

3.091SC Introduction to Solid State Chemistry, Fall 2010  
Transcript – Session 18

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PROFESSOR: OK, OK, Settle down. Settle down. It's 11:05. It's time to learn. All right. Last day we were looking at the emissions spectrum of the target in the x-ray tube. The target is the anode, and it's being a bombarded by electrons that have been accelerated across a potential difference of some tens of thousands of volts, and this was what we saw as the output, intensity versus wavelength.

We see this whale shaped curve which we have attributed to bremsstrahlung, which is the breaking radiation. And then if the voltage is high enough, high enough to do what? High enough to eject inner shell electrons, we will get the cascade, and the cascade will give rise to specific values of wavelength associated with transitions within the target atom.

There's too much talking. I want it absolutely silent or else somebody is going to leave. That's the only way it works here. I talk. You listen. And if you have a problem with that, there's a door here. There's a door there. And there's a door at the back. So let's get it straight right now. It's the only way it works here.

Now what happens is that these characteristic lines are calculable in part. The K alpha line, the L alpha line we saw from Moseley's law, which is up here on the slide. and the leading edge of the whale shape curve, the bremsstrahlung is calculable by the Duane-Hunt Law. The rest of this is not calculable. So there it is.

What I want to do today is harness this radiation. The reason we were studying x-rays in first place was that we said they had a length scale that was comparable to that of atomic dimensions. And so now we want to close the circle here and probe atomic arrangement by x-ray diffraction. And it goes by this three-letter initialization XRD. And in order to use x-ray diffraction to probe atomic structure, we're going to make another model. And this model is going to be simple. And it's going to be inaccurate, but it's going to be good enough to explain the phenomena that we're going to study. So the first thing I want to do in constructing a model that will allow to use x-ray diffraction, is to model the atoms as mirrors. That's the first assumption that we make. We model the atoms as mirrors.

And when we model the atoms as mirrors, this means that we will invoke the laws of specular reflection. So if this table top is a plane of atoms, and I have a beam coming down at an angle, the laws of specular reflection say that the angle of incidence will equal the angle of reflection. So that's all we're doing by modeling the atoms as mirrors. Laws of speculative reflection apply. So that simply means that the angle of incidence, theta incidence equals theta reflection. And you'll see how that comes into play in a minute.

And then the second thing we're going to do in order to get intensities is to use the concept of constructive and destructive interference. OK. So we apply interference criteria. And I will explain what that means in a second with a diagram. But in dense text, it simply means that in phase rays-- it sounds like this rain in Spain falls mainly in the plain-- in-phase rays amplify. And out-of-phase rays dampen.

So at some point, you'll study this in physics, but we need it right now, so I'll give you a little bit of foreshadowing, and then you'll be ahead of the game when you meet this in physics. So what I'm going to do is I'm going to show you two rays, and they both have the same wavelength. And I want to show you in phase. And so I want to illustrate this concept here, in-phase rays amplify.

So let's give one ray here. I'm going to depict it as a wave. All right, so that's ray number 1. And beneath it, is ray number 2. It's got the same wavelength. So that means crest-to-crest distance is the same, and if it's in phase, in phase means that crest lines up with crest, trough lines up with trough. So I'm going to make another one seemingly identical. It's supposed to be identical to the capacity of my ability to draw.

And so what this means is that these will amplify. So 1 plus 2, 1 plus 2 will give me something that looks like this. I'm going to line it up again. Only now the amplitude is double the amplitude of a single ray. That's what I'm trying to depict here. OK. So this is amplification.

Now over here, I want to do the same thing. Only I'm going to have two rays, same wavelength, but out of phase. OK, so in phase is here, out of phase is to the right. So we'll have ray number 3, which does this. And ray number 4, I'm going to line up with the crest of ray number 3, the trough of ray number 4, but it's going to be the same wavelength. So the distance between successive crests is the same. Only they're going to be offset by exactly half wavelength.

So the crest here of wave 3 lines up with the trough of wave 4. The trough of wave 3 lines up with the crest of wave 4, and so on, and so on, and so on. And if I drew this thing accurately, it would be obvious to you. But since I can't draw very well, then we're going to take 3 plus 4. And the sum of the crest and the trough is 0. The sum of the trough and the crest is 0. And so the sum here is 0. All right this is total destruction. This is cancellation.

