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3.091 Introduction to Solid State Chemistry, Fall 2004
Transcript – Lecture 13

OK, let's get started. Settle down. A couple of announcements to make: it is with great sadness that I announced that there will be no lecture on Monday. Yeah, I know. With all the Kleenex consumed, Kimberly-Clark went up two points on the New York Stock Exchange yesterday, which is incredible.

And, in view of the timing of where we are on the lectures versus the homework, and no opportunity to interact with the recitation instructors on Monday, what we are doing just this one time, we're going to slide the weekly quiz over to Thursday.

And, that gives more time for people to contact their recitation instructors. Well, let's get on with the lesson. Perhaps some of you haven't figured out that the lecture has started. And I still hear talking.

And I will invite people to leave if they insist on talking. So, last day, we talked about secondary bonding, and we looked at various forms of secondary bonding. Here's the cartoons, dipole-dipole interactions, dipole induced, dipole in solutions, a little bit of a diversion, induced dipole, induced dipole, which was the London dispersion forces, or van der Waals bonds, and also hydrogen bonding.

And, all of these helped us answer the question, what's the state of aggregation? The reason we want to know the state of aggregation is that this is solid-state chemistry. And we want to know when something is a solid.

So, this helps us get to that conclusion. And, then we came to the point where we realized that three quarters of the periodic table wasn't covered by either ionic bonding, covalent bonding, or van der Waals bonding as a primary form of bonding.

So, we had to come up with something else. And that something else was metallic bonding. We saw Paul Drude's early attempt in 1900 to model metals as a gas of free electrons moving about ion cores, where the ion core, in fact, is a mix of the nucleus plus all the inner shell electrons.

And, we recognize that that didn't take us very far. So, what we want to do is continue the discussion. And today we're going to look at the next installments, which took place about 30 years later as part of the quantum revolution, And, there's really two benchmarks here.

The first one is by Felix Bloch, and this came out in 1928. This was his Ph.D. thesis. What he did for his Ph.D. thesis, which was done under the supervision of Heisenberg at Leipzig, took on an interesting problem.

So far, you've seen quantum theory applied to gases, right? Bohr talked about atomic hydrogen. And, you know the complexities of condensed matter. Bloch's Ph.D. thesis: quantum theory of solids. Let's take quantum theory and apply it to solids, not bad for an opener.

Quantum theory of solids was his Ph.D. thesis. And, here's what he did. You can follow. I'm not going to give you the derivations, but it's quite simple. First, he recognizes that atoms in a metal are arranged in periodic positions.

There is an array. It's not just thrown together in some jumble. So, atoms in solid set in regular patterns. We're going to learn these patterns next week, arrays, and such solids where the atoms are found in regular patterns are called crystals.

So, he took that as one benchmark. The second thing: he says that, remember, Drude says that the valence electrons are free to move around. And, he says, well, if these valence electrons are free to move around, what would they be subjected to? They would be subjected to a potential.

This is how we derived the energy levels in even a single hydrogen atom. We've got the positive charge of the core; we've got the negative charge of the electron. So, now I've got an electron, and it sees the net positive charge of the atomic core.

But, it sees an array. It sees periodic variation in potential. So, that's the second thing he says: periodic potential acts on the valence electrons. And then, he invokes wave mechanics. Remember, Schrödinger's equation was only enunciated a couple years earlier, in 1926.

There's a Ph.D. student who hears about the Schrödinger equation as applied to a gaseous atom. And, he's applying it to condensed matter. And so, he solves the Schrödinger equation with these constraints.

And, what does he get? He gets a set of solutions. He gets a family of solutions. And, these give rise to a set of wavelengths of the electron that could move quickly through the crystal, they could propagate.

In other words, by invoking the wavelength properties of the electron, he can rationalize how these valence electrons can move through barriers that classical physics would impose. And so, pretty soon, out falls electronic conductivity.

