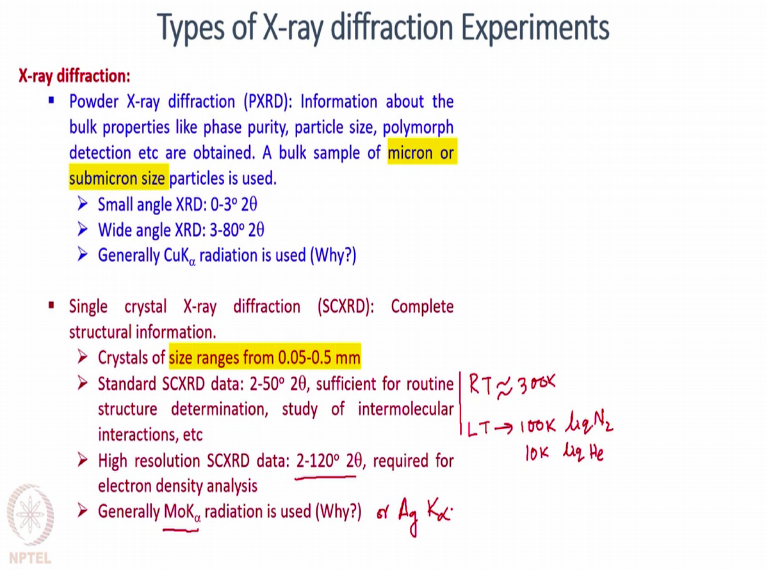

Types of X-ray diffraction Experiments

X-ray diffraction:

- Powder X-ray diffraction (PXRD): Information about the bulk properties like phase purity, particle size, polymorph detection etc are obtained. A bulk sample of micron or submicron size particles is used.
    - Small angle XRD: 0-3° 2θ
    - Wide angle XRD: 3-80° 2θ
    - Generally CuK_{α} radiation is used (Why?)
- Single crystal X-ray diffraction (SCXRD): Complete structural information.
    - Crystals of size ranges from 0.05-0.5 mm
    - Standard SCXRD data: 2-50° 2θ, sufficient for routine structure determination, study of intermolecular interactions, etc
    - High resolution SCXRD data: 2-120° 2θ, required for electron density analysis
    - Generally MoK_{α} radiation is used (Why?) or Ag K_{α}.

$RT \approx 300K$

$LT \rightarrow 100K$ liq N_2

10K liq He

So, using X-rays, what are the different types of experiments that we can do. Suppose, if we have a sample, which is a powdered sample, which is a bulk sample, the collection of particles are in size in the term of micron or sub micron size particles. So, if we want to analyze such samples, we can use a powder diffraction powder X-ray diffraction method that we can apply to characterize that particular sample.

This powder X-ray diffraction is divided into two different types; one is small angle X-ray diffraction, other angle is very wide angle X-ray diffraction. Using small angle X-ray diffraction, (Refer Time: 12:03) studies the diffraction of X-rays in the range of 2 theta starting from 0 to 3 degrees. While in case of wide angle X-ray diffraction, we starting from the generally from 3 to 80 degrees or sometimes slightly higher than that. So, for this particular application when we do powder X-ray diffraction, we use copper K alpha radiation in general. Why? We will come to it at some point of time in then in the following lectures.

When we try to you determine the crystal structure of a substance, then we use single crystal X-ray diffraction methodology, where we get to know the complete structure solution. The disadvantage of this method is that we need a sufficiently large sized crystal which is about 50 to 500 micron in size that means, 0.05 to 0.5 mm in size, which we should be able to handle under microscope. Because these crystals need to be selected under microscope, this should be should have a certain properties, which I will explain in future classes, when we talk about handling of crystals. So, these crystals which are of this size like 50 to 500 micron are suitable for single crystal X-ray diffraction.

For a routine X-ray data for from which one can solve crystal structure, we need a data from about 2 degree to 50 degrees in 2 theta, and that is sufficient for doing the structure determination. Mind you this particular experiment can be done at various temperatures, one can do the data collection at room temperature that is about 300 Kelvin; or if we have facility of doing a data collection at low temperature, we can go down to 100 K using liquid nitrogen. One can go down even to 10 Kelvin using liquid helium. Depending on the nature of experiment, nature of the requirement, one can choose a certain temperature at which we should collect data. And then we use a different set of experimental procedure using different liquefied gas to reach that kind of temperature.

