Symmetry and Structure in the Solid State
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Lecture - 57
Powder Diffraction 2

So, let us look at what are these refinable parameters we are talking about in a profile.

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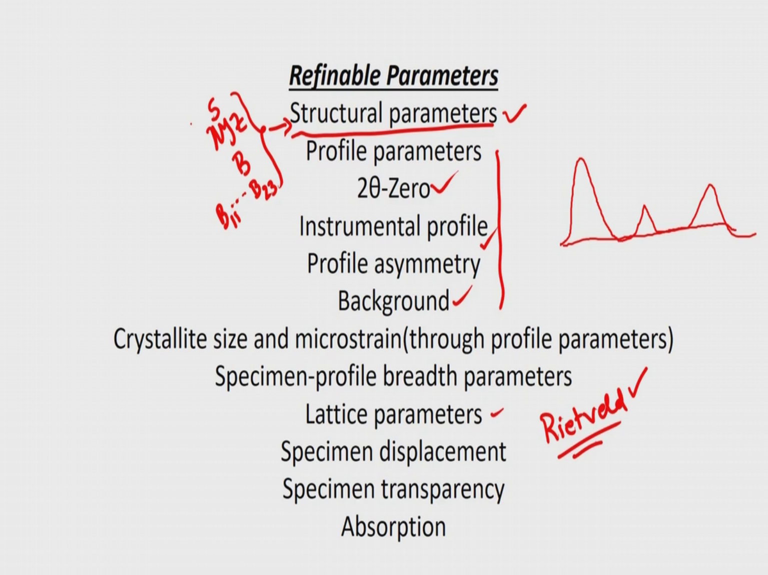

Refinable Parameters

S, xyz, B, $B_{11} \cdots B_{23}$ → Structural parameters ✓

Profile parameters

2θ-Zero ✓

Instrumental profile ✓

Profile asymmetry

Background ✓

Crystallite size and microstrain(through profile parameters)

Specimen-profile breadth parameters

Lattice parameters ✓

Specimen displacement

Specimen transparency

Absorption

Rietveld ✓

So, let me do one small my specialist diagram and draw a profile. It is not looking very bad, but it is a very bad diffractometer on which this profile has been obtained, but it is we can discuss that. So, we have a profile and this profile has to be fitted now. So, it is it has a certain x direction gives us the 2 theta value, the y direction gives you the intensity. So, the x value we read out and it could be 1 peak, it could be 2 peaks, it could be 3 peaks.

So, what are all the refinable parameters which will fit this particular shape of our profile. One of course, is the structural parameter which we do not have we do not know the structure. So, we will not touch it. So, we will keep it separately, but those are refinable remember if you know the structure if you know the positions of the atoms then these are also refinable parameters in the way we discussed in the case of a single crystal analysis the so called refinement procedure.

The profile parameters can be separated out from the structure parameters and those are the 2 theta-Zero which is specific to the instrument. Sometimes the instrument alignment is such that there is a little deviation from what we call as 2 theta-Zero. So, that has to be normally it can be estimated or the instrumentation instrument people will give us that particular value. It can also be ideally determined by collecting a standard data.

For example, if you put silicon and you have to get a reflection at 2 theta 28.65, if the 2 theta is at 0, so, you put silicon on the machine and find out where the peak is coming and that will give you the 2 theta-Zero. If it is coming at 28.6 then you know there is a 2 theta is shift of 0.05 in the in the negative direction. So, that correction has to be applied. So, and it also is a refinable parameter. We can vary it with respect to the length the extent to which we can carry out the structure determination in using 2 theta the profile refinement using 2 theta.

Then there is a typical instrument for profile one of them is caused by me just now. So, it can have a shape throughout like this is a issue which we can be corrected, then profile a symmetry which is very obvious in this profile which I have drawn. Then you know if you now consider the powder pattern to be going from a certain 2 theta value to certain other 2 theta value. So, let me extend it like that. Then there is a background which goes like that.