So in the extreme, you can have destructive interference that dampens to the point of obliteration. OK, so that's the two extremes, full amplification and complete cancellation.

So now, I want to take this concept of planes as mirrors and rules of interference criteria, and now what I want to do is illuminate. And I want to use the full board here. So here's what we're going to do. We're going to take in phase, coherent-- that's what coherent means. Coherent means that the radiation is in phase and monochromatic. What's that mean? Monochromatic means one color, which means single wavelength. So I have something of a single wavelength in phase. Coherent, monochromatic, incident radiation, so I've got a plurality of rays. I have this thing flooded by a beam.

So what I'm going to do, is I'm going to draw some atoms here. And I'll put a second batch on top. And now I'm going to model these as mirrors. So I'm going to have the

incident beam come in like so. The incident beam comes in like so at an angle  $\theta$ . So this is  $\theta$  incident. This is the angle of incidence. And according to our model, the beam is reflected at the same angle. So this is  $\theta$ , reflection of  $\theta$ . Reflection equals  $\theta$  incidence. So that's the first thing that we do.

And then the second thing we do, is we use the laws of interference. So I'm going to take a second beam, and it's going to go down to this atom here. So I'm going to bring it down like so. And it's going to come in at the same angle. And it's going to leave at the same angle. And if you'll excuse the drawing, these lines should be parallel. They should be coming in parallel, and they should be leaving parallel where these angles  $\theta_i$  and  $\theta_r$  are the same.

Now how do we invoke the interference criteria? Well what I'm going to do is put a marker here. I'll put a marker. And I'll call the first one ray number 1, and the second one ray number 2. And what I'm going to show is if I start from ray number 1-- maybe it's time for colored chalk-- so if I start from ray number 1, to show that it's in phase with ray number 2, I'm going to draw this little waveform, and they're both lined up. So you can see crest lines up with crest. Trough lines up with trough, and they both have the same wavelength. So that makes the point coherent, monochromatic.

But now things get interesting, because you can see that ray number 1 travels a shorter distance than ray number 2, and we can put on some coordinates here and mark the geometry, so we can say that the point at which the ray number 2 has to start traveling a longer distance, I'll drop a normal down, and I'm going to call this point A. This is point A. The bottom here is point B. And then up here where it catches up with ray number 1, the reflected ray number 1, I'm going to call this point C.

So you can see that ray number 2 has to travel this extra distance, AB plus BC. And now, if I want to get out to here where I'm now in the reflected zone, and I want ray number 1 reflected and ray number 2 reflected to continue to be in phase, there's a geometric constraint on the dimension of AB plus BC, isn't there?

That length, AB plus BC must be a whole number of wavelengths. It must be an integer number of wavelengths of whatever this thing is, otherwise, these two will not be in phase. So that's the interference criterion. And  $n$  can equal 1, 2, 3, and so on, so this is called the order of reflection.

And then we can go through the trigonometry. I'm not going to do it in class. It's just a waste of time. It'll bore everybody to tears. But if you want to do that at home at some point when you've got nothing to do, you can go through. You've got all the numbers here. You know the value of  $\lambda$ . You know the distance AB, and you know what this distance is. This distance between successive planes is your  $d_{hkl}$ , isn't it?

So if you go through all of this analysis, you will show that  $n\lambda$  is equal to 2 times the  $d$  of the  $hkl$  spacing times the  $\sin$  of  $\theta$ . And this is called Bragg's Law. And Bragg's Law governs the reflection of incident radiation by a crystal.

Now you'll notice I didn't put an apostrophe here. Some people put the apostrophe here, because the man's name was Bragg. Some people put the apostrophe here because, in fact, it was father and son. And they both together won the Nobel Prize

in 1915. Now there have been people who lived to see, as Nobel Prize winners, one of their children win the Nobel Prize. but this is the only time in history a father and son team together won the Nobel Prize for the same work. And there are undoubtedly people sitting in this room who think the fact that the father and son could work together in physics for an extended period of time alone is deserving of the Nobel Prize.

