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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Session 15

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PROFESSOR: OK, OK, settle down. It's time to start learning.

One announcement. Tomorrow we'll have the weekly quiz. In lieu of the Tuesday celebration, we're going to move to Thursday, since the holiday moved everything, compressed the week.

So last day, we were talking about doping of semiconductors, and I want to finish up that unit. Just to refresh your memory, we looked at how we could change the behavior of the semiconductor by introducing impurity atoms. And when the behavior of the semiconductor is dominated by the impurity atoms, we term that behavior extrinsic. In other words, it's not the behavior of silicon itself, but it's the behavior of silicon as determined by the presence of some dopant atom.

And we looked at the special case of doping with a supervalent impurity. And here's the energy level diagram for that situation, where we've got the valence band down here, we've got conduction band up here, separated by an energy gap. That's all characteristic of plain vanilla silicon. But then when we dope with the supervalent impurity, there is an extra electron. And that is put into a donor level that lies just a tiny bit below the bottom of the conduction band.

And then, thanks to thermal excitation, which gives us an average energy of about $1/40$ of an electron volt, we get, for all intents and purposes, 100% excitation of the electrons that sit in the donor level, excitation up into the conduction band. And this is what electrical engineers term ionization. And I also reminded you last day that this is the donor level, and for each donor atom, there sits a donor level at the same value of energy, but these are so far apart point, owing to the dilution, the dilute concentration of the impurity, that we don't violate the Pauli Exclusion Principle. So these are all sitting at the same level and that's why they've given temperature promotes all of them up into the conduction band, where they are mobile.

And then, just to complete the review, we call this n-type because, thanks to doping, we generate electrons in the conduction band, and electrons are negative. Supervalent doping gives us n-type. Then the total number of electrons in the conduction band is the sum of those that would have been generated by plain old thermal excitation. Thermal excitation operates all the time.

So with thermal excitation, recall, we promote from the valence band up into the conduction band. So we break one of these bonds, shoot an electron up here, and leave a hole behind. So this generates the pair. Hole in the valence band, and electron in the conduction band. That's always operative, but owing to the energies

involved, the band gap is on the order of one electron volt, whereas the donor level sits only about 1/50 of an electron volt below the conduction band. So we get very, very little promotion at room temperature.

And in fact, it's something like 10^{-19} is the fraction of promotion, and if you say roughly 10^{23} per cubic centimeter, that means you've got about 10^4 electrons per cubic centimeter due to this thermal excitation from the valence band to the conduction band. Normally, when you dope a semiconductor, you dope it around parts per million level. And parts per million, that's 10^{-6} . If you take 10^{-6} times 10^{23} , you get about 10^{17} . Now you can see, 10^{17} is vastly larger than 10^4 .

So for all intents and purposes, once you've doped something, this contribution is essentially 0, and so the electron population, the conduction band, is that dictated by the impurity atoms, which is why we say that this is exhibiting extrinsic behavior. The intrinsic properties are not visible, they're not palpable. They're immeasurable. So intrinsic is substantially less than extrinsic.

Now, the last thing I wanted to do for you before we say goodbye to this fascinating topic, which lays the groundwork for everything that we know in the modern electronic era, parenthetically, is to look at the other type of doping. I've showed you how to make an n-type semiconductor. How do we make a p-type semiconductor? So in that case, what we can do is dope with a subvalent impurity.

What do I mean by subvalent? Well, the valency of silicon is 4, so I want something less than 4. So a good example is boron into silicon. So boron is group 13, or 3, all right, if you look on your periodic table. And silicon is group 14, according to the IUPAC notation.

So let's go back and take a look at how that might appear. So I'm going to draw the silicon crystal. Remember, this is going into a single crystal of silicon. So silicon is sp^3 hybridized, and we have silicons everywhere in the structure. So we're going to put silicons. And I'm trying to show sp^3 hybridization. So this is 3 legs each in the plane, then you've got 109 degrees here. So that's silicon, and so on. I get the three of them just to complete enough of the picture.

And now what we're going to do, is introduced boron. And boron goes into the silicon lattice and covalently bonds. It doesn't go sit in some void space in between the silicons. It actually sits on a silicon site and substitutes for the silicon. Now, boron is group 13. It's got 3 valence electrons. And so it forms bonds with 3 silicons.

And now there's a fourth silicon here, and that silicon has an electron, but the boron doesn't have a fourth electron. Here's where it gets interesting. The driving force to complete the picture here is so great that the system will actually pull an electron out of a silicon-silicon bond-- and so I'm going to use a different color chalk, and I'm going to indicate, just for argument's sake, that we're going to pull an electron out of this bond here, break this bond, and shoot that electron over to here. That way, we get 4 bonds around the boron. It says p^3 hybridized. It just doesn't have that extra electron.

