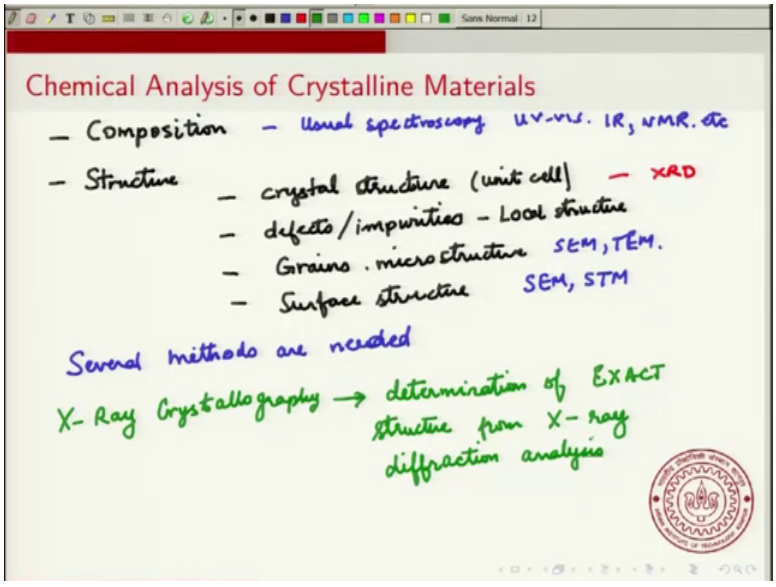
Solid State Chemistry
Prof. Madhav Ranganathan
Department of Chemistry
Indian Institute of Technology, Kanpur

Lecture – 43
X-Ray Crystallography

Now, I will start the 3rd lecture of the 9th week of this course. In this lecture I am going to talk about X-ray Crystallography ok. So, far we have looked at powder X-ray diffraction and we have looked at how to analyze the diffraction patterns ok. Now X-ray crystallography is the most advanced method for determining the structure of compounds and in X-ray crystallography you not only determines the crystal structure, but you also determine the location of each and every atom in the crystal ok.

And in order to do this you need a very accurate instrument, fairly sophisticated instrument that can accurately give you all the important peaks in the diffraction pattern ok. So, week 9 lecture 3 will be about X-ray crystallography and let me also mention that lot of this is highly automated ok.

(Refer Slide Time: 01:23)



So, I will just give a general overview of some of the concepts related to X-ray crystallography ok. So, the general philosophy of chemical analysis of crystalline compounds is the following, that when you say you want to identify a crystalline compound or you want to analyze it ok, then what are the things that you need to do? So,

the first thing you need to know is what is the composition of the compound ok? You need to know what it is composed off what are the elements in it, what are the if there are some important organic functional groups what are they? And typically for this you can use the usual spectroscopic methods.

So, usual spectroscopic methods are used like UV visible IR, NMR etcetera IR NMR etcetera you can use mass spectrometry and so on. So, there are several such techniques. Now, but for crystalline compounds in addition to the composition we also need to know the structure, the crystal structure and the structure when we say structure we mean several things ok. So, you mean the crystal structure that is what is the unit cell ok; what is the unit cell what are the parameters of the unit cell what are a b c alpha, beta, gamma of the unit cell ok?

Then you need to know within the unit cell are there the presence of defects or impurities or color centers and so on ok. As we know that I mean we already saw when we were discussing defects and impurities, that small amount of certain impurities can give a completely different color to materials.

