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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Session 13

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PROFESSOR: OK. Folks, I may not look like Don Sadoway, but for today, I am Don Sadoway. So let's-- I guess you can hear me pretty well, right? OK. Professor Sadoway is in a faraway, terrible place. It's called Vienna. Yeah, I know. We're here. What can I say? And he'll be back next Tuesday.

And so my name is Ron Ballinger, and I'm taking his place. Put a muffler on that. OK, great. I'm sure you're all anxious, before we get started, to see that. Right. The average-- it was about 66, which is about 10 points lower than the last five or 10 quiz ones. So it's a little bit lower. It was a little bit harder test. I'm sure Professor Sadoway will mention this when he comes back, but for those of you who are below the 50 mark, it's time to do something about it, and when I say do something about it, I'm sure your recitation instructors will be very happy to help out in any way possible, but there are other options, not the least of which is a tutor.

And so if you think you need one and you need to be kind of ruthless about examining yourself-- if you think you need one, go down and see Hilary and there are tutors which are available for individual instruction. So I think it's a great time to take it take advantage of that because I can guarantee you that test number two will not be any easier. In fact, it'll be considerably harder because it'll be pretty much new material. OK. So that's enough for that. Last day, we were-- I wasn't here. I was in Washington.

They're actually trying to build what's called an exoflop computer. Does anybody know what exo means? 10 to the 18 th. 10 to the 18 th floating point operations per second. Why do they need that? Because when you go beyond 3.091 then starting modeling these atoms-- especially f-block atoms-- you need a supercomputer that large and to do one run on a petaflop machine takes 100,000 CPUs 10 hours for one atom. So solving the Schrodinger equation's a bit tricky. OK.

Remember last time, we talked about metallic bonding and we're sort of sneaking up on it. Remember, Paul Drude-- well, let's look up here. These are the characteristics of metallic solids. They have high electrical conductivity. They have high thermal conductivity. They shine and they have ductility. So we're going to deal with the first three today, and later on in the course, we'll talk about the ductility part.

But recall that Paul Drude modeled the solid as a series of cations, which amounted to the nucleus plus the inner core electrons and then allowed the electrons-- the remaining, the outer shell electrons, the valence electrons, to float around, called it a free electron gas. And that model explained the temperature dependence of heat capacity, but it was not so good when it came to electrical conductivity. It explained

the fact that you get electrical conductivity, but not the fact that some materials are conductors and some materials are insulators.

So we need to deal with that and for that, we need to talk to two sets of folks. The first one is Felix Bloch and he was a 1928-- he was a-- he got his PhD under Heisenberg. Boy, it would've been nice back in those days, working for those great folks. And he applied quantum mechanics to solids. He said, OK, let's consider that in a solid, the atoms are arranged in an array.

What's an array? Well, it's actually called a crystal. It's an ordered array of atoms. We're going to say a lot more about that as we go along, but-- and then he said, well, then let's apply the Schrodinger equation to this system. Now it's a big difference between the Schrodinger equation for a single atom in a gas and multiple atoms in a solid. It's a different set of boundary conditions, different set of conditions all together. And when you do that, you get a set of solutions for the valence electrons which is, as you might expect, it's periodic. It's periodic and it invokes wave-like properties of the electron and you end up with a set of values of the wavelengths for the electron that are such that it allows mobility, which is, after all, what we're after. These electrons got to move through the solid if we're going to have conductivity. And this is an example where classical physics wouldn't allow that. So you can't get this kind of behavior with classical physics. So that's one piece.

And the second group, two guys. Walter Heitler and Fritz London. We know Fritz London from London dispersion force-- the same guy. These guys were very, very productive. And he did a post-doc-- that's another word for slave labor, by the way. Folks will know that here. For guess who? Well, he did it for Schrodinger. Interesting story, I guess. These guys showed up for their slave labor at Schrodinger's lab, only to discover that Schrodinger had taken a position at a different university. So these guys showed up and he said, goodbye. Anyway, that's a bummer. OK.

And they sat down and they said, well, OK. Let's see if we can go at this from an energy point of view as opposed from the quantum mechanical point of view and let's see if we can apply LCAOMO-- now don't break out in hives because of the test-- to a solid, to large aggregates. Large what? Of atoms. How big is large? Well, I don't know. Dream up a number-- say, 10 to the 23rd. Lots of atoms. And let's see what happens.

Well, we've already done a little of this in the past. We looked at the energetics of the stability of hydrogen or the stability of helium. So we can take that and we can kind of add up and we'll see what happens.