But now it rips the electron out of this silicon-silicon bond. And what's the consequence of breaking this bond? What's the electrical feature that we've created

here? A hole. So now we've created a hole somewhere else in the crystal in order to satisfy the desire of boron to get that fourth bond. And now can you see that for every boron that I introduced into the crystal, I'm going to make a hole somewhere in the crystal.

And on the energy level diagram, where do those holes live? Those holes live in the valence band. So let's go make the energy level diagram. So up here we have the conduction band, and downstairs, we have the valence band, as before. And I'm going to assume that we got the thermal promotion. But it's so tiny in comparison to the amount of boron we're going to put in. I'm not going to muddy the water here and show that you've got pair formation. Because the extent of it is so small, it doesn't make any difference.

So now what happens? Now, I know I'm going to generate holes here, and I've got to show this energy level. And this bonding level is different from this bonding level. Agree? Silicon-silicon bond has different bond energy from boron-silicon bond. So that means the top of the valence band is different from-- because this valence band is silicon-silicon-silicon.

So it turns out that, and this is not to scale, that the energy level of this bond is just a little bit higher. And this is an energy level that involves the accepting of electrons, whereas in the other case, we were donating electrons. Hence, that's called the donor level. This is called the acceptor level. And it's about 1/50 of an electron volt above the top of the valence band.

And so what happens is that in order to make this bond, we move something out of the valence band up into the acceptor level and generate a hole. And so for every boron that we put in, we have another broken bond. And all of these lie at the same level, but the dilution is so high, that they're so far apart, that they don't violate the polyexplosion principle. They're thermally promoted up, and away we go.

So now, under these circumstances, the number of negative charge carriers no longer equals the number of positive charge carriers. Because I've got all these positive charge carriers. Thanks to the introduction of boron, p is greater than n . So we've made a p -type semiconductor, by the introduction of a subvalent impurity.

And we can redo the entire central part of last day's lesson, which was the Bohr model. Now, this is the sexiest part of the Bohr model I've ever seen. This is really, really cool. The hole is mobile! The hole is mobile! And the boron is a little bit shy of protons, right? It's 3 in a land of 4. So it's negative. So I've got a stationary negative center, and I've got something positive revolving around a negative center. This is an inverse Bohr model! Because the Bohr model has a honking big positive center with a dinky little electron revolving around. We've got the immobile negative center, and the mobile hole revolving around. Go through, you get the same set of quantum-- I mean, there's a whole bunch of quantum levels in here. Fantastic! How far that Bohr model can take us.

So now you know how to make a p -type semiconductor, you know how to make an n -type semiconductor. And then what you can do is put them together. And you can put, say, boron-doped silicon opposite phosphorus-doped silicon. Be careful here. The fonts are really critical. This is uppercase P , for phosphorus. This is lowercase p , for positive doping. So don't go, oh, P , phosphorus, that means it's p -type. No, P

gives you extra electrons. It's n-type. So that's what uppercase P. This is a lowercase p. This is p-type.

So now I've got p-type, n-type, and so what do I have here? I've got a p-n junction. And this is the beginning of solid state devices, rectification of A/C current, diodes, you name it. And it all starts with this, the chemistry. This is the birth of the transistor, and all the modern electronics that we have based on that. Later on, we'll show you how you get the boron in, and how you get the phosphorus in. You don't just come in and sprinkle it on top, and hope that it goes to the lattice site. There's a lot of processing involved.

OK. So this is where I want to hold for the unit on semiconductors, and how it fits into the grand scheme of things. So in the books, you'll see-- this is a very crude drawing, because this is showing n-type semiconductor with grossly exaggerated numbers of donor electronics up here. There's no mention of the donor level. So this is sort of semiconductivity, sort of pre-3.091. This is extrinsic semiconduction for idiots, I guess you'd call it. And then, same thing here. You see all of the holes in the valence band. We know better, because we know there's an acceptor level and there's a donor level. OK.

So now we're going to switch gears. Now here's the big transition, right now. If the last two lectures didn't leave high school behind, today we leave high school behind. So those of you who have been coasting up until now, thanks to your very good high school background, start paying attention. Because it's high school no more.

So just to remind you where we've come. We started over here, at the beginning of the semester. And the big theme is going to be, electronic structure informs bonding, which informs state of aggregation. State of aggregation is solid, liquid, or gas. So I want to show you how we get to where we are.

So we did all of these topics, right? Bohr, or Sommerfeld quantum numbers, multielectron. And then we came to octet stability. And with octet stability, we went a long way. We got into ionic bonding. We got into completing the valence shell. And in fact, all of this is a consequence of the octet stability. And that led us into the various types of primary bonding. Ionic, covalent, metallic. And in some instances, van der Waals. Solid argon is van der Waals bond. It's the only kind of bonding, so it's the primary bonding.