So, this is pretty good for an opening volley, not bad for a Ph.D. And, he eventually took on some faculty positions, and then in the 1930's, when the Nazis came to power, Bloch, as did many of the scientists from Europe left and came to the United States.

And, he settled at Stanford. And, eventually he won a Nobel Prize, but not for this work. This was OK, but he got a Nobel Prize in 1952 for work he started in 1945 that had to do with magnetic moments in the nucleus.

So, he had more than one good idea. So, that's the first thing we need to take into account in the band theory. The second was a pair of gentlemen: Walter Heitler, and same man as from last lecture, Fritz London.

This was before he came up with the dispersion idea. Dispersion bonding was 1930. But he and Heitler decided to go in 1927 to Zurich, and spend a year postdocing with Schrödinger. Little did they know that Schrödinger had negotiated a position at Berlin.

And, they no sooner arrived than Schrödinger left. But anyways, that's what brought them to Zurich. And they decided, let's take this idea of linear combination of atomic orbitals, and instead of asking rinky-dink questions like, is lithium-2 stable? Is helium-2 stable? And looking at bonding versus anti-bonding, he said let's ask, if we take Avogadro's number of wave functions and blend them in something like copper, can we make sense of what's going on? So, this is what their contribution was.

It was linear combination of atomic orbitals into molecular orbitals for large ensembles. And so, here's how that goes. Let's take a look at the cartoon. You recall last day we looked at something like if we wanted to ask whether A blends with another A to make A2, we can start at some level.

I'm going to just look at the valence shell, OK? So, I look at the valence orbitals. This is atomic orbitals. And, when these two come close together, when these two atoms become close enough that they're operating as one system in order not to violate the Pauli exclusion principle these energies have to shift a little bit.

Otherwise we run the risk of having more than one electron with the same set of quantum numbers. So, these will rearrange themselves into what we call anti-bonding and bonding orbitals, where anti-bonding are at slightly higher energy than the parent atomic orbital, and bonding are at slightly lower energy than the parent orbital.

So, this is A2. Now, suppose I do this one more time. Suppose I take A plus A2, and I want to make A3. What would happen if I took A plus A2? Well, again, not to violate the Pauli exclusion principle, this initial, whatever this orbital is, let's call it ns, I don't know.

Maybe it's 3s, whatever, it's going to have to allow for that number of states. And, I think you can see by analogy, this is what Heitler and London did. They kept going until they got An, where n is large.

How large? Oh, a crystal about the size of your thumb, on the order of a cubic centimeter, in other words, a block of metal. So, when n is large, what happens? So, this thing keeps going. There's a little bit of a broadening.

But, this is what happens. We have many, many levels here starting at the highest anti-bonding down to the lowest bonding. But now, the space, the energy difference between successive levels is getting vanishingly small.

And in fact, you can think about it. How many atoms would there be in a cubic centimeter of copper? Well, let's think about that. If I've got a cubic centimeter of copper, I can look on the periodic table.

If you look on the periodic table, the molar volume, they call it atomic volume, but the molar volume of copper is 7.11 cubic centimeters. So, there's Avogadro's number there, right? Who is buried in Grant's tomb? Grant.

How many atoms in a molar volume? One mole. So, this contains N Avogadro atoms. So, divide in. So, N Avogadro atoms, you can divide through and pretty soon, you figure out how many states there are.

If I go 1 cubic centimeter, it's roughly 10 to the 23 atoms per centimeter cubed. So, that means I'm going to have 10 to the 23 states here. And, what's this energy difference? It's on the order of some tens of electron volts.

So, suppose I put in here. I'll even give you 1,000 electron volts because I've got a lot of protons in the nucleus. Suppose this is on the order of ten to the third eV, but it's divided by 10 to the 23rd contributors.

So, what's the delta in here? It's about ten to the minus 20 electron volts, which is about ten to the minus 40 joules. I mean, this is less energy than the movement of the eyeball of the mosquito.