Now in 3.091, I'm going to keep it simple, always choose first order reflection, always  $n$  equals 1 in Bragg's Law. So therefore, we will write Bragg's Law as  $\lambda = 2d \sin \theta$ . And to make the point, the  $d$  is specific to a particular set of planes. So it's a  $d$  spacing of the  $hkl$  planes. And it's the  $\theta$  associated with the correct reflection of the  $hkl$  planes.

Now how does destructive interference come into play? Destructive interference comes into play should there be a situation where I have a third ray. I'm going to bring a third ray in also at the same angle of incidence. And that ray is halfway between these two rays. And what situation could that be? That could be a situation in which the crystal structure has in a plane out from the board, an atom that sits halfway between these other two atoms.

And if that happens, you can see. We can go through the derivation. But there's going to be a path length difference that's exactly  $1/2$  wavelength different. That's bad. It's not just there's going to be some measure of reduction. It's going to be total cancellation. And so by going through the set of crystal structures and recognizing that when you have  $1/2$  wavelength difference, you get destructive interference. And therefore, you will see no line. The incident radiation will come in at this angle, and at the reflection angle for that particular plane, there will be nothing detected.

So you can say that you have a combination of selection rules that involve the integral of both the rules of interference and interaction with the crystal structure. So let's generalize this and say if we take interference criteria plus the crystal structure, that is to say, the instant relationship of atom positions for a particular specimen, the combination of that will give rise to the set of expected reflections.

So only when you satisfy the Bragg criterion do you get reflection. So you move the specimen. And only at that special angle will you get the reflections, will you get constructive interference. So this, in fact, is a fingerprint. This is a fingerprint of the crystal. In this case, we're not getting the chemical identity. We're getting the structural identity. So we can determine if something is BCC, FCC, and so on.

So for example in BCC, that's exactly the case that I just illustrated. So in BCC we have atoms at the eight corners. And we have an atom dead center. There's a central atom. And the central atom lies in  $002$  plane, doesn't it? The base of this is  $001$ . And the top is an  $001$ . But the central atom is an  $002$ . And  $002$  is halfway between successive  $001$ .

So can you see that light that comes in? And it's going to be constructively reinforced. Off of  $001$  is going to be destructively reinforced off of  $002$ , and the result is that in BCC, no  $001$  reflection observed.

The same thing happens in face centered cubic, right? What's the face of face centered cubic look like? It looks like this, doesn't it? So there's an  $001$ . Here's an  $0$

0 1. What about this space centered atom? Where is it? That's an 0 0 2. It's halfway between 0 0 1.

So at the angle where you would've expected, if you use the Bragg Law and calculate the angle at which for your particular crystal, because you know the d spacing. You fix the wavelength of your x-radiation coming out of the generator. At the angle where you would expect to see reflection off of 0 0 1, you will see nothing, because 0 0 2 is canceling 0 0 1.

So you don't have to worry about all this. This has all been tabulated for you. Somebody has gone through and done all of this. Well, this is just making the point. See, there's a simple cubic. All the planes are reflecting. There's body-centered cubic. That's  $a/2$ . There's face-centered cubic  $a/2$ . 0 0 2 is going to cancel 0 0 1. You're not going to see anything there.

So people have gone through. And they've made this set of rules for reflection. So simple cubic, you get reflection from all the planes. Body-centered cubic, you just get these planes here. And it turns out that there's a simple rule that compactly represents which planes are going to reflect in body-centered cubic. And in BCC, the hkl, it's the planes for which h plus k plus l is an even number. h plus k plus l is even. And 0 was counted as even.

So for example, 0 0 1 h plus k plus l is 1. It doesn't reflect. 0 0 2, 0 plus 0 plus 2 is 2. It does reflect. And so on. You just go down the whole line. And so these are in ascending order of h squared plus k squared plus l squared, because that's a nice way of deciding how to add them up.

And now in FCC the selection rule is a little bit different. In FCC you get reflection from planes when you write the HKL such that h, k, and l must be either all even numbers, or all odd numbers, or some people like to say unmixed. Some crystallographers say unmixed, meaning you can't have a combination of even numbers and odd number. So for example, 0 0 1 won't work because 0 is a zero. That's even. 1 is odd. But 0 0 2, h plus k plus l all even or all odd, there you go all even or all odd unmixed. So this will work. And then so on. So you can go through and see which ones work. All right.