So, the background which is goes going like that need not be a straight line. It can be falling off with respect to sin theta it may be a first order function, may second order function. So, we have a polynomial which takes care of fitting the background. So, we can now use those as the refinable parameters. Refine the functions of the polynomial to account for the background and this is a very important factor. How you account for the background now will tell you how many how accurately you can get the peak positions and their intensities. Suppose, you put the background way up here then you lost all the reflections.

So, essentially background selection is a very crucial factor and the way it is done is to choose the background along the 2 theta directions starting from one of the low angle regions to the highest one and choose some 20 or so points which are definitely not coming under any peak indication even if there is a little kick here we do not take it as a background point. So, thus background points now are fitted with a polynomial so that the peaks and the peak position stand out. And, so, this is this is a little tricky issue, but again these are refinable. So, profile refinements will handle this kind of a phenomena.

Then of course, crystallite size and microstrain and this we one once we have the profile parameters analyzed we can look into those issues. Specimen profile breath parameters this is due to the nature of the specimen itself as I mentioned in the beginning the choice of the sample preparation. So, if there is no such preparation done somebody throws the powder on the diffractometer. Each powder particle you can call it as a particle will have different sizes.

So, the size of the grain will be different and if different size grains are there it will also introduce a certain breadth associated with the peak. So, the peak become wider. It has nothing to do with the fact that it has the size effect. It is because of each crystal has a different size.

So, if you have the sieve experiment which we discussed yesterday, then it is possible to look at the sieve experiment and then get uniform sized particles and then it is it will not have this difficulty of specimen profile breadth parameters, but if that does exist we can refine them. And, of course, the most important thing is the lattice parameters see we determine some abc, alpha beta gamma by indexing hkl peaks. We identified and we identified maybe 20 maybe 30 depending upon the quality of your diffraction data. That is probably not an indicator of the correct lattice parameters. So, lattice parameters also can be refined under the profile parameters.

So, profile parameters are so many, specimen transparencies, specimen displacement these are all issues and of course, the major thing is the absorption. Because it depends upon how many heavy elements are there in your material if there is a heavy element. Particularly when you are doing a pharma analysis and your excipient is let us say titania; it has titanium in it and as a consequence one has to be worried about the absorption effects. So, this absorption is also a refinable parameter and so, when once we refine all these parameters we can do the profile fit.

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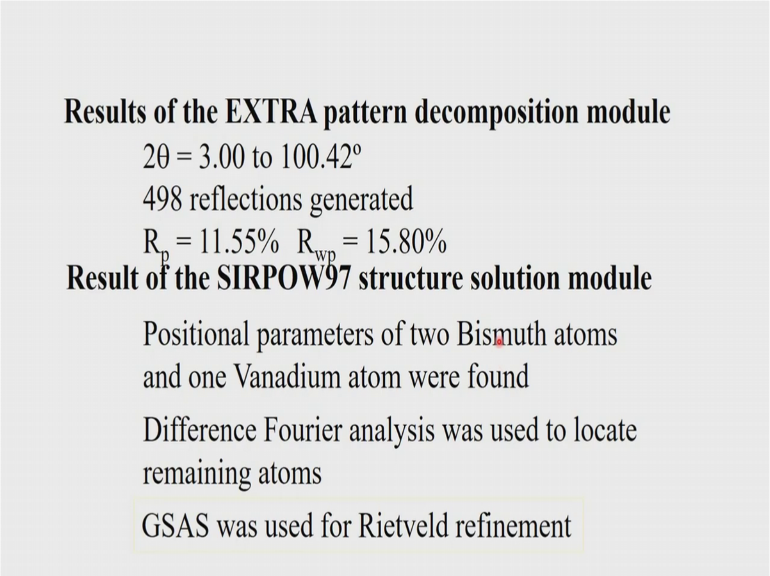