There's nothing here. There's nothing. So, from a distance, if I get up really close, this is still Aufbau principle. So, the electrons come in two by two just as Noah's ark, from the bottom up to the top.

These are all distinct quantum states. But from a distance, they are so close together that this appears to be a band, almost a continuum, a band. So, the band is a set of very closely spaced orbitals.

And now, you see how to populate, and for something like copper, we know copper is argon 3d104s1. So, copper is two by two coming in. And, they'll fill up to the halfway point of the band because I can put two per orbital.

But, I only have one per copper. So, if I blow this up, what do I have? I've got this band that's half filled. This is the S band, and it's half filled. And then, the next level is a vanishingly small energy difference.

And so, if then I apply a potential, let's say I make this side of the crystal negative, and I make the side of the crystal positive, it takes a tiny bit of energy to pull an electron out of the topmost orbital, put it up here, and now it's free to move about the crystal.

So, this accounts for the high degree of metallic nature of materials because the energy levels are so close together. In the past, we saw for classical gas phase atoms, it took a substantial amount of energy to move something out of its ground state.

In this case, to move out of ground state takes a trivial amount of energy. And, I think I've got some cartoons that indicate this. This goes back to Drude with his cation. Some books will actually call the atomic core as cations.

But, they're being sloppy with the terminology because it's the ionic core consisting of the protons of the nucleus plus the inner shell electrons. But, in electrical engineering, they'll refer to this as cations and then the sea of valence electrons.

So, here's a cartoon showing what's happening as you progressively add larger and larger numbers, and not to violate the Pauli exclusion principle. You have to keep shifting the energies. And, since you only have one electron here, as you move out in this case, sodium, you will find you are filling two by two, and all of the bonding orbitals are filled with a tiny energy difference.

And, this is out of the reading. This is the same idea, only it's done in the case of lithium. And lastly, this is the idea I was just trying to get across that here's the metal sitting at rest. And now, there is an electrical potential put across it, which wants to move electrons, and even with a modest potential, that's enough to disrupt the bonding here in the uppermost levels, and cause electrons to rise, and then move along the anti-bonding orbitals quite freely.

So, that gives us a sense of what's going on in the conductivity of something like copper or sodium. But, now let's think about something like magnesium. Magnesium is a metal. But let's think about what's going on with magnesium.

Magnesium has 3s, but it has 3s2 in the case of magnesium. Magnesium is 3s2. So, if we start filling magnesium s-band, we're going to fill two by two all the way up to the top. If this is s, and the p's are up here, what happens when the p's split into the bands? That's the real issue.

And, mercifully, what happens in the case of magnesium is this is the s-band. But for magnesium, the p-band, the bottom of the p-band lies below the top of the s-band. So, in the case of magnesium, this is now the p-band.

And, the p-band energy levels are available so that when we fill the top of the s-band, we can continue to move into a range of energy that allows for motion. So, we are able to account for both unpaired electron atoms, and paired electron atoms by this overlap of energies.

And, I think there's a cartoon in your reading that indicates that. Yeah, this shows what happens with the energy levels as a function of distance. And, you can see that the p-band is now dropping below the top of the s-band, and so it allows for continuous filling into more states.

And so, this now accounts for not only such things as electrical conductivity, but reflectivity. Metals have luster because the photons of visible light have the capacity to excite electrons, which immediately cascade down and reflect back.

So, band theory became widespread in popularity. In the 20s, it was known only about a few physicists. In the 30s, the scientific community knew it. In the 40s, it infected the popular culture. If you talk to your grandparents, they'll refer to the 40s as the big band era because of this.

Maybe you thought that the reason the big band era was named the big band era was due to people like Glenn Miller, Benny Goodman, Tommy Dorsey. No, it was due to Felix Bloch, Walter Heitler, and Fritz London.

So, I don't want you thinking about those bandleaders anymore. This is the band. This is the big band right here. All right, so now let's go on to something a little more interesting. One of the other shortcomings that was not addressed by Drude was the ability to distinguish between metals and insulators.