But in some cases, like HCl, how do you get liquid HCl? How do you get solid methane? So we had to invoke secondary bonding for some of these covalent molecules, and that invoked dipole-dipole interaction, the London dispersion force, which is the same as the van der Waals bond, but I decided to mix things up, so that both men get a little bit of attention, none of them feel slighted. And finally, hydrogen bonding, in those special instances. And that allowed us to then determine whether something was a gas, a liquid, or a solid. And when it's a solid, we're happy. Because this is 3.091, and we're interested in the solid state.

By the way, what is a solid? Well, here's an operative definition. That which is dimensionally stable, has a volume of its own. It doesn't distort in a gravity field. All right? Liquids will distort. Fluids, gases will distort.

Now, there's two ways of classifying solids. One is bonding type. That's what we did here. But the second way of classifying solids is based on atomic arrangements. All right? So let's look at that.

There's only two types of atomic arrangement. Ordered and disordered. I love these taxonomies that split everything into a choice of 2. That way, you just sort of go through life and decide, is it left or is it right? Is it up or is it down? Is it ordered or is it disordered?

So what are the characteristics of an ordered solid? It has a regular atomic arrangement. That means it's got a long-range order. And I'll show you that in an ordered solid, I know not only where my next nearest neighbor is, where my tenth nearest neighbor is. I know where my hundred and fifty second nearest neighbor is, because it's an ordered solid. And we have a simple Anglo-Saxon word for an ordered solid. It's called crystal. So when I say something is a metallic crystal, I don't mean it's something that's got magical properties, and if I put it over my head, I get powerful or something. It just means I've got atoms in an atomic regular arrangement.

Now contrasting to that is a disordered solid. And in that case, we have a random arrangement. But I put an asterisk here because, as they say in California, it's not totally random. It's only random up to a point. No long-range order. There may be short-range order. In other words, I know what my next nearest neighbor is, but I probably don't know where my tenth nearest neighbor is. Because the coordination shell is established, but the next coordination shell, and the next coordination shell, they're not established. And I'm going to show you, with examples, what that means

So we call those kinds of disordered solids amorphous solids, as opposed to the regular solids, which are crystalline solids. And there's a plain Anglo-Saxon word for a disordered solid. It's glass. Now you might think, well, gee, doesn't glass mean that it's transparent in visible light? No, no. Maybe up until now, but I want everybody who's ever taken 3.091 from me to be disabused of the notion that glass means transparent. How do we think about the question of transparency? And here I mean transparency vis-a-vis visible light. I'm not going to say, what's transparent to x-rays? That's pedantry.

So how do we think about whether something is transparent to visible light? We just ask ourselves, is the band gap greater than 3 electron volts? The band gap is greater than 3 electron volts, visible light zooms right through. It doesn't have enough energy to excite the electrons, be absorbed, and re-emit. So that's what transparency means. So I can have the kind of material that's used in things like eyeglasses. It's transparent to visible light because of its high band gap.

Diamond, diamond is transparent to visible light, and you wouldn't dare insult diamond by saying that diamond is glass! In fact, watch the old gangster movies from the 1930s, that was the derogatory term for fake diamonds. You call them glass. So how is it that diamond, which is crystalline, it's transparent to visible light, and yet the window glass that we have is transparent to visible light?

It has nothing to do with state of order. Has everything to do with this. In fact, David, if we could shoot to the document camera, I'll show you a piece of glass that's not transparent to visible light.

How do we zoom in on this thing? OK. Auto focus.

So what I'm showing you is a piece of obsidian. It's a naturally occurring mineral. It's rich in silica, and it's turned dark because it's got some iron impurity, and the iron absorbs in the visible. And this is clearly not transparent to visible light, and yet, it is a disordered solid. This is a glassy solid. In fact, the white speckles there are devitrified obsidian. It's actually started to crystallize. So the crystalline form is the part that's transparent. If you could peel off this crystalline form, you'd actually end up with something that's transparent to visible light. So here's an example of where the crystalline form is transparent to visible light, and the glassy form is opaque. So glass has nothing to do with transparency. This is how you think about the question of transparency.

OK. So let's cut back to the slides, David, please.

So we're now going to start by looking at ordered solids. So we're going to take next several lessons and talk about ordered solids, and then after that, we're going to take a few more lessons and talk about distorted solids.

Now first of all, what's the term crystal? Where does it come from? It comes from the Greek word, *crystallus*, which is the Greek word for ice. That's where we get the term crystal.