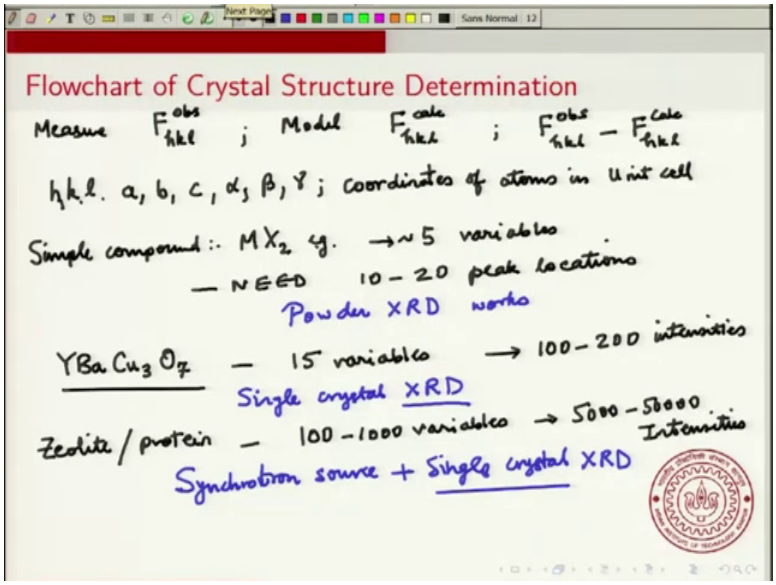
So, these are related to the local structure and again these can also be determined using the spectroscopy methods. Whereas, overall crystal structure determination is usually by XRD ok, then you could also ask what is the structure on a larger scale ok? So, for example, the grains, what are the sizes of the grains? The microstructure, you could ask about the surface structure. So, what I want to emphasize is that you need several methods ok, you need several different methods to determine these. So, several methods are needed and I will not list all the methods that are needed ok. But I will just say that you know for example, if you want to determine the surface structure you might use microscopy like SEM.

For grains microstructure you might use again SEM, TEM etcetera these are we will talk about all these microscopic techniques. This is a scanning electron microscopy transmission electron microscopy, you can also use Scanning Tunneling Microscopy STM ok, again I do not, I will come back to all these as we go along ok.

Now, coming to X-ray crystallography ok; so, this refers to the determination of exact structure from X-ray, its essentially X-ray diffraction analysis ok. So, this is what is meant by X-ray crystallography and this is one of the most accurate and most reliable

methods that is used ok, now we need to know what kind of, what is the general framework of x of this X-ray crystallography ok.

(Refer Slide Time: 07:01)



So, if you want to determine the crystal structure what you need to do is you from the X-ray diffraction pattern ok. So, you measure F of F observed the structure factor, the form factor and then you try to take construct some model for and then from that you calculate this F of h k l ok. And you try to look at the observed structure factor minus the calculated structure factor and you try to minimize this difference, try to make this difference as small as possible. So, that you say that whatever you have calculated is what is observed and then you conclude what is a structure ok.

Now, so clearly as we had already seen that you need that there are a lot of things to be determined ok. So, if you have to determine h k l abc and then you have to determine the coordinates of all the atoms in the crystal, all the atoms within the unit cell. So, you need h, k, l; a, b, c and alpha, beta, gamma. So, these are the unit cell parameters and coordinates of atoms in unit cell ok. Now if you have a simple compound ok and let us say you have an idea that you know, you have some idea of the about the structure let us say for example, if you have an M X 2 X is some; X is some other element ok. So, if you have a compound like MX 2, like let us say it can be calcium fluoride ok.

So, then you need to know as we said that there are a lot of things that we need, there are several parameters and usually you it turns out to be only about only a few parameters

that need to be determined so about 5 parameters, 5 variables ok. So, what I mean is that you might know the, you might have some idea about the crystal structure. So, you might know that it is cubic, let us say; let us say if you know that its cubic then you only have one constant that is a to be determined ok.

And further, but you also have to determine the location of the atoms, the coordinates of the atoms. So, typically about you know of the order of 5, I mean maybe 3, 4, 5, 6 something like that ok. Now what I want to emphasize is that if you want to determine so many variables then you need 10 to 20 peak locations ok, you need the 2 theta value from about 10 to 20 peaks in order to do this and this can be done; can be done using powder XRD. So, powder XRD is fine, a usual laboratory scale powder XRD works. Now on the other hand if you have a more complicated compound; a more complicated compound for example, let us say you have; let us say you have something like YBa Cu 3 O 7 ok.

Now, this is a perovskite structure ok, it is actually a distorted perovskite. So, this typically has about you have lot of atoms. So, typically you can see that there are 7 plus 3 10 plus 2 12 atoms and you will typically have about 15 variables to determine in order to determine the structure completely ok. And if you have 15 variables ok, typically you need about in order to determine these 15 20 variables you need about 100 to 200 intensities. You need to need you need to know about 100 to 200 intensities, always what is done is you know you match it with several peaks and then you try to fit them ok.