So, let's see if this theory can do that. So, let's go to something like diamond. So, if we start with diamond, here's carbon as a single gas molecule, and we start off with 2s and 2p. And we know that this, then, hybridizes to maximize bonding capability.

So this is now sp3. And, I'm going to put a two here for reasons that will become apparent in a minute. So, this is now carbon in the diamond configuration has a single gas molecule. Now, I know this is sort of the sound of one hand clapping, but this is the lone carbon that is waiting to form diamond.

And I'm going to skip over the di-diamond and the tri-diamond. That's just go to diamond crystal. So, what will happen is these levels will divide, and in accordance with Pauli exclusion principle, will start up here with the anti-bonding, and we'll start out here with the bonding.

And, what happens in the case of diamond is that when the population of anti-bonding descends, there is energy gap between the bottom of the anti-bonding orbitals and the top of the bonding orbitals.

So, we have two bands here. Before, we simply had a single band. This would have given us an s band. This would all come from sp3 forming sigma bonds. But, in this case, there is a big divide here.

So, this is the energy gap. Or, some people call it the band gap. And, the energy here is given a symbol, E sub g, the band gap energy. And, in the case of diamond, the band gap energy is 5.4 electron volts in diamond.

So, what happens now? Now, let's fill this, one, two, three, four, and if we count this properly, see, we've got single occupancy. We fill to the top of the valence band. This is known as valence band because these were bonding orbitals.

We fill to the top of the valence band, and now if we want to apply an electrical potential to cause these electrons to come out of the bonds and move up and down the crystal, we've got to come up with 5.4 eV, which is a substantial amount of energy, and doesn't happen.

So, as a result, this is an insulator. So, we now have the capacity to distinguish between metals and insulators. Insulators have high band gaps, typically on the order of about three electron volts.

Metals have no band gap, continuous availability of these closely spaced orbitals. And, while we're in the neighborhood, this upper band that consists of all of the anti-bonding orbitals is called the conduction band because this doesn't involve bonding.

So, if an electron is in this upper band, it's free to move, and under the influence of electrical potential, it will do so. So, we have valence band, conduction band, band gap. Now, let's look at one other one.

Let's look at silicon. Let's look at silicon. Silicon is in the same family. It's group four, sp3 hybridized, only in the case of silicon, we're going to start with 3s atomic orbital. And, the 3p atomic orbitals, which hybridize to give us sp3, but now n equals three.

And, if we bring a large number of silicons together, we will form, as in the case of diamond, a valence band and a conduction band. The difference here is that - let's think about the strength of these bonds.

The bonds are down here in the valence band. Electrons in pairs, these are covalent bonds all the way up to the top of the valence band. This is n equals three in contrast to n equals two. So, what do we know about the relative strength of a bond in n equals three versus n equals two? Is it going to be stronger or weaker? Expected to be weaker.

It's farther from the nucleus. And, indeed, this is manifest by the fact that the separation between anti-bonding and bonding is not as great because we know that when something moves from atomic orbital to molecular orbital, this is the change in energy, going from the atomic orbital to the molecular orbital.

So, if I have a stronger bond, doesn't it stand to reason that the energy difference between an atomic orbital and the molecular orbital will be greater for a stronger bond/ This is weaker. So, therefore, this separation isn't as great as it is in diamond, and indeed, the band gap in silicon is on the order of 1.1 electron volts.

And, 1.1 electron volts is on a special range. What else do we know that's on the order of several electron volts? That's really critical here. Critical here is visible light. Visible light is on the order of two to three electron volts.

So, what happens in this case with respect to visible light? If visible light shines on diamond, it's transparent because the energy gap is 5.4 electron volts. If visible light shines on silicon, it's absorbed because visible light has greater than 1.1 eV.

And, this is an 800 millimeter silicon crystal. This has been cut and polished from a giant single crystal salami, cut, and this is down to one atom fidelity. But, you can see it appears black because the visible light that reaches it is absorbed.