The advantage of doing data collection at lower temperature is to reduce the thermal motion of atoms and molecules inside the lattice. So, at lower temperature, we get the data collected with a very very small thermal motion. But, then if we need further information other than just the structure solution, if we want to know the electron density distribution in a molecule, if you want to identify the hydrogen bonds, if we want to model the intermolecular interaction regions, and determine the electron density distribution between the two molecules, how they are interacting.

We need how high resolution single crystal data; and in that case, the data that we collect it has a much wider range from 2 to 120 degrees in 2 theta, and this is required for electron density analysis. And here you please note that in general we use MoK alpha radiation, or nowadays we use silver K alpha radiation, if you remember in my previous slide. We had these wavelengths; one is about 0.7 angstrom, the other one is about 0.6 angstrom. Compared to the copper, which is about 1.54 angstrom. So, by lowering the wavelength, we can achieve much higher resolution in X-ray diffraction data.

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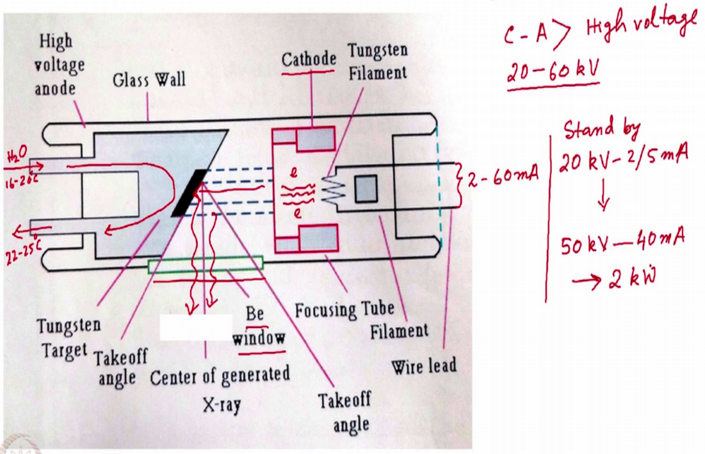
Generation of X-rays



Schematic diagram of X-ray tube

Now, this is the generation of X-rays, and what we are trying to understand now is how the X-ray tube is built. And what are the parts that we have in an X-ray tube. So, this X-ray tube is a glass walled tube with which is kept under high vacuum. And there we have a tungsten filament, which is used to generate electrons inside this evacuated chamber. And those electrons are then emitted from the filament, and they are then allowed to run towards the tungsten anode or any anode that is of use, because in X-ray crystallography we generally use copper molybdenum or silver as anode because of their characteristic wavelengths.

So, we use a suitable anode at that point. And what we have here is a cathode, and the anode, so what we do is between the cathode and anode, we cannot generate we create a high voltage that is a high potential difference is generated there. So, it is in general about 20 to 60 kilo volt in case of different laboratory sources. So, what happens under the influence of that very high potential difference, these electrons which were emitted from the filament run at very high velocity towards the anode and goes and collides with the anode.

So, in that process what it does is that it removes one electron from the innermost shell of that anode, and immediately the vacancy is filled with the electrons coming down from the higher atomic orbital's to the particular atomic, or 1s atomic orbital by releasing that energy. And what kind of the transition happens, and all that we will see in the next slide. So, in this tube what are the other parts, we have a glass wall, we have a beryllium window, which is transparent to X-rays. So, when the electrons come and impinge on the anode, the X-rays are generated. And that X-ray is emitted in this direction outside the tube, and this beryllium window allows the passes of that X-ray beam.

What happens when these electrons are falling on the glass wall at very high velocity? The transfer all their kinetic energy to this tungsten target or metal target, so as a result this metal target gets heated up very soon. So, to cool that metal target, we need to supply cold water at about 16 to 20 degree centigrade, so that the cold water goes in cools the backside of the anode, and comes back through a tube at slightly elevated temperature like 22 to 25 degree centigrade. And then this water is then circulated using a water circulating chiller which maintains the temperature of the input water at about 16 to 20 degree centigrade.

