

**PROFESSOR:** Since  $z$ , that's straight up. And that is going to provide for you a cell that has the shape of a square prism. This would be  $a_1$ . This would be  $a_2$ . And this would be  $a_3$  - I'm sorry, this would be  $c$ . And if you took the choice for the third translation as  $1/2$  half of  $a_1$  plus  $1/2$  of  $a_2$  plus some amount  $z$  up above the base of the cell, and then redefined a  $T_3$  prime that would be equal to-- sorry. What am I doing here? Yeah. This is right.  $1/2$  of  $a_1$   $1/2$  of  $a_2$ , and  $z$  straight up. Define a  $T_3$  prime as  $2T_3$  minus  $a_1$  minus  $a_2$ .

And that will define for you, again, a cell in the shape of a square prism with  $a_1$  and  $a_2$ . And now the translation that went up directly over the center of the base of the net below. Twice that minus  $a_2$  minus  $a_1$  brings you back to a third translation  $T_3$  prime that's normal to the base.

So both cells have the same shape. This is a primitive. This is a body-centered tetragonal lattice. And the symbol that's used to represent the body-centered lattice is  $I$ . One of the few cases, again, where one has to be bilingual. The German word for body-centered is *innenzentriert*. So there's Schoenflies at work again. So primitive body-centered represented by  $I$ .

And that brings us to one final case, and that is the plane groups that have a hexagonal shape. And here we have a funny situation in that the same choices of the third translation do not work for all of the plane groups. If you have a base to the cell-- and again, the two edges of that net are identical by symmetry-- if it has a three-fold axis in it and nothing else, than there are two choices. You can either have  $T_3$  be equal to  $0a_1$  plus  $0a_2$  and an amount  $z$  straight up.

And that will give you a cell that is a primitive cell. This would be  $a_1$ . This would be  $a_2$ . And just as we did for tetragonal, we'd call the third axis  $c$ , This will work for a three-fold axis. So there is a space group  $P3$ . This will also work for all of the other groups. So there's  $P3M1$  and a  $P31M$ . And a  $P6$  will work. And a  $P6mm$  will work. So look it here. We've got five additional space groups in addition to the lattice type.

This is the primitive hexagonal lattice.

For a three-fold axis, we have another choice. We could pick  $T_3$  so that it took the origin three-fold axis and put it directly over this one. Looks as though you could have a different distinct lattice if you move the origin lattice point over the three-fold axis that sits at a location  $1/3, 2/3$ . This one is at  $2/3, 1/3$ .

Let me demonstrate, I think convincingly and clearly, that those two choices are exactly the same thing. And the way that I can show that is, once again, to draw this net  $a_1, a_2$ . And suppose I pick the part of the offset of  $T_3$  that is within the plane of the net as going from this lattice point to this one here. Then if I go twice that translation  $T_3$ , that's gonna put me directly over this three-fold axis. And if I go three translations  $T_3$ , I'll be directly over the lattice point on the ground floor. So putting the original lattice point over this three-fold axis or this three-fold axis is exactly the same thing. And I can change one into the other just by flipping this thing 180 degrees. So it's obviously the same choice.

This description of  $T_3$ , if I define the direction of  $c$  now as  $3T_3$  defined in this fashion, minus  $a_1$  minus  $a_2$ , is gonna be a funny situation. It's gonna be a peculiar sort of double body-centered cell. Of course, along the long diagonal of the hexagonal cell, I'll have one lattice point that's  $1/3$  of the way along that long diagonal, and another interior lattice point that's  $2/3$  of the way along that long diagonal. OK.

This double body-centered cell, so to speak, actually can be redefined in terms of a primitive cell, not a primitive cell that is this particular description of a primitive hexagonal lattice. This is not a primitive hexagonal lattice. But suppose I go from this interior lattice point along the long diagonal of the cell to this location and call that  $a_1$ .

Remember that there is a three-fold axis sneaking down through the center of this triangle, goes through the lattice point, and comes out the center of the triangle below. If I go up to this lattice point and up to this lattice point, I have three translations that are straddling the three-fold axis. And that three-fold axis rotates

one into the other.