And you say, well, what's the reflectivity from? Well, there is a thin oxide film, and that's the topic of another lecture. But, the material itself is dark because the energy level here is less than anything that you'll find in visible light.

You know, that got me thinking. If a photon comes in like this, a photon of visible light, what will happen? Photon of visible light will hit an electron sitting here, and excite the electron, won't it? But that electron is going to be the same thing that happened in Ballmer and Angstrom's gas tube.

This is a one shot deal. The electron rises, but it's not sustained. So, what happens immediately thereafter? The electron falls back down and reemits. So, this is photo-excitation. And, if this energy, if this E incident, if this is greater than 1.1 eV, suppose it's 1.5 eV, things get more complicated.

We're not going to go into all the quantum mechanics, just suffice it to say, that excess energy will go up into the crystal and will be dissipated as heat. And, as far as 3.091 is concerned, if the incident energy is greater than the band gap energy.

Expect excitation, loss of excess energy, and then this electron will fall back down and give us an emitted photon at exactly equal the band gap energy, right? This would be hc over lambda directly band gap.

You know, there's something here that's intriguing. You've got this electron up here. Wouldn't it be cool if you could take the backside of the silicon, and connect it to an external circuit, and shine light on the silicon, and then cause the photons to excite electrons, which could then power something? That would be photovoltaics, wouldn't it? That would be how a solar cell works, wouldn't it? If you wanted a sensor that took visible light, that strikes it, and then captures that electron, and then sends it to a detector, and maybe if you made an array of these, and so that light that comes at different intensities on different pixels sends currents at different intensities, that would be interesting too, wouldn't it? Can you see why the band gap, being 1.1 eV versus visible light is really important? How about this? What if instead of having light coming in, what if I connected this to a power supply, and I pumped the electrons out of the valence band into the conduction band from which they would fall, and then emit photons? So, I could make a light emitting device by pumping things up and having them fall down.

This is why this class of materials is dominating the modern world. Materials with a band gap around the value of the energy in visible light are called semiconductors, for reasons you'll see shortly in terms of their conductivity.

Their electrical conductivity is the least appealing of their properties. It's their ability to interact with radiation that makes them so exciting. And, actually, you know, we could actually do a test.

We could actually measure what these band gaps are by tuning the value of the incident radiation. So, for example, if we did this with long wave radiation, keep moving, moving, moving until we get to a value of photon energy that causes excitation, we could have a sensor that detects when the incident radiation is being absorbed.

And, we could plot that energy as follows. We could have this as, say, the lambda of the incident energy, lambda the incident energy, and this as the percent absorption. This is the percent absorption by the crystal.

And, this would go from zero to 100. So, energy moves from right to left. It goes inversely with lambda. So, high wavelength is low energy. So, at low energy, we expect materials to be transparent.

At high energy, they will absorb, and at some critical value of energy, absorption begins. And this value here is called the absorption edge. So, out here at very, very high wavelengths, or low energies, the material appears transparent because E incident is less than E of the band gap.

And, at high energies, the material appears opaque. Its absorbing because here E incident is greater than E of the band gap. And, this roundedness here is due to defects. It's not a perfectly sharp edge.

And so, what I did is I said, OK, well let's do the calculation. Soy compared silicon and diamond. So, the band gaps in electron volts, for silicon it's 1.1. For diamond it's 5.4. And then, all I did is just said, well, band gap energy is now converted to photon energy.

So, just do hc over lambda. So, lambda of the absorption edge, this is equal to, band gap is equal to hc over lambda of the absorption edge. For silicon, it's way out in the infrared. It's 1,125, I'm going to use these ugly units, nanometers, and diamond is down at 229 nm.

And, where is visible light? Visible light is, round numbers, 400-700 nm. So, you can see that this is out in the IR. And, this is down in the UV. So, we could make a plot here. If this is 400 nm, this is 700 nm.