So, in this X-ray tube on the filament, we apply current from about 2 to 60 milliamps, and as I indicated the voltage is about 20 to 60 kilo volt depending on what kind of X-ray tube that we are using. So, when we are using a standard X-ray tube, we keep it at the minimum that is 20 kV 2 or 5 milliamp, whatever the settings of the tube may be and this is called the standby settings. So, when we do not use the diffractometer when we are not collecting any data at that point, we always keep the generator at the minimum voltage and current, so that the tube is always kept warmed. And we do not switch on, and switch off these tubes every now and then.

But, when we try to collect a data, we increase the voltage to 50 kilo volt current to about 40 milliamps resulting into a power of 2 kilo watt, this amount of energy is then used to generate high intensity X-rays for X-ray diffraction experiments. This is true for both single crystal, and powder X-ray diffraction methods depending on what kind of X-ray tube we are using copper or molybdenum.

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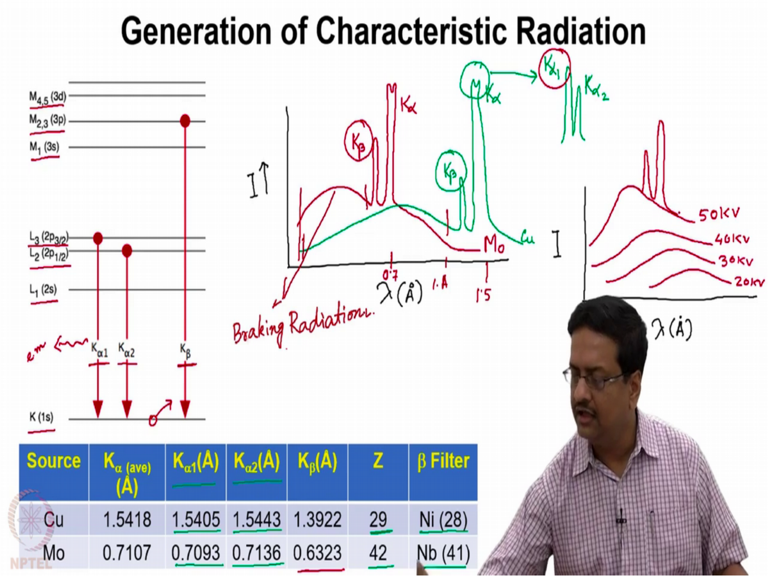

Generation of Characteristic Radiation

Source	$K_{\alpha\ (ave)}$ (Å)	$K_{\alpha 1}$(Å)	$K_{\alpha 2}$(Å)	K_{β}(Å)	Z	β Filter
Cu	1.5418	1.5405	1.5443	1.3922	29	Ni (28)
Mo	0.7107	0.7093	0.7136	0.6323	42	Nb (41)

In this slide, now I will try to explain, how the X-rays are generated and the characteristic radiations are obtained. See this here the energy level diagram shows that the 1s shell has the lowest energy, 2s has a slightly higher energy much higher energy, 2p has two levels; 2p half and 2p 3 by 2, from where the electrons should jump. And the next higher levels are at much higher energy which are corresponding to 3p, 3s, and 3d orbital's. So, when the highly accelerated electrons come and collide with the anode, it removes one electron from the 1s orbital, and makes a vacancy at that level.

So, immediately that vacancy has to be filled; it can be filled by a jump of electron from the level L3, which is 2p 3 by 2 to 1s. These particular jump; when the electron falls from higher level to lower level, it emits electromagnetic radiation falling in the range of X-ray, and that is called copper K alpha 1. When an electron jumps from the level L2 which is 2p half, it has a smaller energy difference. So, the radiation has a different wavelength, which we call copper K alpha 2, and has a slightly larger wavelength.

There are possibilities of having an electron coming down from M 3 or M 2, which is 3p, so that jumped from much higher 3p orbital to 1s orbital results into an emission of a copper K beta radiation, which is again much smaller.