Results of the EXTRA pattern decomposition module

$2\theta = 3.00$ to 100.42^{o}

498 reflections generated

$R_p = 11.55\%$ $R_{wp} = 15.80\%$

Result of the SIRPOW97 structure solution module

Positional parameters of two Bismuth atoms and one Vanadium atom were found

Difference Fourier analysis was used to locate remaining atoms

GSAS was used for Rietveld refinement

And, there are packages that are available to do both the pattern decomposition as well as the structure determination. Now, what I will do is I will take the profile refinement examples when we discuss the polymorphic issues. Here I am going to take you directly to the structure determination protocol. This is ab initio structure determination protocol; that means, you have no idea of the structure you recorded the powder, you did a pattern decomposition using this package called EXTRA, the program you can do the pattern decomposition. And, this pattern decomposition is done in the following way. We consider the data from 2 theta 3 to 100.42 degrees and a given some particular compound we are we are collected the data I think the picture of that is somewhere here.

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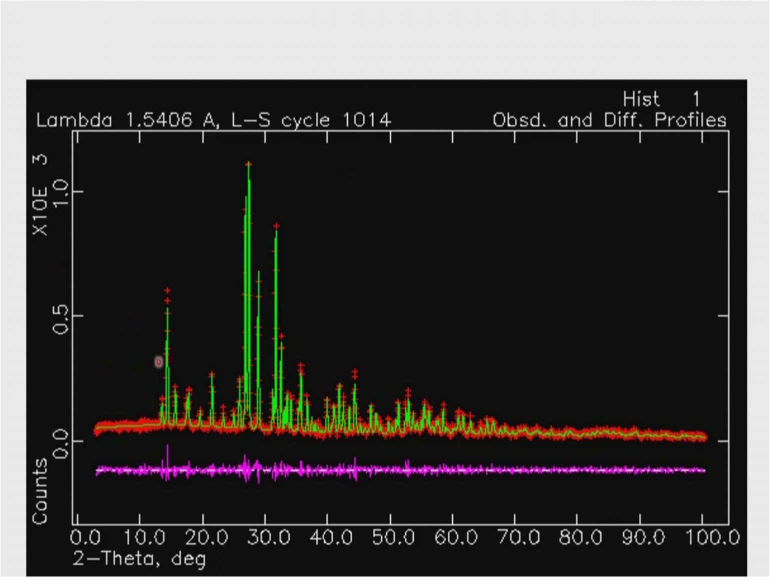

So, this green line is the powder diffraction pattern. The green line which you see here is the powder diffraction pattern of a compound. This is bismuth vanadate and vanadate different kind of bismuth vanadate. It is not a direct bismuth vanadate, it is a substitute at bismuth vanadate a compound for which the structure was not known and you see it is a very complicated pattern. In fact, it indexes as a triclinic system.

So, we have this powder pattern. So, we now want to determine the structure of that compound. How are we going to do that? What we do is we now go back and look at the 2 theta values. We take the 2 theta values from 3 to 100.42 and the data are collected at 0.02 degree intervals; that means we have a very large number of observations and what we do here is to consider each one as an observation.

So, whether it is a peak or otherwise each measurement is now considered an observation. So, we have so many measurements that are available with respect to 2 theta. And, so these measurements now which appear here with on the green line or the powder diffraction pattern of that particular compound.

So, the example here which is given here is that we that we were able to isolate and identify 498 reflections. So, it is not just the peaks if you count the number of peaks here it is 1 2 3 4 5 6 like that if you count maybe about 35 to 40 you will get. But, if you do this fact that we if you do this analysis of where each and every hkl can come in this crystal system when once you have indexed the pattern, the pattern has been indexed.

The abc, alpha beta gamma is known. So, we can calculate how many reflections will come up. So, each and every reflection is assigned to the corresponding 2 theta value and that particular 2 theta value is now considered a reflection and the intensity is considered as a measurement. So, when we do that as a intensity measurement, then we will get the 498 reflections generated. Let me take you back here to show what I mean by that.