So this new definition of a cell that is in fact primitive  $a_1$ ,  $a_2$ -- and they're all equivalent by symmetry. I always get in trouble when I try to draw it, but that actually defines a cell with a shape that we've not seen before. That is a cell that has the shape of a rhombohedron. And as I say, I always get in trouble when I try to draw it. It's got three translations like this and three translations skewed by 60 degree sitting on top. Everybody can see that's a rhombohedron, can't you? Say yes. Be nice.

So this is another primitive cell that's a choice for this triple cell. And this consequently gives its name to this lattice. This is called a rhombohedral lattice, regardless of whether you pick the primitive cell in the shape of the rhombohedron or this peculiar double body-centered cell. So this is a rhombohedral lattice. And this is represented in a space group symbol by the letter R, standing for rhombohedral. So just the three-fold axis with this choice of translations, that would be space group  $R\bar{3}$ .

**AUDIENCE:** [INAUDIBLE]?

**PROFESSOR:** Yeah.  $a_1$  like this.  $a_2$  like this.  $a_3$ , I'm taking a right-handed system, comes from the centered lattice point. So let me draw it in projection. It's easier to see. Here's the outline of the hexagonal net. Here's the three-fold axis. And I've taken  $a_1$  coming up like this. I've taken  $a_2$  coming up out of the board like this. And I've taken  $a_3$  coming out like this. OK. So these are the three edges of the rhombohedron.

Notice that I cannot have that lattice with a lot of the hexagonal plane groups. I cannot do it for six-fold axis. Because a six-fold axis--  $P6$  and  $P6MM$  have a six-fold axis here and three-fold axes in the middle of the cell. So I cannot have a rhombohedral lattice for  $P6$  or  $P6<M$ . The primitive hexagonal lattice is the only thing that works.

And then we have this curious situation with the two alternative settings of point group  $3M$  in a hexagonal net,  $P3M1$  and  $P31M$ . For  $P3M1$ , I have symmetry  $3M$  at both the origin lattice point and in the center of these two triangles. So for  $P3M1$ , in

addition to a three-fold axis, I could put in  $3M1$ , stack up plane group  $P3M1$ .

But I cannot do this for  $31M$ . That's impossible. Because if you look at  $P31M$ , there is symmetry  $3M$  at the origin and only symmetry  $3$  in the center of the triangles. So if I try to pick this as a third translation for plane group  $P31M$ , I'm taking symmetry  $3M$  and plopping it down on top of symmetry  $3$ , and that wrecks the plane group. So for the rhombohedral lattice, I can only have  $3M1$  or  $P3$ .  $P6$  has a six-fold axis at the origin lattice point. The two centers of the triangles are three-fold axes. So primitive for the six-fold axis, either  $P6$  or  $P6MM$ , is the only choice.

So if anybody's counting-- and I wasn't-- we've got 11 lattices so far. And the only ones that we haven't been able to get by simple stacking of the plane groups are the systems that you all know as your favorites. The cubic or isometric stems for the fact that the translations are identical in all three directions.

Let me quickly dispose of those by starting with a four-fold axis coming out of one face of a tetragonal cell and saying now if this is a cubic symmetry, I have a three-fold axis that comes out, sort of, in the direction of a body diagonal. But this three-fold axis is gonna rotate that four-fold axis to this direction and to this direction. We've seen that if I look down along the diagonal of an equally axed tetragonal prism, the three-fold axis takes this face, rotates it into this face, and rotates it into this face.

So I have to have a four-fold axis coming out of every one of the faces. And having that arrangement of four-fold axes means that not only will the two translations be identical in the base of the cell, as is the case for tetragonal, but if I put in that three-fold axis as an extender, all three edges of the cell have to be identical by symmetry.

So I can do this for a primitive tetragonal lattice. And that's gonna give me a primitive isometric lattice. I can do this for a body-centered tetragonal lattice. So that would be indicated by the symbol  $I$ . So it's a body-centered cubic lattice.

And if you add up everything we've done to this point, there are 13 space lattices, a

very unlucky number. And as you all know, there are 14. We've missed one. So what have we not done? We stacked up all the plane groups in all possible ways. We've taken the four-fold axes out of the face normals, all three face normals of a tetragonal cell. And that forced it to become a cubic lattice. What have we done wrong?

Actually, we can get the fourteenth space lattice by a little bit of sleight of hand that is not obvious. Let's say that this is the base of a tetragonal lattice that we used as the parent for our cubic lattice. Let me change that primitive square in the base of the tetragonal cell and change it into a centered square. There'd be no reason for doing that for a plane group.