So the next one here is in the sequence. This sums to 1. And what would sum to 2? It would be 0 1 1. And 0 1 1 doesn't work either because zero is even. And 1 is odd. The next one of the sequence is 1 1 1. These are all odd. So that one reflects. So in FCC, you don't see 0 0 1, 0 1 1. But 1 1 1 does reflect. And then 0 0 2, which is the next one, because 0 squared plus 0 squared plus 2 squared is 4. This is even even. So that one works. So there's the sequence.

And so now what we can do is use this technique in order to make measurements. But before we do so, I want to show you the experimental measurement, one way. There's several ways of conducting the measurement. And so the first way I'm going to show you is called diffractometry. And you can do this over in Building 13. If you get yourself a UROP, you might be assigned to make some measurements.

So diffractometry is a form of x-ray diffraction. It's one of the techniques. And the way it works is you fix the wavelength and vary the angle of incidence, you don't rotate the x-ray generator. You rotate specimen and present continually varying angles to the thing. So this shows the technique in operation.

So you have a specimen sitting here. The specimen can either be a thin film, or in other instances, we have a finely ground powder. So each of the powder grains presents a different angle. And coming out of the collimator is the monochromatic. We want a single wavelength. So this collimator means it's monochromatic and coherent.

So that beam comes and strikes the specimen. And for historical reasons, instead of calling this the angle of incidence, and this the angle of reflection, they call the angle that goes to the detector  $2\theta$ . In other words, the projection of the beam, this is  $\theta$  incident equals  $\theta$  r. So this is really  $2\theta$  incident, or it's  $2\theta$  reflected. It's the same thing.

So you'll see x-ray data usually reported in units of  $2\theta$ . And here's the detector. And then all you do is you rotate the specimen. And by rotating the specimen with a detector, you're able to get the entire set of reflections. And whenever you move through an angle that satisfies the Bragg Law, you get a peak in intensity.

And here's what the output would look like. So you're plotting intensity as a function of  $2\theta$ . So somewhere along here at around, it looks like about 38 degrees, you have satisfied the Bragg angle, and you get constructive interference. When you move off of 38 degrees, destructive interference reigns supreme, and you get almost no reflection. Then you get to the right angle for  $200$ , you get reflection. Well, all you get is these lines. You don't get these numbers. These numbers you don't get for free.

So here's the experiment that we're going to do. We're going to run our x-ray generator with a copper target. Why do I tell you the copper target? Because you're going to fix the wavelength. And you fix the wavelength by choosing the target. So we've got copper target in our x-ray generator, OK?

So remember, the sample is not the target. The sample is what is being irradiated. This is being bombed by the electrons in the tube, copper target in x-ray tube, and that means that the  $\lambda$  of the radiation is  $\lambda_{\text{copper}}$ . And I'm going to use  $\lambda_{\text{copper K alpha}}$  because I know it's wavelength to five significant figures. It's 1.5418 angstroms.

And here's the data set. I looked this up in the literature. Here's the data set from the experiment. And that's all you get, a set of  $2\theta$ s. So here's my challenge to you. I'm telling you you've got an unknown sample that's cubic, and there's your data set. The task for you is determine two parts to the question. And we're going to do it together.

First part, determine the crystal structure. So it's either FCC, BCC, or simple cubic. And the second part is determine the lattice constant, the value of the lattice constant. So you can get quantitative measurements. So I'm going to show you how to do it.

So how are we going to do it? We're going to use this technique. This is my self-help book for you. And here's the key. Here's how I came up with this. There's a way to unravel this. And the way you unravel this is to take these two relationships. You have  $\lambda = 2d \sin \theta$  is 1. And you also know that  $d$ -- in fact, I'm going to keep writing  $hkl$  subscripts here-- you know the  $d_{hkl}$  is equal to  $a$ . That's this

lattice constant. Be sure this is lattice constant. This is the cube edge measurement lattice constant divided by the square root of  $h^2 + k^2 + l^2$ .

So what I do is I combine the two. If you combine these two, you can end up with this relationship. If you combine the two, you get  $\lambda^2$  over  $4a^2$  equals  $\sin^2 \theta$  over  $h^2 + k^2 + l^2$ .