So, this is visible light. Then, this would be silicon out here at 1,125 nm, And diamond over here at 229 nanometers, and visible light right in between. And I thought, well, there's probably another chemistry lesson here.

So, first of all, just to summarize, we've seen here that the metal has no band gap. So, there's no gap between the top of the bonding and the bottom of the anti-bonding orbitals. In an insulator, there's a huge band gap, and in the semiconductor there is a moderate band gap, where moderate is defined literally in reference to visible light.

Now, this was an interesting thing. Here's your group 14, or group four off the periodic table. And, these are the values of band gap energy. I've already showed you that diamond is 5.4, and silicon is 1.1.

And, again, now germanium is going out to n equals four so that sp3 hybridizes. This is 4s2, 4p2 forms four sp3 hybrid orbitals, 0.72. Tin: it may surprise you. Tin has two different crystallographic forms.

They are called allotropes. One of them is metallic, and the other one is sp3 hybridized. So, tin actually has a semiconducting form. It's a tiny, tiny band gap, but it's nonzero. And then, lastly, lead has got so many electrons, the valence electrons are so weakly held that there's no propensity for covalency, and so it exists only in metallic form.

But you can see the trends very nicely scaling with the intensity of the bonding as exemplified by the pull on the nucleus on the outer shell electrons. OK, well, I talked about photoexcitation. There is another way to excite electrons, and that's by thermal excitation.

Just the energy in the environment could lead to promotion of the electrons from the valence band to the conduction band. So, I'd like to look at that process. Let's look at thermal excitation. So, again, I'm going to simplify this.

The upper anti-bonding orbitals represented here as the conduction band, and the lower filled bonding orbitals are represented as the valence band. There is fine structure in here. These are electrons, two by two, all the way up through here, all right? So, let's suppose we have enough thermal energy so that E thermal is greater than band gap energy.

If the thermal energy of the system were greater than the band gap energy, we would have the ability to break these bonds and promote electrons across the band gap. So, what happens? Let's look at that process.

So, I'm going to rip an electron out of an orbital here, rip an electron out of an orbital, and send it up to the conduction band. So, one electron is now moved from the valence band to the conduction band leaving behind a half filled orbital so it's pretty clear that we now have a new carrier in the conduction band.

So we have a negative carrier in the conduction band. But, what's interesting is what's happening down here in the valence band. This broken bond, this single electron in a bonding orbital is like a hot potato.

Nobody wants this thing. It's highly unstable. And so, what will happen is if we put this crystal between two electrodes, and so let's say we polarize the right electrode negative, and the left electrode positive, it doesn't surprise you that the electron will be repelled by the negative electrode and drawn to the positive electrode.

It will move from right to left. This broken bond, I'm drawing it here as in energy space, but you can imagine a lattice full of silicons. This broken bond will actually propagate. And since the broken bond is a zero in a land of minus one, it has an apparent charge of plus.

And, this represents essentially a vacancy in a bonding orbital, and is termed a hole. This is termed a hole. It's designated lowercase h, and it has charge plus one. We've got minus one in the conduction band.

We've got plus one in the valence band. And so, under this same influence of electric field, the hole will move from left to right. So, one promotion thermally generates two carriers. We get an electron in the conduction band, and a hole in the valence band.

So, now we have some conductivity that is quite different from what we're used to. And in fact, the numbers are equal, right? The number of electrons that we generate is equal to the number of holes that we generate.

Electrical engineers will represent this in a more compact notation. They don't want to know the chemistry. Electrical engineers historically were afraid of chemistry. They just classify these things on the basis of their functionality.

Electrons are negative carriers. Holes are positive carriers, so in electrical engineering parlance, you'll see this equation, n equals p, meaning the number of negative carriers is equal to the number of positive carriers.

So, this comes out of thermal excitation. And, so now, we could say something intelligent about conductivity. We can say that electrical conductivity must be related to this. So, I know I was using sigma over there for bonds.

