Happy Monday everyone! How you all doing? You  know it's good because it's a goodie bag day   and so I'll get to what you have in your hands in  this lecture. Today-- So we've been talking about   these things for a while now, right? We've built  up an understanding of the stamp and the basis,   and then we understood how to talk about it  like in terms of the planes and the symmetries,   and then we shined x-rays on it, and now we're  going to start taking them all apart. And so don't   be sad, don't be sad, because actually that's more  real-- that's more real. And that's what we'll   talk about today. So what our plan is-- you know--  So today we're going to start creating defects   in the perfect order that we've had so far. And  in your goody bag you have a defect generation   machine, which we'll talk about. And then on--  And so today we're gonna talk about one kind   of defect, that's a point defect, and then  on Wednesday we'll talk about line defects,   and then we'll just mess the whole thing up,  and we're going to make it amorphous. So that's   where we're going. And beyond that if you  want to know more about where we're going,   there's the concept map up there for exam 3.  Which again, you know we don't pick these dates,   so this date came later in the semester that  we wanted but it's that's what it is. I think   it's all the way up in early December. But--  Because of the fact that there's a Thanksgiving   holiday in between and there's one topic here  we have to start before the exam. It's not here   because it won't be on the exam but we're going to  start polymers but won't be on the exam. I'm going   to spend the whole lecture before exam three just  reviewing for exam three, because we're gonna have   that Thanksgiving break and all that. So that's  what's not listed here these are just the topics   that are covered on exam three. Okay. Good. If  anyone has any questions please do let me know.   The concept map. Now the thesis of 3.091  you have seen in multiple different ways.   I have tried to convey to you that  the electronic structure of atoms   is the key to life. It's the key to chemistry.  It's the key to understanding and within that   you get things like this which is what we've  been talking about recently like composition   and arrangement. Right? That's these  crystals  that's these different-- BCC FCC. Okay.   And then the chemistry you put inside. But  you see the other thing about it is defects.   Because the thing is that defects, which is the  topic of today and Wednesday, they are absolutely   crucial for understanding the properties.  If they're there and I just told you they're   always there. The question is how much are they  there? And so if you don't know about defects--   if you don't know about defects then you  really cannot fully understand properties.

There is a very strong correlation between the  two and that's why we have to talk about them.   We have to understand them. Now I love  this quote from Colin Humphreys he said,   "Crystals are like people, it is the defects  in them which tend to make them interesting."   Yeah. And that's actually really true because  defects, right, defects sound you know... 'I   don't want to defect.' No, actually oftentimes  you do want defects. Sometimes you don't. So   there are some kinds that are kind of like  maybe not things you want in your crystal   and then there are other kinds that actually you  are engineering purposefully to be there. Either   way you got to understand them. Right? And that's  what we're doing today because --Gesundheit-- so   you know if you take this three layer-- We talk  about graphene. It's a one atom thick material.   Pretty cool-- every atom's on the surface. