**PROFESSOR:** Today, we are going to change gears after the first hour to a very different set of topics. What I wanted to do today was to take a look at notation for space groups. And this is a question that is far from trivial. There are conventions, and we'll see the reasons for them with a few examples.

And then I would like to pass around representations of some non-trivial space groups. First, as they appear in the old *International Tables for X-Ray Crystallography,* Volume 1. And then second, to give you a look at the larger, heavier, and much more expensive Volume A, which gives much more information which is both its liability and its advantage. There are things in there that are not in the international tables. But there's so much information and so cluttered that it's really overwhelming. But I'll give you a chance of what their representations of the space group look like.

Let me begin by passing around an example of the information in the *International Tables,* Volume 1 for one of the orthorhombic space groups. And it all fits on one page. It's not terribly complicated. But it is considerably more complex both in the arrangement of atoms and in the cluster of symmetry elements, compared to the very simple monoclinic space groups which we looked at in their entirety and in considerable detail.

So first of all, some indication of what's on the lower part of the page. This is exactly analogous to what you've seen and presumably are familiar with for the two dimensional plane groups. There are many possible origins that could be selected for the 0, 0, 0, position relative to which the atomic locations are expressed.

So the first thing, just below the picture of the arrangement of atoms and the depiction of the arrangement of symmetry elements is a statement of where the origin is. So it says, origin at the inversion center 2/m. And if you look at the arrangement of symmetry elements, there is nothing but the representation for screw axes normal to the page. But there is, off on the right-hand side, a solid

chevron, and that is the indication for a mirror plane.

Something again that is nowhere stated, but always assumed is that the two variables x and y or the axes a and b are assumed to run from upper left to lower left for a and the coordinate x and from upper left to upper right for the axis b. And therefore, plus c comes out normal to the plane of the projection.

Here, for the first time, we're seeing a complex space group that really requires the full range of symbols for representing the atomic locations. You will see, for each circle, a vertical line dividing it in half. These are two atoms then that are superposed in projection. One of them, corresponding to the little comma inside the circle, is the enantiomorph of those circles which are unadorned with that little comma. And they are, therefore, of opposite handedness.

Alongside of each circle, you will see two symbols giving the elevation of that atom within the cell. The one at the furthest upper left corner says 1/2 plus. So this says that the coordinate is z, whatever that is for the representative atom, plus 1/2. The half of the circle that has the comma inside has a minus sign next do it. That means that it is at an elevation minus z.

Well, where is the representative atom? This is tucked just inside the corner of the cell where the vertical line divides the circle into 1/2. That is a plus, so that's an atom at plus z. The right-hand side of that circle has a comma. It's an enantiomorphic motif, and that exist at 1/2 minus z.

So you find labels on all of the atoms in the cell. There are a total of four clusters of eight. So are a total of 16 atoms within the unit cell.

If you look at this pattern and reflect on it for a moment, so to speak, you can see that the same cluster of eight sits at the corners of the cell as in the middle of the cell. Exactly the same. So therefore, this is a lattice that is side-centered. There's a lattice point at the corner of the cell and one lattice point, in addition, at 1/2, 1/2, 0, in the center of the cell.

The c-axis comes out of the plane of the paper. This then is a side-centered c-

lattice. And that is the capital letter symbol that appears first in the symbol for the space group. It is a side-centered lattice, and the extra lattice point is in the middle of the face out of which c comes.

Then come, in the space group symbol at upper left-- this is the abbreviated form-- mcm. And what I wanted to go over this example specifically for, there are three directions in an orthorhombic symmetry, no one any more or less special than any other. So if you look at the arrangement of symmetry elements, there's a 2 sub 1 screw axis coming out in the direction of c.

The symbols running left to right, arrows and barbs, the arrows stand for two-fold axes. The barbs stand for 2 sub 1 screw axes. And running up and down parallel to the a-axis, again, arrows that indicate two-fold axes and barbs that indicate 2 sub 1 screw axes.

So which is the special direction? Which one should come first? It's not like a cubic symmetry, where the direction of the four-fold axis is always along the edge of the unit cell, or a tetragonal symmetry, where the four-fold axis is always taken to be the direction of c. Here, that's not specified.

So again, the first convention is that the magnitudes of the translations determine a, b, and c in orthorhombic. Because there's nothing more or less special about the symmetry of these three orthogonal directions. And the convention which we've mentioned earlier is that the magnitude of b is greater than the magnitude of a. And then seemingly logically, c is the smallest.

So if this is the direction of a and this is the direction of b, then c comes up. And this is the intermediate length translation. This is the maximum translation. And normal to the blackboard is the shortest translation.

What symmetry goes first? And here again, for orthorhombic, we need a convention. And the space group symbol has-- I [INAUDIBLE] I use lambda for this, but-- a symbol for the lattice type. And we've seen that the capital C that comes first indicates that there is a c-centered lattice.

And then what one does for orthorhombic is give the symmetry elements in the order abc. So the axis that is parallel to a over the plane that is perpendicular to a. Next, the axis that's parallel to b over the plane that is perpendicular to b. And then the axis that is parallel to c over the plane, if any, that is perpendicular to c.

So then this is a convention for orthorhombic. And again, this is the only crystal system where conventions this elaborate are necessary. If this were tetragonal, 4 or 4/m would always come first because that's the direction of c. So even the order of the symmetry elements is different.

But we've got another problem. If we look at the axes, if any, that are along a, we've got this symbol that stands for a two-fold axis and this single barbed arrow that stands for a 2 sub 1 screw. So what kind of axis is along a? There are two different kinds of axes.

So in here, we could put either a 2 or a 2 sub 1. And if we look at the planes that are perpendicular to a, there's two of them. There's a dashed line, and this is a glide where the direction of tau is in the plane of the paper so that we're looking edge on in the glide plane and perpendicular to tau. And then there is a solid line. That's the symbol for a mirror plane.

This would be a glide in which tau is a long b, so this is a b-glide. So those are the two sorts of symmetry planes that are perpendicular to a. Again, there are two of them.

So we could put in either m, or we could put in a for the plane that is perpendicular to a. So already, there are four different possibilities for the first character. So obviously, what I'm leading up to is the fact that we're going to have to have conventions of necessity to come to a symbol on which everyone agrees.

I think you get the idea now, so let me move along quickly along the direction of the arrow for a two-fold axis, a barb for 2 sub 1 screw axis. So again, there are two kinds of symmetry axes that could go in here for the axes that are parallel to b, either 2 or 2 sub 1. If we look at the planes that are perpendicular to b, there's a

dotted line.

And this is a glide for which tau is directed upwards. We're looking directly along the orientation of tau. The axis that is normal to the board is the c-axis. So this is a c-glide.

And then appears a dash-dot line alongside of it. The dash-dot line is a glide plane where you're looking neither perpendicular to tau nor parallel to tau, but halfway in between. So this is a glide plane where tau is equal to 1/2 of a plus 1/2 of b.

And that's a diagonal glide represented, just to confuse the innocent, by the symbol n. So two choices for axes along b. Two choices for the glide plane, either c or n.

And finally, mercifully, along the direction of the c-axis, which is easiest to visualize, because things are either along it or parallel to it, we've got only a 2 sub 1 screw axis. So this is the only symbol which is not ambiguous. And then perpendicular to that, we have the symbol for a mirror plane, the solid chevron off to one side. And then the chevron adorned with a diagonal arrow and that is, again, a diagonal glide n.

We notice that the center of the cell at z equals 0 is the same as the grouping of atoms at the corner. So that is a side-centered lattice. The centered lattice point is coming out of the face which c emerges from. And so this is a c-lattice. You have a question?

**AUDIENCE:** Professor, for the first term [? x of the ?] plane perpendicular to a, why is it a and not b?

**PROFESSOR:** I'm sorry. You're absolutely right. I wrote it down as a b-glide. Perpendicular to a is a b-glide. Good. Congratulations.

So we need a convention. And the convention for establishing a hierarchy of symbols is easy to remember. It's if you have both a two-fold screw axis and a two-fold axis, the order of preference is that the 2 is chosen in preference to the 2 sub 1 screw symbol.

So by this greater than, I mean the preference for choosing it is greater than the symbol to the right. So we get rid of the 2 sub 1 here. We pick the 2. Get rid of the 2 sub 1 here, and that stays at 2 sub 1.