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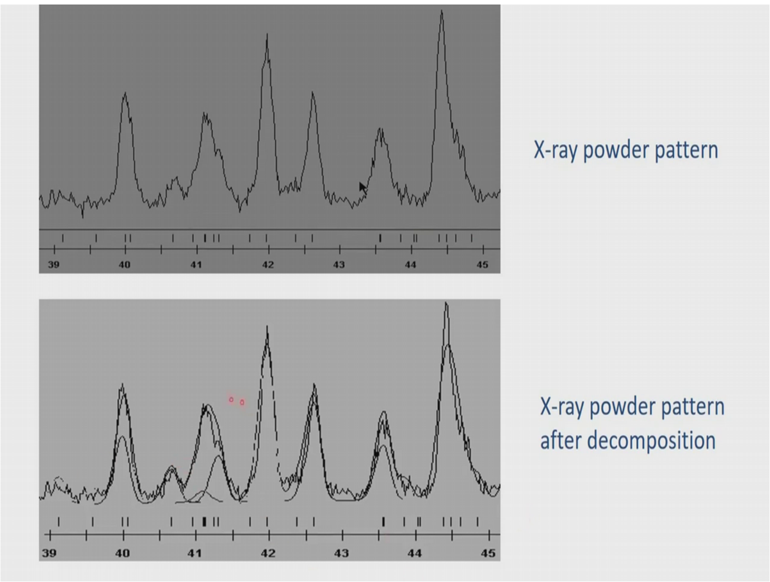

X-ray powder pattern

X-ray powder pattern after decomposition

So, if you look at this one if you look at the counter peaks 1 2 3 4 5 6 7. So, in this case there were seven peaks on the powder pattern, but if you look down here and count the number of reflections that are possible you will see 1 2 3 4 5 6 7, a overlapped peak 8 9 10 11 12 13, overlapped peak 14 15 16 17. So, you have a very significantly larger number than what you have there and of course, the overlap peaks will remain overlap. So, we have to do the pattern decomposition to identify individual ones and we have done that through profile analysis. So, if we have done that exercise we will end up getting 498 reflection. So, it is as though you have a single crystal data now which has given us 498 reflections.

Then you calculate the profile R. The R factor associated with the profile, how do you do that? The R factor that is associated with the profile can be obtained in the following way you have the powder pattern. Now, based on the idea of where the reflections should come we have assigned the intensities. The assigned intensities will generate reflections and those reflections are marked as plus here. So, all these are possible positions of where the intensities can come in this powder diffraction pattern.So, the points plus is therefore, the I calculated and this is the I observed. So, for every point we have a I observed and I calculated. So, what did we do in the least squares refinement in the single crystal case we took the modulus of f of hkl minus modulus of the observed f hkl minus the calculated f hkl the modulus and then we made it a minimum quantity by doing the refinement protocol and then we calculated an R factor.

So, similarly we calculate an R factor here and that R factor is now associated with the profile. So, we call it as the profile R factor. Of course, the each and every measurement is now benefit is has a different advantage because at lower angles we have more intensity at higher angles we have less intensity. So, we need a modifying function and that function is the weight factor. So, we attach what is known as a weight factor and therefore, we have two R factors the profile R factor which is 11 percent here 11.55 percent which is pretty good for a powder diffraction pattern and the weighted R profile is 15.80 percent.

So, when we have this kind of a situation we can believe that the 498 reflections are reasonably well generated. So, we now have a list of hkl and the intensity 498. It is still not sufficient you know in a single crystal as you all know by now you have thousands of reflections for a unit cell of a defined value. So, here we get still not that kind of numbers, but 498 reflections is not a bad idea. So, using these 498 reflections we can either use the Patterson methods or direct methods to hope and get the positions of the atoms.

So, in this particular case luckily for us with the example which we took, in fact, this is the structure which was determined as the first ever structure in India for a ab initio measurement and this was done in our laboratory by a person by name Digambar Porab who is now teaches in Goa. So, this compound we know is a bismuth vanadate ok. So, it has two bismuth atoms and one vanadium atom according to the molecular structural formula and using that information we now went on to use the Patterson synthesis.