And this is the key. Why is it the key? The value of  $\lambda$  is set by you. You chose the target. The value of  $a$  is set by the sample. That's the lattice constant. So the ratio of two constants is a constant. Agreed? So this is a constant. So if the left side of the equation is a constant, the right side of the equation must be a constant. But  $h$ ,  $k$ , and  $l$  vary. And  $\theta$  varies. But the ratio of the variation, when mapped into  $\sin^2 \theta$  over  $h^2 + k^2 + l^2$ , this must be a constant. And that's going to be the way I work through this delightful problem.

So let's see. Start with 2  $\theta$  values, and generate a set of  $\sin^2 \theta$  values. That's what Sadoway says first. So I took 2  $\theta$ . And all I did was make 1  $\theta$ , and then took the sin of it, and then took the square the sin. So this is the data set transmogrified into  $\sin^2 \theta$ .

All right, what's the next thing he says? Normalize by dividing through with the first value. So I'm just going to take this whole series and divide it by 0.143. And now I end up, instead of 0.143, 0.191. I have 1, 1.34, and so on. That's what I mean by normalize. Normalize to the first entry.

OK, What's next thing he says? Clear fractions. Clear fractions from the normalized column. So I'm going to multiply this by a common number. Because 1.34, remember this is experimental data. It's noisy. 1.34 looks like  $4/3$ . Doesn't it? It's fuzzy logic. And 2.67 looks like 2 and  $2/3$ , 3 and  $2/3$ . That's roughly 4. 5 and  $1/3$ . The 3 looks like a magic number. So if I multiply this column by 3, I get 3, 4, 8, 11, 12.

What does it say next? Speculate on the  $h$ ,  $k$ ,  $l$  values, that if expressed as  $h^2 + k^2 + l^2$  would generate the sequence of the clear fractions column. And then that's going to take me to the selection rule. So I say, well how do I get 3? It's 1 plus 1 plus 1. 4 is 2 squared plus 0 squared plus zero squared. 8 is 2 squared plus 2 squared plus 0 squared. So I'm generating this thing.

And now it's pretty obvious, right? Because now I've got to use these. And what do I see here? Well, 1 1 1 are all odd. 2 0 0, all even. 2 2 0, all even. Gee, this looks like it conforms to the selection rules for Bragg reflection from an FCC crystal

And then to make sure that I'm on to something, what I do is this. Compute for each  $\theta$  the value of  $\sin^2 \theta$  over  $h^2 + k^2 + l^2$  on the basis of those assumed values. What I'm doing is I'm saying if my hunch is right, whatever I choose for the  $\theta$  and the assumed value  $h^2 + k^2 + l^2$ , that should be a constant that doesn't change. So let's test it. And sure enough, look. 0.0477, 0.0478, so it looks like I'm on to something.

And furthermore, I know what this is. That 0.0477 is this. This is 0.0477. And I know my  $\lambda$ . That's 1.5418. So now I can calculate my  $a$ . So now I've determined that it's FCC. Plus if I go ahead and I calculate the  $a$  value, I get 3.53 angstroms.

And if it's FCC and it's 3.53 angstroms, I bet it's nickel. So that's how you index this stuff. So there we are. There are the selection rules.

Now here's a little trick. Let me show you. Because when I go to index this, the first thing I do is I go for low hanging fruit. If you start looking for whether it's simple cubic, face-centered cubic, or body-centered cubic, let's look at the sum. So I've got simple cubic, body-centered cubic, and face-centered cubic. So the first plane on simple cubic, it's going to give me everything. It's going to give me 1, 2, 3, 4, 5, 6.

And FCC, what does it give us? If you start looking down there, it gives you 3, 4, 8, 11, 12. Well, this is so different. 3, 4, 8, 11 is so different from 1, 2, 3, 4. What does BCC give you? It gives you 2, 4, 6, 8, 10, 12.

Can you see you have a problem here? It's pretty easy to pull out FCC. But look at these two. Since you don't know, you're just normalizing. You can't tell. If I give you a number sequence that is in the order 2, 4, 6, 8, 10, how do you know that that couldn't be 1, 2, 3, 4, 5?