But let me notice now that if this is the direction of a four-fold axis, rather than having the three-fold axis come out of this direction relative to this super double square, I can make the three-fold axis come out in this direction. Ah-ha. So what I have now is a cell that is centered, has a center in the base and has translations that are perpendicular to the base like this. And if this is the direction of the four-fold axis and this is the direction of the three-fold axis, that three-fold axis is going to put a centered lattice point on the remaining faces of the cube.

So it's only if I notice I can make a double square base to the cell again, put the three-fold axis of a cubic symmetry along the direction of the body diagonal, I generate lattice points in the middle of the other faces as well, and this gives me the lattice known as F, the face-centered cubic lattice. And the edges of the cell here are all identical, equivalent by symmetry. So they're labeled  $a_1$ ,  $a_2$ ,  $a_3$ .

Have you ever seen a lattice constant for a cubic crystal  $a_0$ ? Has anybody ever seen that? A lot of people do it. And if you see that notation in a publication, you will be entitled to sneer at it knowingly. It's logical, three, two, one, zero. By extrapolation, if you've got an  $a_3$ , an  $a_2$ ,  $a_1$ , you gotta have an  $a_0$ , right? Well, not necessarily. That sort of algebra doesn't apply to labeling of cell edges.

It comes from a curious historic precedent. Come back, again, to the fact that for literally more than 100 years, people developed symmetry theory and had a pretty

good idea that crystals were based on packing of units, molecules, whatever they were, that were on the nodes of a lattice. But they couldn't measure the size and shape of the lattice.

And that was the brilliance of the famous experiment by Max von Laue because that, in one fell swoop, show that the mysterious radiation x-rays were just electromagnetic radiation of a very short wavelength. And that's what he really gained notoriety for. But at the same time, he proved for the first time, unequivocally, that crystals were based on a lattice.

And that was the other side of his double-edged accomplishment. Up until that time, people learned about crystals by studying the morphology and measuring the angles between crystal faces and recording different faces on a crystal. I mean, I can just see one of these old guys working a little bit before his wife made him come down and sit for supper because it was getting cold. And he'd let out a, whoop, huh? A 13 27 face. What the hey. It's a new face on potassium tartrate, something like that. This was the way these guys got their jollies.

And on the basis of the angles between faces, as I said on several occasions, they could determine a ratio of axes, a ratio of a to b to c, if their assignment of indices to faces were correct. And how did you know? Well, along came x-rays, a and you could measure for sure.

So what people started doing to distinguish a to b to c ratios determined from crystal morphology, they put the zeros on it to indicate real values from diffraction. And when little people came afterwards and they didn't realize the reason for doing that-- nobody's done this for over 100 years because everybody determines lattice constants using diffraction-- but some people have seen these zeros. So they say, I'm not doing proper notation.

And you know how furious crystallographers get if you don't use proper notation. So let me write  $a_0$  as the lattice constant of my cubic crystal. You see this commonly. And there's been no need for it for 100 years. So anyway, that's the origin of the subscript zero. There are a lot of dumb things that take place among normally

rational people.

I said a moment ago-- and I crossed my fingers when I said it-- that  $c$  is the label that is assigned to the unique axis, the axis that is unique because of symmetry. Sometimes you see monoclinic crystals, which have a two-fold axis and/or a mirror plane perpendicular to the two-fold axis, labelled with this as  $b$ , this is  $a$ , and this as  $c$ , and the angle between them-- that's the general obtuse angle-- as  $\beta$ .

There is a story behind this lapse of standardness in notation. How do people decide on what proper notation is? Well, there is an organization called the International Union of Crystallography, which is the equivalent of the International Union of Pure and Applied Physics and the International Union of Pure and Applied Chemistry. And they meet every three years. And there are special commissions for people who like to fight and argue out conventions and nomenclature.

And this is such a silly abomination that there was a move made when they came out with their new edition of international tables to change this and do it the way you do for all of the other crystal systems, namely  $a$ ,  $b$  with  $\gamma$  between them, and  $c$  coming out this way as the direction of the two-fold axis. And this would be the mirror plane. And that would put this in accord with tetragonal and hexagonal and everything else. And it was logical and seemed the right thing to do.