So, 498 reflections we use the Patterson method we also use the direct method and then we in both cases we were able to identify two bismuth atoms and one vanadium atom uniquely because these are standing above over and above the oxygen atoms which are present. So, when once we have this information we cross checked with using both the methods in Patterson gave directly the two bismuths and one vanadium. We verified this by running the direct methods also and found out the two bismuths and vanadiums are reasonably well located with a good R factor over all R factor associated with this 498 reflections.

Then what was done was to use this approach to do a difference Fourier. So, what we did was we accounted for two bismuth and vanadium and did a difference Fourier map and this difference Fourier map on this program that was used is program called GSAS that was used for the refinement of the structure later. But, at this moment Patterson and direct methods gave the positions of the heavy atoms. These every items were now subjected to difference Fourier analysis; that means effectively we remove the bismuth and vanadium and see what is left in the density.

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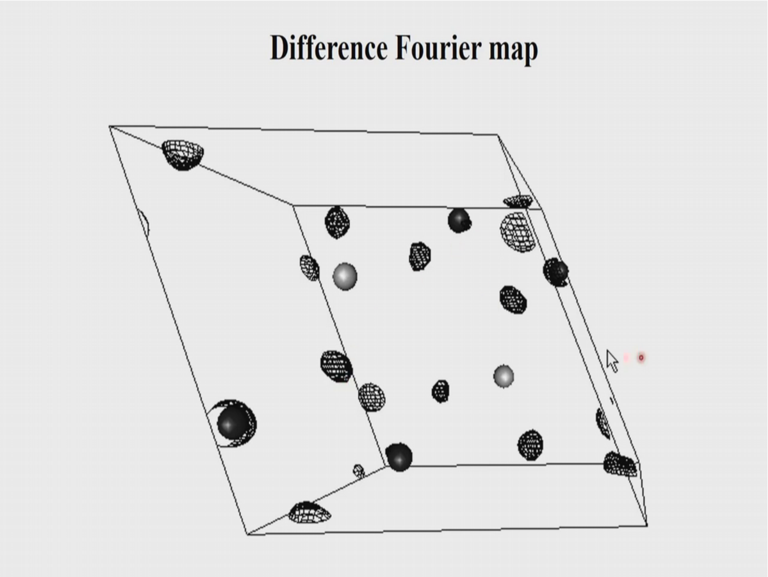

Difference Fourier map

And this picture which is shown here gives us the difference Fourier map and you see the two bismuths here and the vanadiums here, the vanadium here, the bismuths there and so, this is a 3-dimensional plot of the difference Fourier and whatever is the density which is coming up here represents now the oxygen positions. We then identify these atoms, got the oxygen positions and put all the heavy atoms as well as the light atoms together and theta refinement. The refinement was a profile refinement, but with the structure information available with the structural parameters put in.

So, what are the structural parameters we are talking about? The structural parameters are the same as the structural parameters we always refer to that is the position coordinates xyz and then the thermal parameter which could be isotropic B or unisotropic B 11 to B 23; the 6 parameters and of course, the scale factor. So, these now define our structural parameters.

Now, we here what we are doing is to put the bismuth and the oxygen positions into this one and do a refinement and then do the difference Fourier map. And, that difference Fourier map of course, every time as we do the structural parameters we should also refine the profile parameters. The way it is done is in fact, very well organized and that is known as the Rietveld refinement due to a person called Rietveld.

So, what we should remember particularly when people loosely talk about Rietveld refinements in many cases because Rietveld refinement is in the phrase itself is a refinement technique; that means, you should have a starting model the starting model in this case came from our position of the bromine, the position of vanadium and then the difference Fourier map given the positions of oxygen's. So, we are not doing any other aspect. See we took the powder pattern and decompose the powder pattern and identified some 498 reflections use the Patterson approach and the direct method approach to get to the heavy atom positions. After that the heavy atom positions were put in and refinement was done.