Well, remember, we had atom A and now let's only deal with the valence electrons. And so this would be 0 and there's another atom A-- 0-- and this would be A² and we've been through this before. Let's just take-- we know that we get splitting and we get a sigma bonding orbital and a sigma star anti-bonding orbital.

Well, let's start adding some atoms here, additional atoms. What do we get? Well, let's just try for A_N-- lots of atoms. What do we get? We end up with lots of states. Remember, we have to have conservation of states. So for every atom we add-- let's say this is copper, for example, which has an s¹, one s. It's an odd number of electrons. So every time I add a copper to this, I add extra states. And then what do I do? I start filling them using Aufbau, just like we've done in the past. Well, if we keep going, and by the way, not to scale, it starts looking like a whole

bunch of states. And this energy level here, these energies, what? We know for hydrogen, this is what? Minus 13.6 electron volts.

So what are we dealing with here in terms of state differences? Well, let's take 10^{23} atoms and let's see if we can calculate energy. Well, let's take for copper-- the molar volume of copper is what? 7.11 centimeter cube for mole. All right. And that's N to the 23rd-- actually, 6.02 times 10^{23} atoms.

And let's just ask ourselves, what's the sort of range here? Well, we know it's 13.6 here. We know that's 0. We're all friends. So let's call it 10 eV, just for grins. Not a bad number. And let's ask ourselves, well, if we've got 10^{23} atoms and 10 eV-- let's take 10 eV over 10^{23} and you get what? Well, 10^{-22} eV per state. That's small. That's really, really, really, really small and if you convert that to joules, you end up with 10^{-41} joules. That's really small.

So what are we saying? We're saying that this organization here-- when we and put a lot of atoms in there, we end up with what amounts to a band. A band of states. And what do we do? We populate this band just like we did using the Aufbau principle, but what does it really look like? Well, in the case of copper, you remember, copper has a 1s electron. Copper is $3d^{10}4s^1$. If we start filling start this band, we're going to get-- and so we start filling and we get up here and we find that we end up with a half-filled band, because there are states that are not occupied. But remember, the distance between this guy and this guy, an occupied and unoccupied state, is only 10^{-41} joules. So that's pretty small. 10^{-22} electron volts.

To give you an example, 0.025 electron volts, which is, if you want to convert that to temperature, that's about 300 degrees Kelvin. So very, very small energy. So that means if I were to take and if I were to apply a potential here, then what happens? Well, I add a little energy-- and I don't have to add much energy-- and it's very easy for me to promote one or more of these electrons up into the above here and then I can get migration.

So the endpoint is that if we apply a potential, we end up with conductivity, which is what we were after. Moreover, we can say a few more things. If I shine-- now this is a sort of mixed metaphor here. This is an energy diagram and this some plates on an electrode so be a little bit careful. We shine photons on this thing. What happens? What's the energy of the photons, of light? Between 200 or 400 and 700 nanometers. It's about one electron volt. So there's plenty of electron volts here. I'm going to-- with a metal, not only will I have conductivity, but there'll be enough energy here to promote electrons and those electrons will move around and we'll end up with re-emission and we end up with opaqueness. In other words, we absorb light and readmit it and so we end up with, in the case of a metal, luster. So there's a couple of things.

So if we recall back here-- we're talking about high electrical conductivity. We had-- we need to say a lot more about that, but we're OK here. But Drude, it was OK as well. High thermal conductivity, Drude did that. That was fine. Luster. OK, So it works for copper, seems to be OK. But what about another one? Like, say, beryllium. What's with beryllium? Well, beryllium is $2s^2 2p^2$. So now let's draw the thing for beryllium. We have beryllium. We have-- must be a 2s and now it's 2p and we populate this. And now we want to add a beryllium-- n beryllium atoms, all right?

What's happening? well, it'll be a little bit. We got this band that we've talked about earlier.

Now we go to fill it. So we're filling these guys and we fill it, and lo and behold, we find out that we fill it all the way to the top and so we're screwed. We have no conductivity. What I can imagine now is there's 100 computers in here. 50 of them have Skype. Guess what's going to happen? By the end of the day, there'll be 50 things up there. So we know beryllium's metal and it has conductivity.

So what's the deal? Well, it turns out that while beryllium has the 2s band full, the 2p orbitals still are there. They're still there and so there's going to be a band unfilled. There's going to be a band for the 2p orbitals. Well, guess what? It turns out that the way I've drawn it, the 2p band overlaps the 2s band. And so what that means is that I can promote into the 2p band and I can achieve my conductivity. So that's another-- so we solved the problem of the filled s-orbitals, and we've got conductivity in both cases. So we're OK so far, but Drude wasn't far behind.