So we're going to start with a history lesson. That's how we start everything in 3.091. A history lesson. So we go way, way back to Isaac Newton's time. The Reformation, Charles, Oliver Cromwell, all those exciting times.

In merry old England, there was Robert Hook. You know him from Hook's Law, in mechanics. So he was doing military research in 1660. He was trying to understand what was the optimal way to stack cannon balls. So when you're on a battle front, you want to figure out how to keep your material compactly arranged. You don't lie them on the ground.

So from that, he concluded that crystal that is a regular array must owe its shape to the packing of spherical particles. So that's what he was thinking, or trying to imagine. Remember, Democritus said that we have these indivisible particles, but no one had ever seen them before.

Then in 1669, a Dane by the name of Steenson who was working in Italy was looking at quartz crystals. And he was studying various quartz crystals. By that I mean, quartz crystals of different sizes. And what he observed was, didn't matter what the size of the crystal was. They always had the same angles between corresponding faces.

So if I give you a big crystal and a smaller crystal of the same material, and a smaller crystal, and they all have the same shape, Can you imagine that you might conclude that that is reflective of something down at the atomic level, and if you could get down to the atomic level, that spacial arrangement would hold right now? Because that's how it grew, right? It started from a small number of atoms and grew, grew, grew. Why would it start with one shape, and all of a sudden change to another shape? It doesn't make any sense. At least, not to me. And certainly not to Steenson.

And then we go to Holland, 1690. Christiaan Huygens. And he was studying calcite crystals. And he drew drawings of atomic packing and bulk shape. This is 1690. I'm going to show you an image from his book. This was drawn in 1690. See, this is stacking of cannonballs, but he was looking at a calcite crystal. Actually, Dave, could we cut back to the document camera? We're going to do a fair bit of this.

I'll show you calcite crystal. This is what he had to work with. It looks like this. To give you a sense of scale-- what do I have? Do I have anything you'd recognize? OK, here's a soda can to give you a sense of scale, OK?

This is one honking big calcite crystal. I got it as a gift from someone who watched 3.091 lectures on OpenCourseWare. And he said, if I ever come to town, can I attend your lecture? I said, sure. And he showed up, he attended the lecture. He was a man probably in his early 40s, and as a pastime he collects gemstones. And he gave me this giant calcite crystal, because the one I was using before was so pathetic. He said, I've got to give you one.

And then, I thought, jeez, if I could ever come upon somebody who's in the gold business-- and you know, he might give me a big honking crystal of face-centered cubic metal called gold-- which broke \$1,000 an ounce yesterday, but-- anyways, if you're out there, and you're watching these lectures, I'm here. It's 8201, and you can see any anytime. My assistant's name is Hillary, she'll take the call.

All right. So let's go back to the slides. Dave, could we cut to the slides, please? Thanks.

All right. So now-- oh, I'm going to show you a few others. Remember, here's the idea, that we're looking down to the elemental level. So if you look on your periodic table, it says 10, you see, 10, it's supposed to be tetragonal. So here's a crystal of 10. Dave, cut back, please. We're going to go back and forth today a lot. There's a piece of ten 10. So you might look at it and say, gee, that looks kind of cubic. But if you look carefully, the vertical dimension is greater than the horizontal. In fact, it's got a square base. And then, this is the tall one. Which, if we cut back to the slides, let's see. And that's what tetragonal looks like. And we'll study all of these in a few minutes.

These are some giant crystals I didn't dare drag in. This is sort of human-sized scale. This is balsalt, which is a magnesium iron silicate. It's on a coast of Iceland. Dave, let's show them a few more. Here's one more, if we go to the document camera. This was beryllium aluminum silicate. This is a barrel. And you can see, this has got a hexagonal habit.

So something's going on at the atomic level that's different as we go from one crystal structure to the other. What else have I got here? Here's some calcite, here's some fluorite. Look at this one. This is square pyramidal but it's ionic. So don't give me any of that sp³ d² stuff. Because it's not going to work here.

All right. Let's go back to the slides, please.

So then we jump to 1781, to France. Rene Juste-Hauy was at the Sorbonne, and he was studying the cleavage of calcite crystals. In other words, he was taking these things and breaking them. So he'd go to work every day and break things. And he studied the shards, and he found that the shards were all rhombahedral. the same

shape as the parent crystal. No matter how small the shards got, they always looked like this. He didn't end up with cubic shards. He didn't end up with long slivers. He always ended up with rhombahedral slices.

So the other thing is that he didn't end up with any voids. No matter how he cut this thing, he never got voids. So he reasoned that this must be the way things are packing in three space perfectly. So then he said, gee. If they pack perfectly rhombahedrally-- we all know that we can stack boxes together perfectly, cubes together. So he, being a Frenchman, said, what's the mathematical formulation? They were steeped in mathematics there. That wasn't a slur against the French. It's a compliment. He said, what are the mathematically distinct shapes, that if we stack them together in three space they will fill three space with no void?