We are running out of characters. We've burned the Latin alphabet. We've burned through the Greek alphabet. But here we are. So, sigma now represents electrical conductivity of the specimen. And, we know the electrical conductivity of the specimen must be related to the number of carriers.

Population of carriers, all right, and it must be related to the charge on the carriers. In other words, if I had plus one, all other things being equal, plus two, all other things being equal, the plus twos will get me double the conductivity of the plus ones.

So, charge or, let's say, charge on unit carrier, and then lastly there is a term called mobility of the carrier. What's the mobility? The mobility is the ease with which the carrier can move through the crystal.

You can define mobility as the velocity per unit electric field. So, if I have two carriers, one is in copper. It moves very quickly. One is in silicon, moves very slowly. I apply the same voltage across equally sized specimens.

I find one moves more quickly than the other. The concept that captures that is called mobility. So, if I take the product of the population, the charge, and the mobility, I end up with something that gives me conductivity.

And, what I'm going to do is I'm going to sum this over all of my carriers because each carrier contributes. A negative current going from right to left will contribute to a positive current going from left to right.

OK, so we can now write this. We can write in the case of this crystal here, we only have two carriers. We've got electrons, and we've got holes. So, we can say it's the number of electrons times the charge on the electron - absolute value - is the unit charge times the mobility of the electron plus the number of holes times the charge on a hole, which is the unit charge, and the mobility of the hole.

So, we also know that the number of electrons equals the number of holes in thermal excitation. So then, that allows us to write, this is n sub E. It's the same, times the elementary charge times the sum of the mobilities.

And, those mobilities in many instances in this crystal are roughly the same. So, we can get a measure of what the conductivity is from this. Now, I'm going to show you an equation that we're not going to derive from first principles, but from the more elaborate form of quantum mechanics, allows us to estimate the number of electrons that have been thermally excited in a crystal, and it looks like this.

It's got a pre-factor times absolute temperature to the three halves, and an equation that has a ratio of the binding energy and the disruptive energy. And that's done through an exponential where we put the band gap energy in the numerator, and some measure of thermal energy in the denominator.

And, the way we characterize thermal energy is the product of the Boltzmann constant, and absolute temperature. So, this is a measure of the binding energy, all right, and this is a measure of the disruptive energy.

And, we've seen that notion before and we're going to see it again where we make an exponential. There's going to be a minus here. And, because we get two carriers for excitation, there will be a two here.

And now we are ready to elaborate. This kB, just to be clear, is the Boltzmann constant. And, the Boltzmann constant is 1.38 times ten to the minus 23 joules per Kelvin. It's the amount of energy per degree rise times temperature will give us an energy term.

We know the band gap energy, and so by evaluating this, it turns out for silicon at room temperature, the value is ne for silicon at room temperature is equal to 1.3 times ten to the tenth carriers per centimeter cubed.

1.3 times ten to the tenth, you say, well, that's 10 billion. Well, how many carriers are there in copper per cubic centimeter? In copper, per cubic centimeter, we did the calculation. For copper, we have one carrier per copper atom.

And we said for copper, we've got roughly Avogadro's number of copper atoms per cubic centimeter. So, in copper, that analogous quantity is going to be on the order of ten to the 23rd per centimeter cubed.

So, what's the difference? The difference is that silicon, native silicon, pure undoped silicon has a value of carrier concentration. Ne of copper to ne of silicon at room temperature is at the order of about 10 trillion.

And so, you can see the power of band theory because it's now allowing you to make sense of the various values in conductivity. I showed you last day, copper is up at 5.9 times ten to the seventh Siemens per meter.

So, if we take now the conductivity of pure silicon in the same units, we're down here at ten to the minus four. And if you take the ratio of ten to the plus seven over ten to the minus four, it's about ten to the 11th.

And, this is giving us ten to the 13th. And, all I've done is look at this first term, population of carriers. We're talking about the same carrier, same charge. Clearly there's something here that's in the mobility.