So, now if we want to visualize the actual situation when the X-ray is emitted from a given tube, I would like to draw a figure. We have plotting here intensity versus the wavelength of radiation in angstroms. When the electrons are accelerated inside the tube under a very high potential difference, they are running at enormous leave a large velocity towards the anode.

But when they are approaching the anode, they fill a deceleration. As a result, the electrons are decelerated the velocity is reduced. And in that process, the charged particle when it is decelerated, it is continuously emits some X-ray radiation. And that region looks like this, which emits quite X-rays over a range of wavelengths. And then at a given point, we see a radiation peak. And then immediately after that we see another radiation peak, which is like spitted like a snakes tongue at the tip.

Suppose, these particular graph is for molybdenum tube. So, as we can see for molybdenum, the K beta radiation is about 0.63 angstrom, and K alpha radiation is about 0.71 angstrom. So, this region is about 0.7, this radiation is K beta, and that one is K alpha for molybdenum. If we were using a copper tube, what you we would have seen is slightly different the copper has the wavelength that much higher value and we see the characteristic peak feature for a copper tube; And for that K beta lies on the left, and K alpha lies on the right.

So, now you see that in both the cases, the tip is split. And that split is because we have alpha 1 and alpha 2, as we see on the left hand side figure that alpha 1 has the higher energy, which means a smaller wavelength. So, alpha 1 if you see for both copper and molybdenum, the wavelengths are smaller than the corresponding wavelengths of alpha 2. So, what we see the expanded version of this tip is like this, this one is K alpha 1 at a lower wavelength, and K alpha 2 at a slightly higher wavelength in both case of both copper and molybdenum.

So, if one wants to do any X-ray diffraction experiment, the experiment has to be done using one particular wavelength and not all these characteristic wavelengths that we are getting that is alpha 1, alpha 2, beta and so on. So, to do that one has to use a filter. So, for copper which has atomic number 29, we use nickel with atomic number 28 to remove the corresponding K beta of copper. This is interesting, because the nature has provided us this filter. Nickel absorbs K beta radiation completely and allows K alpha to pass through. So, we can eliminate K beta using a nickel filter.

In the same way for molybdenum which has atomic number 42, we can use niobium having atomic number 41 as a filter, which will then remove the K beta of molybdenum. Now, the question is how to separate K alpha 1, and alpha 2. For that we need a crystal monochromator, we will discuss the function of a crystal monochromator when time comes; So, in that we will then show how a crystallized crystal monochromator a particular plane of a crystal can be used to separate K alpha 1, and alpha 2. And one can then use only K alpha 1 radiation for a particular X-ray diffraction experiment, then we get a monochromatic source of X-rays.

When the electrons are decelerating what we can see here, we have a region of continuous radiation in both the cases. This continuous radiation as I indicated comes from the braking of the electrons that is deceleration of electrons. So, this region is called the braking radiation. So, this braking radiation is also called bremsstrahlung in German, which means the decelerating electrons are emitting the electromagnetic radiation of a wide range of wavelengths starting from about 0.1 angstrom to about 0.6, 0.6 two angstroms in case of molybdenum. And for copper, it goes even beyond that and it is something about up to about 1 angstrom. And for copper, the peak appears at about 1.5 angstrom.

So, this is how the X-rays are generated and characteristic radiations are obtained from a given X-ray tube. Now, we would like you to also understand that what is the importance of using very high voltage? If we were using an X-ray tube with a variety of potential difference is applied, we would have seen the feature that I am going to draw here with very small potential difference like 20 KV, the braking radiation should have come at much higher wavelength with very low intensity. If we increase that potential difference to something like 30 KV, the maxima shifts towards the lower wavelength, and the intensity of the radiation that is coming out has also increased.

So, in the same manner if we use even higher 40 KV wavelength the 40 KV voltage, then the maxima shifts further back towards the look smaller wavelength. And when we use 50 KV for our experiment, we get a much much larger intensity of the braking radiation. And simultaneously, immediately about the end near end of the braking radiation, we should start seeing that characteristic radiations. And we should then use the characteristic radiations for our X-ray experiment.