And the answer is seven. Seven space-filling volume elements. By the way, the gabled milk carton isn't one of them. And so he called the crystal system, so I call seven distinct shades of milk cartons. And these are the seven crystal systems, and they're described geometrically, and you'll get a chance to go through them. The cube is one of them. Tetragonal. Here's the calcite, rhombahedral. There's barrel, hexagonal, and so on. The seven different ways you can fill three space. And this is from the archival readings of my predecessor, Professor Witt.

Actually, just to give you a sense, here's the two-dimensional analogy. If I said to you, we're going to open a company, and we're going to make bathroom tile, and we want to make it sort of an upscale company, you know, not everybody wants boring old square tiles. But definitely, I can cover two space with square tiles by putting them side by side, one on top of the other. What's another way I can fill? I can go with rectangular tiles. So this dimension is different from that dimension. What's another way? I can use a rhombus, right, at 60 degrees. Or I can use just a plain old parallelepiped at some arbitrary angle.

And if you go over to the Stata Center, to the Gehry building, take a look at the shape that they chose as the unit cell. This is the repeat group, if you like, or the unit cell, because that's the one that's going to be cookie cutter replicated, side by side. When you're putting the skin on a building, you have to make everything fit with no holidays, right? Because you don't want gaps. what they chose was this area element. And all the pieces of stainless steel are cut to this shape. And that's how you make things fit.

How you take something and make it fit around a three dimensional object is tricky. It's the same thing as the clothing problem, right? How do you take a flat piece of cloth and make it fit the contour of the human body? At least, you know, in men's clothes, you know, we've got dimensions. We've got sleeve length, got waist, chest. We've got all these numbers. For a woman, 8. One number? One number? Fashion designers don't know crystallography! If they knew crystallography, they'd know how to specify the shapes! If you understand this, you can start your own business and make clothes that fit. And I guarantee you, there's a market out there for clothes that fit.

What about this one? Pentagon. We're going to make pentagonal bathroom tile. Well, when we install these, we're going to have to use two different colors. You can see this up here, right? This is pentagonal bathroom tile. It doesn't fit. You've got all these white spots. So this is not a unit cell. This is not one of the crystal systems for

two dimensional. So this one's no good. We better put an x through it, in case someone fell asleep, and wake up, and then tell me that that's OK.

All right. So then we move about half a century forward, to the turbulent year 1848, also in France. Auguste Bravais. And what Bravais did, is he said, all right. This is just filling space. But where are the atoms? I haven't told you where the atoms are, right? You know, as far as you're concerned, maybe there's one atom in each of these boxes. Or maybe there's atoms at the corners of the box. Or maybe there's atoms at the corner and the center of the box. Where are the atoms? I've simply told you that I can fill three space with boxes, or with these rectangular boxes, and so on.

So he set out mathematically to prove how many different arrangements of points there are in space. It's sort of like saying, if I want to tell you where all the apples are in the orchard, I'm going to tell you where the trees are, and I'm going to tell you where the apples are on a tree. So where do the atoms go inside these boxes?

Turns out there's 14 different arrangements. And what do I mean by that? This is a good example. So we've already established that the cube is a space-filling volume element. It's one of the seven. But look. If I'm one of the atoms at the corners here, I've got six nearest neighbors. This is also a cube, but it's got atoms at the corners and an atom in the center. You might say, well, what's the big deal? If you're in the atom in the center, and you look to the nearest neighbors, you've got eight nearest neighbors. Here you only have six nearest neighbors. So this is spatially differentiated from this.

So what why don't we keep going? And by the way, the same environment of that central atom that's coded green is the same environment of any of the atoms on the corners. They're all symmetric. So both are cubes, but they have different space point environments. And here's a third one, where we put atoms at the corners and atoms on each of the faces. So this atom on the face, you can see, it's got one, two, three, four atoms in the plane, three behind, three in front. It's got 12 nearest neighbors. This has got eight nearest neighbors, this has got six nearest neighbors.

So Bravais went through and he said, let's take those seven crystal systems. Let's put atoms in distinguishable ways. How many distinguishable ways can we come up with atom arrangements? And the answer is 14.

Now, what we're going to do in 3.091, is we're just going to confine our conversation to the cubics. Because you use orthogonal vectors, they're all the same length, the mathematics are simple, and the principles are the same. And by the way, boatloads of materials are in the cubic system. So it's not as though we just chose something that's convenient but irrelevant.