For planes, you pick m in preference to an a-glide, in preference to a b-glide, in preference to a c-glide, in preference to a diagonal glide, in preference to a diamond glide, assuming you have a choice of two different planes. So in this case, we picked the m in preference to b. Here, we've got a c-glide and an n-glide. We picked the c, and it's in preference to the n. And here again, for the plane that is perpendicular to c, we picked the m in preference to the n.

So the full symbol would be C, 2 over m, 2 over c, and 2 sub 1 over m. Now I'll peek and see if I got this right. Yes, I did. How about that?

And the short symbol would be simply Cmcm, which indeed is what we see listed in the upper left-hand corner of the page. This is a space group based on the point group 2/m, 2/m, 2/m, which is D2h. And there is the large number 17 in the superscript, which is the 17th orthorhombic space group, which Schoenflies was able to derive in the order in which he did them. Any questions? Yes.

**AUDIENCE:** If you look at the other symbols to describe the space group, would we construct the same space group using that function [INAUDIBLE]?

**PROFESSOR:** Yes, you could. And let me say, yes, it's possible. But also to answer a question, you might have about the short form of the symbol, we're throwing away information.

We've thrown away the fact that there are two-fold axes, and a pair of directions, and 2 sub 1 only in the third direction. Is it possible that two space groups could have exactly the same three symbols in the short form? And the answer is no.

Because if you think about it, you start with a lattice type. If you put a mirror plane in one orientation, a mirror plane in the other orientation, that really is all you have to specify in order to determine every other symmetry element that's present. You simply combine those operations, and you find that when you've taken these

symmetries and rotations and combine them with the lattice translation, it comes out to one and the same unique result.

So your question was what happens if you take another three symbols. You end up with the same result. Three of them, really, are enough to specify what the group will turn out to be.

Now the other thing I wanted to do was to show you how remarkably the symbol for the space group will change if you take a different set of axes simply because the relative lengths of the cell edge for this arrangement of symmetry elements have changed. This takes dominance. This determines the labels that go to the axes.

And then the symbol for the plane group, and what is a b-glide, and what is a c-glide follows from this choice of axes. So let me take another example. And I think if you follow what I've done so far, I can zip through this a little more quickly.

Somebody pick a new direction for this axis. Let's not pick a. We have used that for this. So somebody pick a b or a c. Do you want to pick a b or a c?

**AUDIENCE:** [INAUDIBLE].

**PROFESSOR:** b. So we're going to change this direction to b. Somebody want to pick a label for this axis?

**AUDIENCE:** c.

**PROFESSOR:** c. And nobody gets to pick this axis. If you think you can, you're out of here. Because that now has determined the coordinate system. So we've got b this way, c this way. We want a right-handed abc convention.

So a goes up. So abc right-handed system. So exactly the same arrangement of symmetry elements except that we've now changed the labels on the axes. So we have changed the name that we have to apply to the glide planes.

So let me now proceed to write down here the new collection of symbols which would appear for this setting of exactly the same space group. First of all, the

centered lattice point is now in the middle of the face out of which a comes. So this is an a-lattice, side-centered a.

If we look along the direction of a, all that we have for an axis is 2 sub 1. Then we have these two planes. One is an m. One is a diagonal glide. So that is m or n.

If I look along b, I have the choice of either 2 or 2 sub 1 as both are present. Perpendicular to b, however, is a glide for which tau is along the direction of c. So that is a c-glide.

And then the other symbol for an axis that's perpendicular to b is a mirror plane. So it's either c or m. Then finally, along the direction of c, I once more have two-fold axes and 2 sub 1 screw axes.

And then perpendicular to c is a diagonal glide. And this is a glide. The dotted line indicates that the direction of tau is along a.

So I have a choice of either a or n in here. So putting down the symbols in the order of preference, this would be A, 2 sub 1 over m, 2 over m, 2 over a. Or the short form of the symbol would be Amma, which I submit doesn't look anything like Cmcm.

And when you start out in diffraction, many people have a first disconcerting experience. You spend probably the better part of a month taking single crystal diffraction patterns. You come up with a trial space group for your particular material.

And then you go to the *International Tables,* and you say, oh, it's not in there, what did I do wrong? And you go back, and you check all your calculations. You look once more at all of the systematic absence of reflection.