There's a hook here, though. Look at the sequence of  $h^2 + k^2 + l^2$ . Do you notice that there's no combination of  $h^2 + k^2 + l^2$  that gives you 7? You get 6. And then the next one is 8. But there is a sequence that gives you 14. So if you have a seventh line, if the seventh line to the first line, the ratio of  $h^2 + k^2 + l^2$  for angle number 7 to  $h^2 + k^2 + l^2$  for angle number 1, if it's equal to 7-- and point of fact it's not 7:1, it's 14:2-- and if it's equal to 8 for the seventh angle-- then it must be simple cubic. And now you've sorted it all out. So you're an expert now. Now you can do it.

OK, so you're going to get some practice on homework. So you can index crystals. You can determine a crystal structure. All right, a couple of other things we can do. There is a second technique. And it's called Laue diffraction after von Laue, who got the Nobel Prize in 1914. He beat the Braggs by one year for this technique.

So he shines. In this case for Laue, it's a slightly different technique. What Laue does, is he uses light x-rays. That means variable  $\lambda$ . So how would you get a fixed value of  $\lambda$ ? Well, you would pick off one of those lines, like maybe the K alpha line because it's a nice, singular line. And repress the bremsstrahlung and so on. But if I want a variable  $\lambda$ , where do I go for variable  $\lambda$ ? I repress the lines. And I go for the bremsstrahlung. So now I've got lines varying all across the x region of the spectrum. So I use variable  $\lambda$ . And I fixed the angle of incidence, whereas with diffractometry, I use a single value of  $\lambda$  and vary.

So here's the cartoon which shows what's going on. I'll do it one more time. So this is called camera obscura, which is darkened room. That's all this means is dark room. So let's say I've got the specimen on the back wall of this thing, and what I've got is white x-rays coming in. So the white x-ray enters through the face. I've got the plate here, and I've got the specimen sitting somewhere in between. And what happens is I get a spot pattern. I get a spot pattern. And the spot pattern is imitative of the symmetry of atomic arrangement.

So I have to say a little bit about symmetry so we know what that means. So let's take a look at symmetry. So I'm going to talk a little bit about rotational symmetries. So let's look at that. So first one I'm going to look at is an 0 0 1 plane. So if I just

take a projection of an  $0\ 0\ 1$  plane, it looks like this. Doesn't it? It's just the cube edge, or the cube bottom. So it's got a and a as the edge. And now, the rotational axis, it's about a normal rotational axis. A normal rotational axis.

So what I'm going to ask is how many degrees do I have to go through before I get this same image back. You can see that you go 90 degrees, it'll come back. If I stop at 45 degrees, it's going to look like this. You're going to say I know he moved the specimen. If I go 90 degrees, you can't tell it apart. So we define fold. The fold is equal to 360 divided by the basic angle of rotation. So we would say that this plane here exhibits 4-fold symmetry, OK?

Let's do a second one. The second one is  $0\ 1\ 1$ . So if I look at  $0\ 1\ 1$ ,  $0\ 1\ 1$  at this plane.  $0\ 1\ 1$  goes across the diagonal. So I'm going to take the diagonal here and plot it like so. So it's going to have an edge of  $a$ . And it's going to have the diagonal, which is  $\sqrt{2}$  times  $a$ . And if I put a rotational axis in the center of that, clearly if I go only 90 degrees, I'm going to tell that the thing is rotated. I have to go 180 degrees before I can't tell that there's been any disturbance. So this one here has 2-fold symmetry.

We'll do one more. Because there's only three major ones that we have to deal with. And that is going to be the  $1\ 1\ 1$  plane. And the  $1\ 1\ 1$  plane. And the  $1\ 1\ 1$  plane, I think I've got an image of it here. You can see the  $1\ 1\ 1$  plane drawn in this cube. So what's the face of  $1\ 1\ 1$  look like? The face of  $1\ 1\ 1$  looks like this. That's face of  $1\ 1\ 1$ . And if you go through this analysis, this is  $\sqrt{3}a$  because it's a diagonal of a difference persuasion. So this is 3-fold symmetry. This has 3-fold rotational symmetry.

And that means if I take a crystal such as this, for example. I've told you before, this is my silicon wafer, and this silicon wafer has been cut from a single crystal. So I'm looking at the edge of an atomic plane. The question is, which one is it? The crystal didn't come with a label on the side. I don't know what the crystal growth axis was. I started with a single crystal, and I dipped it into molten silicon. And just like rock mountain candy, I drop the heating coils and cause the liquid to solidify around the seed crystal. And I grow this salami that's about 8 inches in diameter, about 2 meters long.