What can we say about insulators? It looks like we have a problem. Well, let's take a look at another example. And let's try carbon. Well, we know carbon is what? $2s2p^2$. And so we can go-- and we know, by the way, that most of the time carbon will hybridize and so we'll end up with $2sp^3$. So n equals $2sp^3$ hybridized. So we see that happen. And we also know that carbon's not a metal and that we have strong bonds. In the structure that we're going to talk about, they're covalent bonds and so they're very strong bonds.

So let's do this. Carbon in the gas phase-- we have 2s and 2p. We know that what happens is we end up with hybridization and so we end up and we fill these guys. So that's what we get. Now this would be for diamond in the gas phase. So with this hybridization, we get bands. We start adding carbon atoms to this and what do we get? Well, we get a band that's the 2p band. The sp^3 band is different looking than the bands for magnesium or copper or beryllium in that there's a separation between the sigma and the sigma-star anti-bonding orbitals.

So we start doing these guys up using Aufbau, and we discover that there's an energy gap e sub g between the sigma bonding orbital part of the band and the sigma-star band. So what's happening? Well, that's actually pretty good sized. It's about 5.4 electron volts. Now compare that with what? Visible light is around one electron volt. So now we have a very, very different situation and there's some terminology we need to have here. This is the so-called conduction band and this is the so-called valence band. Valence band and conduction band.

So in order for us to get electrical conductivity, we have to somehow promote an electron across the 5.4 electron-volt band gap. This is the so-called band gap. Now we know that visible light is about 1 electron volt so we know that's not going to do it. And in fact, we might expect that even a diamond is what? Transparent to visible light. So if the photons come in, if there's no promotion, there's no mission, transparency to visible light. So that's a big number.

Let's try another one. Let's try silicon. Now I'm going down group four, where silicon is going to be also sp^3 hybridization. So we can do that, only this time over here, carbon is what? n equals 2. For silicon, n equals 3 and so we can do the same thing. Here's the 3s. Here's the 3p. And we hybridize and we end up with before and then

we end up with a band, same kind of band structure where this is a sigma-star, star, this is e sub g , this is the valence band, conduction band.

Now we have states up here, but in this case, what do you figure? n equals 3. So those valence electrons are hanging out further away from the nucleus. And we know generally that the energy drops off, the valence electron energy drops off as we get further away from the nucleus. So you might expect that the energy of this gap would be a little bit smaller and indeed, it is. Very fortunate for us, it's 1.1 electron volts. Now we're getting close. And so this is 1/4 or even 1/5 of that for carbon and remember, visible light is on the order of one electron volt. So one, one and half electron volts. So what happens? This is close enough so that we get semi-conduction. It's called a semiconductor and we'll make a definition. If the band gap is greater than 3 electron volts, we call it an insulator. If the band gap is less than-- well, let's give it a range. 1 to 3 electron volts, we call it a semiconductor and of course, if the band gap is equal to 0, we call it a metal. So that's a distinction, which is a little bit arbitrary, but pretty good.

So now, if I take a look at silicon, what do I see? Well, if I had a piece of silicon here as opposed to diamond and I looked at it, it would be gray. We would have color and the reason it would have color is because I get some promotion here and I get re-emission and so now I get color. So it's not transparent to visible light.

OK. Let's take a look in general at what we-- what we're talking about is photoexcitation. Now this is a diagram which is-- you should have in your aid sheet. Sooner or later, you should have it in your aid sheet. OK. So let's draw a general band. Here's our two bands. This is the valence band. This is the conduction band and we have a band gap. And now what happens if I were a photon here? Well, I guess it depends. If the photon-- if e photon greater than e band gap, then what happens? I get promotion of an electron up from the valence band to the conduction band. OK.

So then what happens? Well, the photon is quantized. It's one shot. The photon's gone. Now I guess we need to settle one little thing. What happens if the photon is really a lot greater than the band gap? In another words, let's say it's a million electron volts or something like that. Well, for purposes of 3.091, what we're going to assume is that any excess energy goes to heat. Let's not worry about what happens for other things. In fact, that's not far off. Some of these LEDs that you see, they get warm. So there is some heat. So the photon-- once it goes away, I get-- the electron falls back down. Well, if the electron falls back down, then what do I get? I get another photon out, but now I've basically built myself a diode or some kind of device. That photon-- the energy of the photon is equal to what? It's equal to the band gap, which is equal to hC over λ . So I can adjust the wavelength here if I can adjust the band gap. See where we're going with this?