So, before we could do all these things we have done the profile parameter refinement in the beginning that is we have fitted the every powder diffraction peak with a profiles and we have refined the parameters that are associated as is indicated here. So, essentially what I am trying to tell is the way in which we have to do the Rietveld refinement, it is not a structured determination protocol Rietveld refinement will not help you to solve structures there is a misnomer and so, I want to remove that misnomer because Rietveld refinement is only a refinement technique and it uses both the profile as well as the structural parameters.

So, the number of parameters are many more because you have to have 2 theta-Zero, you have to have instrument profile, you have to have background, you have to have lattice parameters everything to be refined. Before that; you in before you introduce the structural parameters into the protocol. So, when you do this refinement therefore, the so called Rietveld refinement you need a starting model. The presence of the starting model can be generated the way we discussed or the starting model can be obtained from the database.

So, if we go to database icd database and look at different kinds of bismuth vanadates, the data that is available on those there is a good possibility that there may be a structure very closely related to the structure with the cell dimensions agreeing nearly the same. So, in such a situation we can take those coordinates and put those coordinates as the structural parameters and go ahead and refine, then it will be a successful refinement.

So, in other words Rietveld refinement can do only small changes in the starting model. It cannot determine a structure find a position of an atom in the in space and so on. And, so, so, the refinement technique which is used under the Rietveld protocol is essentially referred to as a toothless technique because it can only grind it to a certain extent. It cannot grind it to a final structure refinement position final structure refined positions of the atoms.

So, keeping that in mind it is a very extremely useful technique because any powder diffraction pattern in principle its structure can be determined ab initio like the way we discussed or we have to now find ways and means in which we can find the starting models. If we can do that then this Rietveld refinement protocol will do a wonderful job and we will get a good fit as you have seen here all these are the calculated positions marked in marked as red in this particular case.

So, all these marked in red as plus or the calculated positions the values of the intensities I calculated. I observed is from this and then you see the pink display here telling how well it is the well is the feet. So, we can calculate the corresponding R factors and this is a fairly successfully determined structure.

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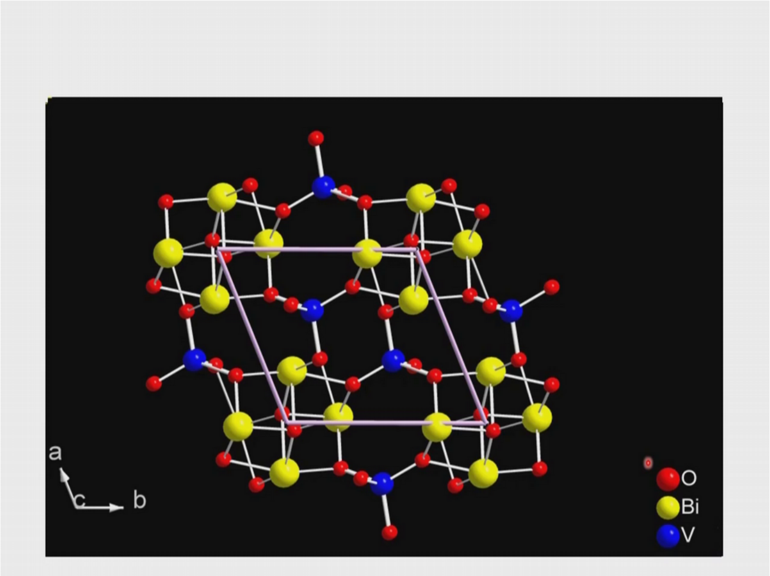

So, the structure is shown here. It is not a simple structure; it is a fairly complex structure this is the biggest structure of in those days determined by ab initio structures. Of course, there is there was a structure of zeolite which was determined around the same year by Lynne McCusker and that is a much much bigger structure and the much more challenging structure. But, this is one of the bigger structures which came from our laboratory. So, this is the structure of bismuth vanadate. The positions of the atoms are very clearly seen here. It is asthough it is a single crystal structure. All the details associated with the single crystal structure can be derived from this.