So here are the different Bravais lattices. So you can see the cubic, there's simple cubic, body-centered cubic, face-centered cubic. With tetragonal, there is simple tetragonal, body-centered tetragonal. There's no face-center tetragonal. If you try to make face-center tetragonal it's degenerate, reverts to one of the other systems.

So these are the distinguishable systems. And everything, including crystalline proteins-- if the protein crystallizes, it forms atomic arrangements in one of these Bravais lattices. Everything conforms to one of these Bravais lattices. And if it doesn't, it means it lacks long-range order, in which case it is a glass. That's it.

So here's face-centered cubic. You can see the placement. But there's something that's been simplified here. Right now what you see is a single atom, designated by a hard sphere. But at each of these lattice points, I can put more than one atom. So let me show you what I mean by that. What I want to do, is put different numbers of atom arrangements at the lattice point. So those positions, the distinguishable positions, are called lattice points.

And now I want to define the crystal structure-- the crystal structure is the complete accounting of atomic arrangement. It's the complete description of atomic arrangement. And we don't have to go too far, because we just have to get the base unit, the unit cell, and then just repeat the unit cell. Complete description of atomic arrangement.

And so how we going to go about this? We're going to start with a Bravais lattice. And what is the Bravais lattice? The Bravais lattice is simply a point environment. And this will mean something to you in about three minutes, when I give you the rest of the description. So it's a set of points in space and the basis. And what is the basis? The basis is the atom group at each lattice point.

So what do we mean by that? Well, let's look at what's up on the board. What's up on the board is face-centered cubic. So let's do all of these. So we're going to say that the Bravais lattice, in this case, in face-centered cubic, FCC. That's what this one is, up on the board. And we've got dots indicate the points. Because really, the points are nothing. It's a concept. See, it's French. It's a concept, right?

What's this? See what I'm holding? I'm holding a Bravais lattice. It's just a set of points. It's like a John Cage piece, you know, a bunch of rests. So if I go to the piano and I play rests in five four time, listen. Isn't that great? Man, it's fantastic. All the different rests, and different--

So this is a set of lattice points. Now I'm going to put something on them. You think I'm kidding. I'm not. All right. Now what's the basis? If I put a single atom, we have what's up on the slide. And so that's the representation of metal. So for example, gold is FCC, with a single gold atom at each lattice point. Aluminum, copper, platinum. These are all FCC metals. So there's a single atom at Bravais lattice point, and so the crystal structure is known as FCC. It's the same as the Bravais lattice. It's called FCC.

OK. Now, we can also put a molecule at each lattice site. So I'm going to put up the FCC here. Here's the FCC. There's the cube, the set of lattice points, and the lattice points are-- I'm going to just illustrate on the front face. One, two, three, four, and a fifth atom at the front face. Now these are the points. I could either put simple atoms there, and the central image there shows what happens when you have the close-packed arrangement, the atoms are so big that they touch.

Or what I could do, at each lattice point, I could put a molecule. So for example, I could put methane. I could put CH₄. A methane molecule. Because when one of you gets to Jupiter, and you see the methane ice, and you go, oh. That's FCC. Because everybody else on the mission hasn't taken 3.091. They don't have a clue what they're looking at. But you go, that's face-centered cubic. And they go, huh? And this is at each lattice site.

You see, my point is, now look, here's the difference. All five of these, the carbon and the four hydrogens, sit at this lattice site. All five atoms sit at this lattice site. It's not that the carbon goes here, one hydrogen goes over at one lattice site, one hydrogen over here. You don't have the methane straddling the unit cell. You have all five atoms here, five atoms here. At every lattice point, I have all five atoms at each lattice point. So in that case, we also have, it's FCC.

So methane ice is face-centered cubic. Because it's spherical. They pack just like gold atoms. You know, from a distance, we can model this as a sphere, as a point. Or we could put an ion pair.

An example of that is sodium and chloride, and this is called rock salt crystal structure. Rock salt. Let's look at that one. So at each lattice point, I'm going to put two ions. Not one, two. This is taken from your text. So you might look at this and say, well, here's the front. You might look at this and say, well, isn't this kind of like simple cubic? Because I've got one, two, three, four, but I've got different atoms if I try it that way.

See, this is taken from a different book. I did some highlighting on it. So this is sodium chloride again. One, two, three, four, five. With this lattice site, I put the chloride atom and the sodium atom. The pair of atoms are associated with this lattice site. You might say, yeah, but this is way over here. Doesn't matter. I'm going to anchor all of those to this lattice site. To this lattice site, I'm going to anchor this and the sodium ion. So this is not simple cubic. Because if I try to call this simple cubic, I have different atoms at different lattice sites, and that's a no-no. Has to be the same.