Where do you think you're going to have much higher mobility of electrons, in a metallically bonded structure, or in a covalently bonded structure? I think you can see that the mobility of electrons in silicon is going to be much lower.

Whether it's 100 times or not is something to be seen, but I think you can see that the band theory is helping us make sense of what's going on. So, I think this is probably a good place to stop. I just want to give you one thing to ponder over the Columbus Day weekend.

I told you that the measure of thermal energy is the product of the Boltzmann constant times temperature. And, if you take room temperature and you multiply it times the Boltzmann constant, this value at room temperature is about one 40th of an electron volt.

Yet the band gap energy is 1.1, which is much, much higher than the thermal energy, how is it that we get any thermal excitation? That's what I'm going to answer next day. Before you go, I wanted to go back to Siemens and show one of his many inventions.

I've shown you silicon, high purity silicon. Where do we get silicon from? This is the silicon age. We live in the silicon age. So, silicon starts on the beach. You start with sand, Quartzite. And, we take silica, and we feed it into this furnace, which was invented by Siemens.

It's an electric arc furnace. It has three carbon electrodes, and these are fed by AC power. And, we put the sand in here with a few other ingredients, and the action of electric current passing between the electrodes actually melts the charge.

So, you have this liquid honey-like goo of silica and some other ingredients, and then the reaction proceeds. The carbon reduces the silica to elemental silicon and generates carbon monoxide. And, the carbon comes from the electrodes themselves so, you consume the electrode.

See, the electrodes are constantly being fed like giant drafting pencils into the charge while they are passing current. And now we make silicon. And the silicon is full of impurities because sand has iron in it.

It's got aluminum in it. It's got Lord knows what else in it. And that's not going to make high purity silicon for microelectronic devices. So, you might say, how are we going to make high purity silicon? We're talking about 99.999999 times.

People talk about six nines, seven nines purity. One part per million, one part per billion, how are you going to get from this glop here that's full of iron, aluminum, and also saturated with carbon? What are you going to do? Somebody might say, why don't we distill the silicon? Well, silicon melts at 1,418 degrees centigrade.

It boils at a temperature above 2,000 C at atmospheric pressure. What are you going to contain this stuff in? How are you going to ensure purity? And, how much energy are you going to consume? That won't work.

So, what happens instead is people get smart and use some chemistry. So, they take this impure silicon and chlorinate it with HCl. See, we've met silicon, it's sp3 hybridized. We've met HCl and it's polar.

And, it forms this molecule, trichlorosilane. And guess what? The inter-atomic, right, secondary bonding is weak in this material. And it boils at 33∞ C. That's below body temperature. You hold this in your hand, and the stuff will start boiling.

So, what can you do? Well, what happens to the iron? What happens to the aluminum? What happens to all the other crud? It doesn't form this. So, now, you can selectively transfer with minimal energy.

The trichlorosilane, fractionally distill it to get very, very high purity, trichlorosilane. Then you go back and you convert to silicon. And, how do you do that? You pass it over a hot wire at high temperature, this is unstable.

So, see, we are playing with chemistry. We are playing with temperature. These are the tricks. This is the playbook. So, now, we've got a high temperature. We've got a hot wire. How do we make a wire hot? With a flame? No.

We pass electric current through it. And, the molecules of trichlorosilane hit the hot wire in the presence of hydrogen, back react to form HCl, silicon tetrachloride, and silicon. And, it's this silicon that comes out of that first operation that then goes for subsequent zone melting to make the giant single crystal from which we cut this piece right here.

And, all this goes back to the 1800s. By about 1870, Siemens was running furnaces like this. There is one other important application for this furnace that's used to this day. It's recycling steel.

Steel is the number one recycled metal by far, not the aluminum beverage can, steel. In this country, there's about 12 million tons of steel consumed for automobile industry, and about 12 million tons of steel go back into recirculation.

And, this is the furnace. You take scrap metal, electric arc furnace, slag on top, remelt, purify, and then it goes back into the marketplace. OK, have a nice weekend.