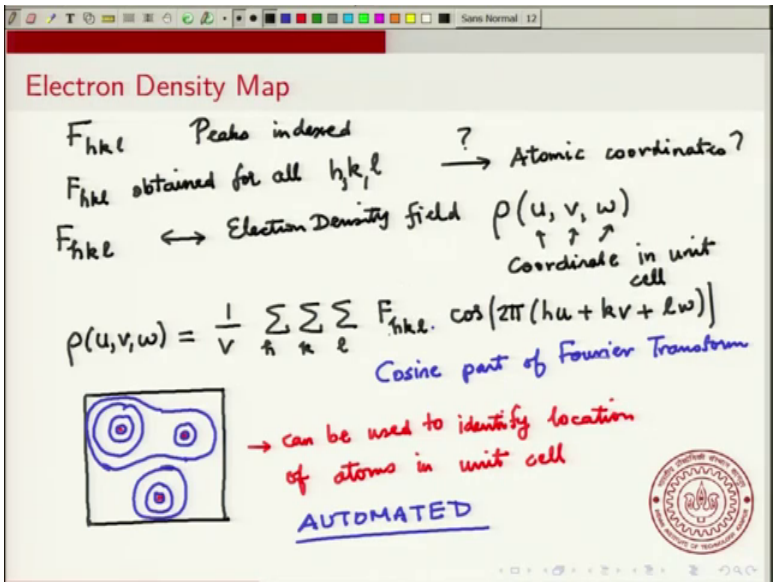
So, you so always the experimental data is lot larger than the number of variables and this is done in order to get accurate values of these variables, now for this you will typically use a single crystal XRD. So, you make a single crystal and then you; and then you put it in the XRD X-ray diffraction instrument and because it is a single crystal you will have to rotate it ok, but when this is done you will get a very good intensity of all the peaks ok. So, this gives much higher intensity and.

So, you will be able to record several more intensities ok, now a more complicated case would be something like a bio molecule. Let us say or you could have a alumina zeolite, protein and in this case you could have you could easily have 100 or more variables, 100 to 1000 variables ok. And you would require something like 5000 to 50000 intensities and here you have to use; you have to use a synchrotron source, synchrotron source plus

single crystal SRD. So, you have to use a single crystal X-ray diffractometer, but you have to use a synchrotron source of X-ray radiation ok.

So, the intensity is very large and you can detect lot of peaks ok. So, now the question is a following, that you have if you are if you finish indexing the peaks ok.

(Refer Slide Time: 15:27)



So suppose you have F of h k l and you know; and you know the h k l and you have identified. So, peaks have been indexed ok. So, you know all the F of h k l ok. So, you know F of h k l for all h k l ok. Now, how do you get the atomic coordinates? How do you get the atomic coordinates from this? You know h k l for and you know the F of h k l. So, how do you get the atomic coordinates ok?

Now, there is its I mean this process is done using the following idea that the electron the F of h kl ok, is related to the electron density and this electron density field; that means, the electron density at some coordinate u, v, w. So, this is some coordinate inside unit cell; that means, you imagine that you look at any point on the unit cell. So, u, v, w is some point inside the unit cell and at that at each point there is an electron density ok. So, at each point in space inside the unit cell there is an electron density and this electron density if you know the electron density at all points in the unit cell you can calculate F of h k l and vice versa.

And the relation is a following. So, rho of u v, w so this electron density is equal to 1 over v sum over h sum over k sum over l F of h k l times cosine the cosine part of the Fourier transform 2 pi h plus k plus l sorry h u plus kv plus lw ok. So, this is like the delta ok, but the delta the phase difference delta was only used for; the phase difference delta was only used for location of the atoms only for the position of the atoms, but this is at an arbitrary point within the unit cell.

So, u, v, w is an arbitrary point within the unit cell and this is actually what is called a Fourier transform. In fact, the cosine part of the Fourier transform ok. So, I will just write this it is the cosine part of Fourier transform and so, the electron density is nothing, but the cosine part of the Fourier transform of the structure factor ok. So, the structure factor, the geometric structure factor F of h k l is the rho of u, v, w is a cosine part of the Fourier transform of F of h k l ok.

So, now if you have this electron density everywhere, if you have this electron density everywhere then you can make up you can make these electron density maps. So, for example, if you have if you look in a plane if you look in one plane you can have these electron density maps and these will typically appear as contour maps ok. So, if you have something like this, if you have something like this contour maps.