Well, what happens if I-- let's say I hook this up to a resistor and I draw a current. Well, as long as I keep the light shining on here, photons, then I can keep promoting these guys, and I can keep drawing current. So what do I have? I have something that I can generate electricity with light. And so that's sort of solar-powered something, isn't it? We can generate current. What happens if I take-- and now instead of doing that, I hook up a battery to this thing and now I pump current in here? I pump current in here. In that case, I can force the electrons up here. So I can force electrons to go in the reverse and I could make a photosensor or I could force the electrons up here and let them come back down and I know this

wavelength here, I can make a light-emitting diode. So just this one little concept here, which is very simplified, gives us the basis for photovoltaics. And that's exactly the way it works. OK.

Let's put this in another way. Let's plot the percent absorption. In other words, if the energy's high enough, I absorb-- versus wavelength this way and since energy is inversely proportional to wavelength, we have energy going this way. Let's put some numbers in here. Let's say this is 400, this is 700 and this is Professor Sadoway's dreaded nanometers. So this is visible light and let's put carbon on there. Well, if you do the calculation, convert it, it turns out that for carbon, with this band gap, you end up with behavior where if the energy is above the band gap, I get-- well, let's call this 100. That's 0, right? I get 100% absorption.

When I get to the band gap, below the band gap, what happens? Well, I drop off and it goes like that. In the case of carbon, this wavelength, right, which is, by the way, called the absorption edge-- that number comes out to be about 229. If I try it with silicon, that number-- so this would be carbon, this would be silicon and carbon-- 1125. All right. So the absorption edge for silicon is 1125, which means it absorbs in the visible range and so that's the way we get the luster. And this would be in the what? Infrared. And this would be in the UV region, if you wanted to-- which would be far hard UV and this would be far infrared. OK.

This is the paper-- Heitler and London's paper. It's in German and you can see in Zurich. And this is their original paper. You can go down to the library and you can get this original paper and if you know how to read German, it's-- we have it. This is some of the original paper. You notice the Schrodinger equation up there. Nasty-- really nasty, but this is the calculations. This is radius. This is energy and you can see a point here where you get an energy minimum and that's where the bands operate. This is another way to look at it. This would be the bottom of the bonding orbital or the top of the anti-bonding orbitals.

This is another way to look at what we've drawn so far. Somebody is talking. Something you guys ought to know, this room is acoustically perfect. If you pass gas in the back row, I'll hear it, OK? So if you're talking up there, I'll hear it. OK. So you can see what's going on here. We've drawn that and this another way to look at it. By the way, there's a mistake in your book that doesn't make any sense. $2s3p$ -- it's $2p$ in the description for beryllium. OK, this is another way to look at it. This is in the archival notes. It's one of the few pieces of the archival notes which I don't understand. So don't worry about that. OK.

Here's what happens when you-- where we illustrated this where you apply a potential. What happens is you depopulate the bonding orbitals, and you populate the antibonding orbitals rules, and you get conduction. This is another-- this is the right way to look at it. This sort of illustrates the things we've gone through the whole time. A metal has no band gap. That no band gap is achieved either by half-filled set of orbitals or overlap between one or between different levels. An insulator has a large band gap and a semiconductor has a sort of intermediate band gap.

Let's get a little-- sort of wet your whistle for your reading for next Tuesday. I think we have Monday lecture on Tuesday. If you go over to the reactor-- they have a reactor here at MIT-- once a week, a truck backs up and it's full of silicon logs. These things are about 12 inches in diameter and they're about this tall and they bring them into the reactor and they're irradiated with neutrons. Well, what do you think

happens? Since everybody in here knows the Periodic Table by heart, what's the next atom-- what's the next element over from silicon? Phosphorus. OK. So guess what? You take and you irradiate the silicon. You absorb a neutron. It adds one to z , doesn't it? And it becomes phosphorus. Well, phosphorus has one more electron than silicon. So I have implanted phosphorus into silicon by transmutation. And there's one more electron that's in there. Now where's it come from? I don't know. The electron bank, right? But what do you figure the energy of that guy is? Well, it's a lot higher than the electrons in silicon. And so guess what? That electron, we'll find out, doesn't reside down here. It resides up here or very close to that. So that's what's called-- and we'll talk about it next time-- it's called doping, only now we're doping it in a special kind of way. OK.