So if I associate the pair, chloride ion and sodium ion, chloride ion and sodium ion, chloride ion and a sodium ion not depicted. It's off the diagram here. And I put these dots at the center of each chloride ion. Can you see that I'm at the face of FCC? So that's an FCC Bravais lattice, but it's got two atoms, in this case, both ions, associated with each lattice point.

I will come to the dogs in a second.

And now there's a last one I can do. And that's got two atoms, but not an ion pair. We're going to put an atom pair. Got an atom pair, and that looks like this. I'm going to put a carbon atom, one carbon atom, and a second carbon atom. And this angle here is 109 degrees. And I'm going to put this pair of carbon atoms together, and when I do that, and I replicate that through FCC, I end up with diamond cubic. And I'll show you a three-dimensional example of that next day.

So just bear in mind that if you have an ion pair, you end up with rock salt. If I show you this pair, this is due to the sp^3 hybridization. And so examples of this one are diamond, not graphite, just diamond, silicon-- so everything that I've shown you about single crystals, and intrinsic and extrinsic semiconduction, is diamond cubic crystal structure. But it's not one of the Bravais lattices. It's an FCC Bravais lattice with two atoms per lattice site. That's diamond cubic crystal structure.

But it extends to two dimensions. So here's an Escher print. It's got all these dogs. In two dimensions, what's the crystal structure here? Well, there's no such thing as body-centered cubic. There's no third dimension in two dimensions. So you've only got simple cubic or face-centered cubic. So what do we have here?

Well, you see, you've got a problem. Because the black dogs are facing the opposite direction of the white dogs. So you can't go one, two, three, four, and make anything that way. So instead, I put dots on the, I don't know what you call this part of the dog. I don't know. This part of the dog. The leg? Whatever you call this thing. Yeah. You put it on the same spot of the dog-- maybe I should have used his eye, I know how to call it.

Anyway. So I put these things up, right? And that means that if I associate the four dogs with this point, the two dogs facing the right, and these two dogs facing the left. So these four dogs are associated with this lattice site. Then I move up here, and I've got the same thing. One, two, three four. Two dogs facing right, two dogs facing left.

So that means I've got a simple cubic bravais lattice, and the basis is four dogs. Four dogs as my basis. And with that combination of a simple cubic lattice and four dogs is the basis, I can make the entire structure. That's what this is all about. That's my unit cell, that's my repeat unit. So there's simple cubic, right there. So instead of a single atom at each corner, or these are spheres that are touching, we got the four dogs. Here's another one. Once I got the Escher, I kept flipping through the book. I don't know what this thing is, but it's creepy. Anyway. It's wallpaper. If it's wallpaper, it's ordered. If it's ordered, it's a two-dimensional crystal. If it's a two-dimensional crystal, it has to conform to one of the 14 Bravais lattices. So which one is it?

So I looked at this for a while, and I took this happy entity here, and I put a dot in its belly. So wherever I found one of these, I put a dot. and then I connected the dots, and what do I get? I got the rhombus.

Now, what's the basis? That's the Bravais lattice. What is the basis? So I went over here and I said, well, if I start from this thing and I go all the way up, I got some tail, blue tail here. And this thing way down here looks like it's missing a tail. So if I start from this, go all the way down to here, and capture all of this material in between and associate it with that lattice point, that can be my basis. And then I take that set of imagery, and I put it on top of this, where it's centered at about this thing's navel, and put it around here. You can see, the translation is obvious there, and the translation is obvious here. There's the wallpaper. So it's part of a Bravais lattice, only in two dimensions, you see? This is crystallography. That's all it is. Crystallography. All right.

So the next thing that we have to do, it's kind of a little bit boring, but you need to know this stuff, because it's formative for the next unit. It's the characteristics of cubic lattices. Now what do I mean, the characteristics? I mean the geometric characteristics. So there's a table here that I've taken out of your archival reading. If you go to the website, there's a set of notes that were written by my predecessor, Professor Witt. And if you go and look this up, this unit on crystallography, there's this table. And it shows such things as the unit cell volume.

Well, what's the unit cell? The unit cell is this cookie cutter cube that's the repeat unit, and it has a dimension here called a , which is the lattice constant. It's the size of the box. So what's the volume of the unit cell Well, duh, it's a^3 . That's obvious, all right? Doesn't matter whether it's simple cubic, face-centered cubic, body centered cubic.

How many lattice points per unit cell? Well, that's-- how many atoms do I get per unit cell? If you look at this, you say, well gee, it's-- you know, if you've got the simple cubic, you've got them at the eight corners, so it's eight, right? Well, no, because each atom on the corner is inside this cell, but it's also inside the neighboring cell, and it's inside each of the eight neighboring cells. So I have eight times one eighth. So the total amount of atom within the cube is only one. That's why you've got to go through this derivation.