See, I have it right. Why is it not in there? Well, the answer is more than likely that you have a different setting for the labels that you applied to the axes. And you have, therefore, metamorphosed the symbol for the space group from one form to a symbol that is very, very different.

How do you tell, when you have a particular space group, what all of the possible symbols for one and the same symmetry might be? So let me now pass out two things. If you have a question like that, you can bet your bottom bippy that it's in the *International Tables* if you look in the right place.

So first of all, let me do something I should have done early on. I meant to hand out a copy of the space group that I drew up here. If I can find it again. It's buried with all of the stuff that I brought in. So I do have a copy for you, but it's gone at the moment.

Let me pass out a listing of all of the possible variants of the space groups for the 230 three-dimensional space groups. And it starts out simple for triclinic symmetries. There's only two possible symbols period, P1 and P1 bar.

And then when you come to monoclinic, the Schoenflies symbol has the marvelous property that it is independent of the orientation and labelling of axes. It depends only on the point group that the crystal has. For monoclinic, either C2 or Cs-- that's a mirror plane-- or C2h-- that's 2 over a horizontal mirror plane.

But the labels can still change depending whether in the first setting either a, b, or the diagonal of the oblique net has to be labeled a and c. So at the top of the column, you'll see the permutation of the two symbols a and b or b and a. And again, the change is significant.

Number eight, as indicated in the left-hand column, can be Am or Bm. And for the groups that are based on 2 over m, you can see, again, there are different symbols. A, 2 over b, A, 2 over a. Again, not at all similar.

Next, come the orthorhombic space groups. And you can amuse yourself by looking through those. Again, what is called the standard setting under the heading symbols for various settings, this is the one that's listed in the tables. But then for various permutations of a, b, and c, you can have five other possibilities.

And you can marvel at how the symbol for the space group changes, as you do

nothing but change the labels a, b, and c that goes onto the axes. So there are tons of orthorhombic space groups because you have three different axes to play with, and three different planes, and four different lattice types. So there is an absolutely mind boggling collection of orthorhombic space groups. It is the most densely populated crystal system.

For tetragonal, no real alternative. Something like P4, 4 is in the direction of the c-axis. There are two-fold axes parallel to that, but the symbol that is used for the symmetry part of the space group symbol looks very, very much like the symbol for the point group. So these are pretty much self-explanatory.

Notice that there are two kinds of lattices for tetragonal crystals, either primitive or body-centered. So you see families with P for primitive or I for body-centered. But notice how many you can get out of a single type of axis and a single lattice. Numbers 75, 76, 77, and 78 are a four-fold axis and a primitive lattice, a 4 sub 1 screw, a 4 sub 2 screw, or a 4 sub 3 screw.

Then you do the same thing with I. And so it goes. Then it picks up at the top of the page again. And you see, again, different possibilities for the symbols.

Continuing still on-- and I think you have the idea now-- same for trigonal crystals. They chose to list those separate from hexagonal. And then hexagonal symmetries. The number is fairly large here because when you take an axis and add it to a primitive hexagonal lattice-- for number 168, for example-- you get P6. Change the six-fold axis to a screw axis. There are five different types of six-fold screw axes. So there's a P6 sub 1, a P6 sub 2, a P6 sub 3, a P6 sub 4, and a P6 sub 5.

And then finally, cubic. A fair number of cubic symmetries. But the edge of the cell is always along the direction of the four-fold axis or the two-fold axis, depending on whether the symmetry is based on 2, 3 or 4, 3, 2. So there are really no alternative symbols for different settings of the symmetry elements relative to the edges.

So there you have them. All 230 of our cast of characters. But in forms of the very different mantles in which they can be cloaked.

What else did I want to do? I want to contrast what is done for us in the old Volume 1 of the *International Tables.* And I will pass out an example for one of the tetragonal space groups. This is the one with maximum symmetry 4 over m, 2 over m, 2 over m.

Sorry. Can you pass those back? And this is something that is analogous to P4mm in two dimensions with the four-fold and two-fold axes extended parallel to the edge of what is now a tetragonal cell. And then there are two-fold axes perpendicular to the four-fold axis.