So how do people decide on nomenclature? This is something that people fight with with more passion than anything else in science. So you make a proposal. The proposal goes to the national committees of crystallography in countries over the world. They discuss it. They fight about it. They vote on it. Then it comes back to the International Union. And finally, if everybody seems agreed, they present it at the next meeting of the International Union Of crystallography for a vote.

And that's exactly what happened with the proposal to standardized notation. This took place maybe, I don't know, in the 1950s. Everybody was in favor. The discussion proceeded rationally. Then this little guy jumps up in the front row, short of stature, balding of head, with a very piercing nasal voice. And he gets up and he enters into this diatribe.

b-axis unique was good enough for Curie. b-axis unique was good enough for Mauguin. B-axis unique was-- and all the names were French. Actually, he wasn't French. He was Belgian. So he went on and on and on. And he so cowed this group of 300 rational delegates, that they didn't cave in entirely. What they did was they entered every entry for monoclinic crystals in the international tables twice, once with this set of labels, once with this set of labels. And to indicate that this was the preferred notation, this is labeled the first setting. And to indicate second-class citizenship no matter what Curie, Mauguin, Bravais, and all of these other guys felt, this was called the second setting.

And I'm not kidding. I'll bring in a copy of the international tables for x-ray crystallography. Every entry for a monoclinic crystals is in there twice.

**AUDIENCE:** And no one in the past 50 years has tried to get rid of the second set?

**PROFESSOR:** No. Actually, the reason is it is expensive to revise these tables. And I brought in on the first day, you don't remember, my copy of international tables for x-ray crystallography, which is about this big and cost \$100. And then the new version which is twice as large dimensionally, four times as heavy in terms of weight, and I think about eight times as expensive in terms of actual cost. So you don't do this casually. If there's something actually new comes out, you make a little supplement that people can stick in the pages somewhere.

**AUDIENCE:** Don't they still have PDFs nowadays or something?

**PROFESSOR:** The last volume came out before PDF, before very intensive use of computers for such data. The journals now are all done online. You submit papers online and they're archived online as well in addition to hard copy. But that's something that was before the time of the publication of the last set of volumes.

Well, I am almost done with talking about lattices. But I have a thought question. You've all heard of this castle in Ireland that has this famous rock in the side of the castle called the blarney stone? And you, to get the gift of gab, have to lean over this rather dangerous wall and somebody holds your ankles and you go down and

you kiss the blarney stone. And that gives you supposedly the gift of gab. But kissing is a dangerous occupation. You've all heard about kissing disease mononucleosis? And with all those people smooching the blarney stone, I've always been afraid the blarney stone might come down with mono. And if the blarney stone became ill in this session, would it have to be transferred to the Mono Clinic? I don't know.

All right. Here in all their glory are the 14 space lattices, or Bravais lattices as they're finally called. The labels a, b, c, et cetera, are not on them, but the c axis is vertical. You'll see that the hexagonal rhombohedral lattice is shown referred to hexagonal axes. In the international tables, you will find all the information both referred to rhombohedral lattices and to the triple hexagonal cell as well.

Now, into these lattices one should drop those of the 32 point groups that the lattices can accommodate. That's gonna be a lot of additions. Besides that, there is the option of having the symmetry elements of the point group not intersect at a common point, but interleave them as we did, for example, with the glide planes in P2GG, and in some of the other two-dimensional plane groups as well.

Then we would do what we also did in two dimensions, take the mirror planes and replace them by glide planes, one or the both. And you might think that we really have an enormous amount of work to do. We haven't considered any symmetry combinations that involve a horizontal mirror plane. For example, we look at what symmetry 2 requires and we found the primitive monoclinic lattice, and the side-centered monoclinic lattice, and the body-centered monoclinic lattice. So there's more than one lattice type into which we can drop a given point group. But what would you have if you had a mirror plane perpendicular to the two-fold axis? What kind of lattice will that require?

OK. Let me, in one masterful swoop, convince you that we have done almost the better part of the work. Let us ask what does inversion require of a lattice? What does the symmetry of inversion, which didn't appear in any of the plane groups at all because that's inherently a three-dimensional point group operation? Well, think

about it. All inversion says is that, if, hey, there's a translation that goes up this way, there should be another translation minus  $T$  in the opposite direction. And any lattice whatsoever can make that claim and satisfy that requirement.