So here's an example for face-centered cubic. You see the corners, one, two, three, four? There's eight of those. Eight times one eighth is one. And then you've got these atoms on the face, and there's one, two, three, four, five, six, right? Six faces. But each of these atoms on the face is only half inside the cube. The other half is in the other cube. So I got six times one half is three, and that gives me four. So that's how you go through, and figure out what's going on.

And then you can look at things like nearest neighbor distance, and what's the relationship between the radius, if you're looking at hard sphere packing. So here's a good example. Here's the hard sphere packing model. So I've got atoms all the same size, and they're packed to touch. And they're packed to touch so that in the end, I end up with a face centered cubic arrangement. And so what's the relationship between the radius and the lattice constant? And it's just simple trigonometry, right? $4r$ equals $2a$ squared, and you go through it, and that's how you end up with all these formulas. So that's what going on.

All right. So I think we're going to move to the last five minutes here.

So just a couple of comments. Today we played music when you came in. It was Burning Down the House. An old piece by Talking Heads. Why was I playing Burning Down the House?

Well, I want you to study this painting. This is a painting by Georges Braques, from 1908, And it's called The Houses at L'estac, or if I speak Canadian, The Houses at L'estac. And you see the thing about these houses? You see the ones in the background have better definitions than the ones in the foreground? And the ones in the foreground are all distorted, and kind of falling over?

Well, when this was exhibited at the Salon, on the critics lambasted it. They said, this thing is absolutely childish. And one of the critics said, this isn't a painting of houses. This is nothing but a stack of cubes. And from this painting, and that negative comment, came the term cubism. And so the entire movement of cubism comes from this. And since we're studying the properties of cubic crystals, I thought the connection was pretty tight. And that's why I chose that piece.

Don't go anywhere yet. We still have a couple of minutes. It's not better out there than it is in here, I guarantee you.

All right. So now I want to show you one of the properties. Why do we care about atomic arrangement Suppose some of you are interested in fiberoptics. One of the things you have to do in fiberoptics is make junctures, because you can't run a cable 100 miles without making some junctures. Well, atomic arrangement reflects microscopic properties. And one of the properties that you can have in a crystal is something called birefringence, depending on the atomic arrangement. So what

happens is if you have a ray that comes in from the left here, it splits into two. And that's no good, in certain instances. In other instances, if you want a beam splitter, you want something birefringent.

So look at all these crystals. Quartz is birefringent. Ice is. You've seen it. Calcite is birefringent. What do I mean by that?

Well, Dave, can we cut to the document camera? Right. So here's a here's a crystal of-- well, this is my handwriting. It's beautiful. Let's write-- here's more. Isn't that beautiful? OK, enough about me.

Now let's-- All right. So this is birefringent. But what happens if we rotate it? We can change the degree. And if we're really clever, and we get it onto the optical axis, we can actually get these things to superimpose.

Here's a piece of cryolite. This is the stuff they make aluminum out of. They dissolve aluminum in it. And you can see that, see, I loaned it to somebody, and they dropped it. And when they dropped it, they damaged it. That's what happens. Look, it's all crunched up there. But anyway, I don't want to get into that. But so you can see, if we turn this and we get it right on the optical axis, we can actually make these things line up sometimes. Anyway. So you can see the property of birefringence.

OK. Let's go back to documents, Dave. One more thing.

Last thing I want to show you. You know gold. Gold looks like this. It's yellow, right? Well, depending on how you, you know, those of you have seen certain wedding bands know that if you want to make a white gold, you add nickel to it. And once the nickel content gets above a certain level, the gold looks white. In other words, just metallic reflective. In Eastern Europe, it was common to add high levels of copper, in which case, you get a beautiful rose-colored gold, or pink gold.

I'm going to show you some blue gold. This isn't a joke. This is 14 karat. It's 40 plus percent by weight gold, and the balance is indium. And when you add indium to gold, you get blue. Document camera, please. Just so that you remember. OK.

That's gold. This is gold foil. Rutherford, et cetera, et cetera. You know, this is yellow gold. Ho-hum. This is white gold. Same deal, but with some nickel. Now it's reflecting off of the yellow gold. Boy, there's a lot of yellow in here. Where's that coming from? It's hard to tell.

All right. Now Let's look at some blue gold. This is blue. So, but it's brittle. So you know, what are you going to do with something that's brittle? You can't shape it. So I have an idea. So here's my idea. See, what we do is-- see this? We do, instead of this, we put this. We drill a hole in it, we put hands on it, we sell it for a lot of money. It's blue gold. It's blue karat gold.

What you can do if you understand crystallography. All right, get out of here. I'll see you on Friday.

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