So actually 4 over m, 2 over m, 2 over m has been dropped in at a lattice point of a primitive tetragonal lattice. The chevron in the upper right of the arrangement of symmetry elements is the mirror plane that's perpendicular to the four-fold axis. The other mirror planes are the same as in the plane group P4mm. And the glide plane, which now would be called a diagonal glide, is exactly the same as in the two-dimensional symmetry.

Notice, however, the exquisite number of general and special positions that are present in the space group. The general position has the letter U. You've gone through almost the entire alphabet before you've labeled all of these positions.

And again, either on the mirror planes, but now there's a vertical mirror plane, a diagonal vertical mirror plane, a horizontal mirror plane, mirror planes halfway along each of the axes, mirror planes halfway along the diagonal translation. So there are lots of positions of point group m. Lots of positions with point group 2mm.

And then finally, 2 over m, 2 over m, 2 over m. And the highest symmetry, 4 over m, 2 over m, 2 over m, which occurs at the origin, at the center of the cell, and at the positions 0, 0, 1/2 and 1/2, 1/2, 1/2.

Then I'd like to pass around one more example of a space group from the *International Tables.* And I know I copied it, and I don't have it with me. I left some stuff behind, which we'll get after we take our break. No, here it is.

This is an example from Volume 1, the older edition, for one of the cubic point

groups. And this is a very high symmetry. This is symmetry 4 over m, 3 bar 2 over m, the highest symmetry cubic point group dropped into a body-centered lattice. So this turns out to be, in the long form, I, 4 over m, 3 bar, 2 over m.

Let me pass these back. So the first thing you'll notice is no picture of symmetry elements. How do you draw something where the symmetry elements are not merely parallel to the plane of the depiction or perpendicular to it? Here, you've got mirror planes that are inclined to the paper, axes that are inclined to the paper. How do you represent them?

You'll notice also the enormous number of atoms in the general position. 96 atoms. Drop in one atom at xyz, and all hell breaks loose. You get 95 other atoms.

And again, when the lattice is centered, they do not list all 96 sets of coordinates. They denote at the top of the page 0, 0, 0, 1/2, 1/2, plus. That means because the lattice is body-centered to those 48 positions that are listed, you add 0, 0, 0, which is easy to do, and then add 1/2, 1/2, 1/2 to x, y, and z. And these are the atoms that hang at the centered lattice point.

Again, because the symmetry is so high, surprisingly, there are not that many special positions. Because all of the symmetry elements can serve as special positions are related by the symmetry that's there. So this is all that you see for the body-centered lattice with 4 over m, 3 bar, 2 over m dropped into it.

And again, you can describe some very, very complicated crystal structures with a very brief set of notes, give the value of the single lattice constant a. And then say, you've got an atom in the general position 96l with x equals something, y equals something, z equals some number. And another atom in position 16f x, x, x, and just the value of x would be given. So you've described a structure that has roughly 125 atoms in it with just that modest specification of atomic positions.

Let me now pass out for you some samples of what the space groups look like in Volume A of the new *International Tables for Crystallography.* Not X-ray crystallography, but just crystallography in general. And I think you will be blown

away because the amount of information that's there is almost suffocating in its detail and its density.

The first sample space group that is given here is, not by coincidence, one of the tetragonal space groups, the one that we just discussed, P, 4 over m, 2 over m, 2 over m. They've done some very useful things. They have specified the asymmetric unit within which you need specify coordinates of atoms.

And here, they say that you have to tell what's in the range x equals 0 to x equal 1/2, y equals 0 to y equals 1/2, and z equal to 1/2, but greater or equal to 0. Then they give a representative set of symmetry operations which generate all of the atoms within the unit cell. The symmetry operations are not independent, but they list 16 symmetry elements.

And now if you look to the next page on the list of 16 atomic coordinates in the general position, you will see a number in parentheses in front of each one. The 15, for example, tells you that you get this atom from the atom at xyz by the operation of symmetry element 15, which turns out to be a mirror plane parallel to the x minus xz direction.

And this is very, very useful if you want to describe a structure and you've labeled your atoms silicon 1 and silicon 2 if they're two different kinds of silicon ion in the structure. And then you're talking about a silicon, oxygen, silicon bond, and it's not at all clear which of the symmetry related atoms are involved in that bond. Well, the presentation of a standard numbering of atoms related by symmetry lets you say that, for example, this is the bond between silicon superscript 5, oxygen, silicon superscript 14. And you can identify the coordinates of the atoms that went into that particular bond angle or bond distance. And that's very nice.