So let me now just quickly say that if we have derived the lattice types, and by implication the space groups as well, for a two-fold axis, for a four-fold axis, for a six-fold axis, and so on, we have automatically satisfied the requirements for any point group that results when you add inversion to a two-fold axis, when you add inversion to a four-fold axis, or add inversion to a six-fold axis.

So it turns out that the requirements of a six-fold axis, which gave us the primitive hexagonal lattice, are also met by  $6$  over  $M$ . The requirements of a four-fold axis, which gave us the lattices primitive tetragonal and body-centered tetragonal, are also satisfied for  $4$  over  $M$ .

So, any one of the point groups that differs from the  $11$ -- from the  $10$  two-dimensional symmetries-- namely  $1$ ,  $2$ ,  $3$ ,  $4$ ,  $6$ ,  $M$ ,  $2MM$ ,  $3M$ ,  $4MM$ , and  $6MM$ -- any symmetry that you get by adding inversion to those two-dimensional point groups is automatically going to be happy in the space lattices that we've derived to this point. So we have done an enormous fraction of the work that's required to derive space lattices, and the space groups as well.

So there is not too much more to be done. And what I will do for probably the next meeting is to derive a few of the space groups for the lower symmetries which are not too complicated, just to show you how the game plays out. And then I will mention a little bit about the special idiosyncrasies of the orthorhombic brick-shaped cells where there is nothing more distinct about one direction and the other. All the inter-axial angles are  $90$  degrees. The translations are general. So there are peculiarities in notation there that are unique to the orthorhombic system.

And then I want to spend, perhaps, one class talking a little bit about crystal chemistry. Have any of you had a class in solid state chemistry or crystal chemistry? OK. One. One of the main uses of space group theory is the description of crystal structures. So I think I might, as a minor digression, take an hour to talk about

packing and some of the concepts used to describe the close-packed structures and ionic structures and give you a problem that ask you, as I already did, to generate a structure, simple-minded two-dimensional structure, and do some interpretation of it. So, I think this will be worth saying a little bit about just so that one of the main applications of symmetry theory does not escape without any discussion at all.

We will, after about two more lectures, have a complete change of direction and start talking about properties of crystals and how these properties are impacted by the fact that crystals have symmetry. So we're gonna use some of our results in symmetry, but not all that much, but develop remarkable mileage in predicting anisotropy in crystals just on the basis of the symmetry which that crystal possesses, that certain physical properties as a function of direction are weird surfaces that have lumps and noses and bulges in them.

And certain properties have this anisotropy universally, regardless of the chemistry or composition of the crystal. Given the symmetry of the crystal, the anisotropy has to be in this fashion. We'll be able to show that some properties simply cannot exist, period, regardless of composition and structure in materials that have certain symmetries. So that'll be the direction we take off in.

I mentioned at the beginning of the term-- you've probably forgotten-- there is a lovely book on tensors and physical properties by a gentleman named J. F. Nye, N-Y-E. And the title of the book is *Physical Properties of Crystals*. This is a nice place to go for further reading. We will go through roughly half of Nye's book with a little more emphasis on the consequences of symmetry than what he does.

But if you want to do some extra reading, I asked the Coop to stock this book. But I suggest that you not rush out and buy it. It's available in paperback, which means it's cheap, but only relatively so. There's no such thing as a cheap technical book, paperbacked or not, these days. It's also on reserve in the library. So, see if you need the extra help. See if you would like to do some reading in Nye. And make sure you want to before you go out and put your money down at the Coop.

The last part of Nye is an elegant, beautiful part of the book. It deals with the thermodynamic relations between different properties. And it's a unique treatment that is developed by Nye. We won't do any of that, but it's a nice thing to have. So don't rush out and spend your money. But if you want additional reading and just going to the reserved book collection is not enough, then Nye is not at all a bad copy of a book to have.

I think most of you have probably seen Nye, not the book but the man. How many of you have seen the famous Bragg bubble raft movie on disk locations, where he floats sheets of bundles and sheers them and you see his dislocation go zipping across? At one stage in that movie, there's an assistant who tiptoes, trying to be unobtrusive, across the background. But the camera catches him scurrying behind Bragg. That's Nye. So if you've seen the movie, you've seen what Nye looks like.

OK. I'll call it quits there for today. And we'll see you next week on Tuesday.