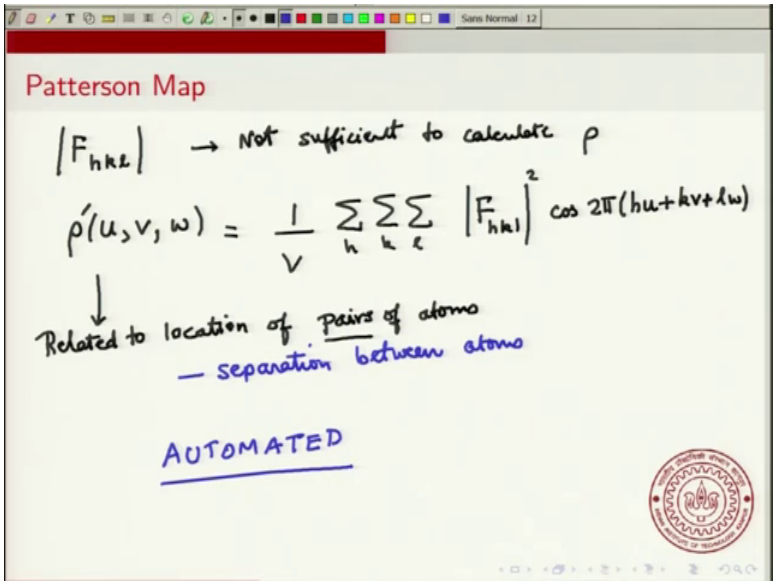
So, basically you can say that electron density is increasing as you go from the, as you go from the out outside to the inside of each of these ok. So, then immediately you would identify that an atom is located right here, these are the locations of the atoms where the electron density is a maximum and so, you can identify the location of the atoms using this electron density maps.

So, electron density map can be used to identify atoms in unit cell ok and this is again I should emphasize that this is completely automated; that means, the instrument will do this for you we will use some software to carry out this analysis and give you the electron density map ok. Now one of the things about the electron density map is that you need to know the F of h k l with a sine ok.

So, the F of h k l you need to know whether it is plus positive or negative ok, but if you look at the X-ray diffraction pattern then F of h kl you only see a positive sign of F of h k l ok. So, for this electron density map you need F of h k l with and you need the

information whether it is positive or negative ok, but often in this X-ray diffraction you only obtain absolute value of F of h k l ok.

(Refer Slide Time: 22:53)



So, this is not sufficient to calculate rho the electron density and to overcome this problem there is something called a Patterson map that is made ok. So, the Patterson map uses the absolute value of h k l and it constructs and a map electrode, this is not exactly this is not actually the electron density, but it is I will call it rho prime. And it is constructed in exactly the same way some over h, some more k, sum over l and now instead of F of h k l I you say absolute value of F of h k l with a square and cos 2 pi h u plus k w kv plus lw ok.

So, it is exactly like the like what was used in the case of the electron density maps, but it takes into account the fact that experimentally we only determine the absolute value of F of h k l and not F of h k l with its sign. And now this turns out this Patterson map is related to location of pairs of atoms ok. So, if you look at a Paterson map and if you look at peaks on the patricians and map. So, just as the peaks in the electron density map were related to location of atoms this is location of pairs of atoms. So, basically the peak corresponds to a distance at which you find 2 atoms, so some separation between atoms.

So, and then using some reference or some fixed atom you can actually determine the entire crystal structure ok, now what I want to emphasize is that both this Patterson map and electron density map are also automated and these are parts of the, these are parts of

modern X-ray diffraction instruments ok. So, the single crystal XRD instruments which have both either Patterson map or the electron density map which are which can be calculated automatically.

So, all you do is you put your sample in, record the spectrum and then analyze and then you send it for analysis ok. So, the spectrum is analyzed by the instrumental software and then you get the entire electron density map at the end of it ok. So, with this I will conclude this lecture. So, there is a 3rd lecture of week 9 ok. In the next lecture I will talk about microscopy techniques. In fact, electron microscopy is again a very powerful technique to analyze crystals and that will be that we will conclude week 9 ok. So, the 5th lecture will as usual be reserved for practice problems and review of the contents of week 9.

Thank you.