So now I go and I cut these things with the diamond wheel. So I'm cutting them normal to the growth axis, but I still don't know what plane I'm looking at. So if I use the Laue technique and put the crystal like so, bombard it with white x-rays, and I look at the spot pattern. The spot pattern is going to give me one of those symmetries. And if I get a 3-fold symmetry, I know I'm looking at  $1\ 1\ 1$ .

I mean, it's not going to be some wacko plane. It's going to be either face, edge, or diagonal. And on the basis of the symmetry in the Laue pattern, I can tell which plane I'm looking at. They use this stuff. They use it to make the devices that are in your cell phone and your computer. I'm not just telling you a story. All right. So let's look at some others.

We'll go back to the Escher prints. Everything has symmetry. OK, so what's this one? See this? What's the symmetry? 4-fold. How about this one? What do you think? 3-fold.

I even went into Photoshop just to show you how dedicated I am. So I took this image. And I told Photoshop to give me 120 degrees rotation. And I got this. You can even see the fold in the book there. So I'm really doing it. It's coming back. It's 120 degrees rotation. How about this one? That's 3.

Now these are real Laue patterns. This is 4-fold. This is obviously 3-fold. This one is hard to see. But it turns out it's 2-fold. The one axis is just a little bit longer than the other axis. What about this one? That's our simple cubic puppy. Yes, 1-fold. Translational symmetry without rotational symmetry. You can make this by just moving them sideways. But you have to go all the way around. So that's 1-fold symmetry translation.

Look at this one? What's going on here? Is that one of the Bravais lattices? This is called Penrose tile, again rotational symmetry without translational symmetry. You can take a patch of this and move it rotationally. But you can't take and cover a wall with it. So that's rotational without translational. See? You can go around this way. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and reproduce this. But you can't use this as a unit cell and keep it hopping laterally and tile a wall with it. Here's another one, not a Bravais lattice.

All right. So I told you at the beginning of this unit that there are ordered solids and disordered solids. We've been focusing on ordered solids. They have a unit cell. They're periodic. And we call them crystals. And next week we're going to start looking at disordered solid. So they have no building block, no long range order. And we call them glasses. For a long time, people thought that solids have to fall into one box or the other box. And then the best thing that can happen in science is not, oh, yeah. That's exactly what I expected. It's, I wonder what that means. And there was one of these moments in 1982. In 1982, a man by the name of Danny Shechtman from Technion in Israel, was over here in the United States working at the National Institute of Standards and Technology, which used to be National Bureau of Standards down in Gaithersburg, Maryland.

And he was looking at a set of aluminum-manganese alloys. So aluminum is a metal. Manganese is a metal. You can make a solid solution which we call an alloy. And these are highly ordered. And what he found in his Laue measurements, were rotational symmetries that are impossible in a crystal. He was getting 5-fold symmetry. You can't get 5-fold symmetry. There is no set of planes here that will give you a 5-fold symmetry.

They lack translational symmetry. They were called aperiodic. And the popular name for them was quasicrystals. So here's the Laue pattern of one of Danny Shechtman's aluminum-manganese specimens. I think this is 25% manganese and aluminum if I'm not mistaken.

So let's count, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10. You can't have 10 or 5. Atoms don't work that way. But he got it. He got it, 5-fold, 72 degrees.

Now this is really, really exciting. This is a shot of his lab book. You're looking over his shoulder. These are the specimen numbers. And this is aluminum 25% manganese, April 8, 1982. So it's just another day at work. You could be doing this. And he can't believe what he's getting. He's wondering what's going on. You can't contribute this to a calibration error on the instrument. This thing is on unassailably

5-fold symmetry. The joke is that this is not far from the Pentagon. Only within shouting distance of the Pentagon would you discover 5-fold symmetry.

So there it is. So where have we come with all of this? We've come with the ability to start with some very simple ideas about x-ray generation. And we've come to the point where we can characterize crystals, get quantitative measurements of their lattice constants, and by using Laue techniques, investigate symmetry.

OK. Let's adjourn. We'll see you on Friday.

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