All sorts of information a la group theory. The maximal non-isomorphic subgroups, the maximal isomorphic subgroups of lowest index, the minimal non-isomorphic supergroups. At one time, I may have known what all that meant, and I've long since forgotten and have never regretted having forgotten. So this is very exotic, higher-level information about the subgroups that exist for the space group.

Notice how much more information is present though, compared to the depiction of the same space group in the earlier *International Tables for X-Ray Crystallography.* Well, more or less at random, I picked out some other space groups.

I, 4 sub 1, amd. So this is 4 over m, 2 over m, 2 over m in which the 4 has been replaced by a 4 sub 1 screw axis. The mirror plane perpendicular to the edge of the cell replaced b an a-glide. The mirror plane for the second mirrors that's perpendicular to the cell edge, the a-glide is diagonal. And then perpendicular to the diagonal, two-fold axis is a d-glide.

Again, the different operations are identified by a number, the glide plane, and the inversion centers, and two-fold axes that are present. And then in the coordinates of the general position, you are given the nature of the symmetry element that produces the atom at a particular set of coordinates from the atom that's in the general position. Now again, the maximal non-isomorphic this, the minimal non-isomorphic supergroup, and so on. Lots of information.

Then some examples of still higher symmetries. P6 sub 3 over mmc based on 6 over m, 2 over m, 2 over m with the 6 replaced by a 6 sub 3 screw axis and one of the mirror planes replaced by a c-glide. If you go on, here comes the really exciting part.

The next page gives you a depiction of a cubic space group. Heroic. What they do is show stereographic projections at locations, such as 0, 0, 0 and 0, 1/2, 1/2, I believe it is.

And then the best part of all, down at the bottom of that page, you see the arrangement of atoms in stereo. And if you're one of these people who can stare at the thing cross-eyed and let your eyes sort of blonk out, you can watch the two halves merge. And all of a sudden, zing, the thing leaps out of the page at you in three dimensions.

If you don't have that ability to cross your eyes and see stereographic projections, you have to get a little viewer. But nevertheless, if you want to see it in three

dimensions badly enough, you can do it. So there you are. For the first time, pictures of the general position in cubic space groups.

I think that's kind of fun. Sometimes I gaze at it for so long I'm afraid my eyes are going to get stuck. And then I'll be in real trouble.

Here's another one. P 4 over m, 3 bar, 2 over m. You notice the problems that they have in indicating the orientation of three-fold axes which are not parallel to or perpendicular to the paper. You have to do that with a little stereographic projection.

And then finally, after we've done a couple of more cubic space groups, you come to the one that I gave you the handout from the *International Tables for X-Ray Crystallography.* I, 4 over m, 3 bar, 2 over m. And look at all the information that is there that no attempt is made to give you in the earlier tables.

So this is for better or for worse what space group tables look like. This is the information that hopefully you'll be equipped to use. If nothing else, if you can't derive these things or reproduce the arrangement of symmetries from the symbol, if you ever have to construct the atomic arrangement from a material from the crystallographic notation in which the atomic arrangement is provided, you can hopefully go to the *International Tables,* know where to look, and how to go about identifying the coordinates of all of the atoms within the unit cell.

Timed myself to finish just at five of the hour. So let me, before you leave, give you one final problem set on symmetry, problem set number 10. And this is related to identifying what the symbols used to give atomic locations represent.

First problem asks you to look at a pair of atoms and determine the symmetry element which has related them. The second problem on the second sheet asks you to do what we did here for this orthorhombic space group. Determine the symbol when a, b, and c are particular translations of the three that are unique. And then change the orientation, and see what the space group symbol morphs into.

Let me finish with one final handout. And that is could you please summarize what we spent the last month and a half doing? Gladly. I have summarized everything

that we did and the theorems that we used to derive it on one piece of paper.

So all of symmetry theory is here admittedly written in a rather tight hand. But here is an indication of everything we did to get from a definition of basic operations, a flowsheet that gets us down to 230 three-dimensional crystallographic space groups. So I'll pass that around for your awe and amazement.

Sorry I gave a big pack out on the right-hand side of the room. They'll come around to you. So let us take our usual 10 minute break.