We've got-- let's keep going. I want to get this one up there. There we go. OK. Now-- so far we've talked about photons. They're a one shot deal. What about thermal excitation? Well, we can make our-- the same drawing we have in the past. We got our material here where we have a valence band, conduction band, and now we put-- we add thermal energy.

By the way, what's the one electron volt in temperature? Just to give you a feel-- one electron volt is 11,600 degrees Kelvin if you convert that to temperature. So one electron volt seems like a small number, but in temperature, is pretty warm. OK. So now the thermal energy is what? It's constant. Unlike the photons, which are one off, right? So it's constant. So what happens?

Now I take an electron from the valence band and I promote it up here. So it looks sort of like-- so far up there with photons. But there's one critical difference. It stays up there. It stays up there because the energy is constant. So what does that mean? Well, it leaves behind a broken bond. And that broken bond has a lot of energy, and in fact, it doesn't like to stick around. So given a chance, it'll move. It's like a hot potato and so that broken bond is called a hole. We're not too imaginative. It's a hole in the lattice. But it has high energy. So what's the deal with this hole? Well, this is-- a hole is a 0 in a land of minus 1. So what does it mean? It's actually net positive.

So now in the case of thermal excitation, I end up with an electron in the conduction band and a hole in the valence band. So I end up with an electron in the conduction band and a hole and the electrical engineers call this p . They're not very imaginative either-- positive in the valence band. So we get 241. We get two charge carriers for every event. That, we get one. This, we get two charge carriers for every event. So now we have what? Let's ask ourselves, what's the-- can we do a little math on this? And the broken bond, by the way, is a hole and so the number of electrons is also equal to the number of holes because it's a one for one, and in the electrical engineering world, they say n equals p .

And so we can now go back and say something about this conductivity. We can do some calculations here and we can calculate the conductivity due to the electrical connectivity, and it's really the sum over i of n of i , which would be the number of the population of carriers times-- that's the value of the charge on the carrier-- times something called the mobility.

OK, so what's the mobility? Well, you could imagine that these electrons have to move back and forth in the lattice and in a metal versus a covalence solid or something like that, it might be a little bit different. The resistance might be different

and so-- in fact, it is. μ_i is equal to the velocity of the charge carrier divided by the electric field. OK. So we're almost there.

Now we need to-- and we can simplify this because of the $n = p$ business, and we can say that the electrical conductivity is equal to what? It's equal to $n \cdot e \cdot \mu_e + p \cdot e \cdot \mu_h$, which would be the holes, the electronic charge, times μ_h . But since n is equal to p , we end up with $n \cdot e \cdot (\mu_e + \mu_h)$. OK.

And so that-- what we really need to get is this. Well, we don't have time to go through that, but from a quantum mechanical calculation, we can get that. $n \cdot e \cdot \mu_e$ is equal to what? It's equal to some constant times $T^{-3/2}$ times the exponent of $-\frac{E_g}{2k_B T}$. So what is all this stuff?

Well, this is a constant. This is the temperature. This is the band gap. So it's a representation of the binding. What's down here? Well, k_B is Boltzmann's constant. This is absolute temperature and so this represents the disruptive force. So it's a balance between how tightly they're bound and how much energy I've got to do this. Well, let's-- we've got one minute. Let's do a quick calculations for silicon, just to close the loop here.

For silicon at room temperature, that number comes out 1.3×10^{10} per centimeter cubed. Say well, that's billions. That's a big deal. What about copper at room temperature? Well, that number comes out about 8.5×10^{22} . Now we're talking big numbers. So there's a 10^{12} difference between these two

Well, let's take a quick look before we finish up. OK. This is the band gap as a function of position in the Periodic Table. Now you guys ought to be able to rationalize this. Lead is a metal, bigger atoms you can see. 10^{22} actually comes in two flavors. Gray and white and one of them-- I think it's white-- actually forms covalent bonds and they use tin for night vision. Think about where that band gap is.

But here's the punch line. We're trying to rationalize this large difference in conductivity. Well, there's copper up there at 10^{22} , there silicon at 10^{10} and ten to the minus 4, 10^{-4} , about 10^{12} or thereabouts-- and so, lo and behold, this-- we were able to rationalize with these fairly simple models, the range of conductivities that go all the way from metals to semiconductors and even diamond. Look at diamond-- 10^{-11} . You can rationalize that the band gap-- where's the band gap? 5.4 electron volts. OK, we're out of time.

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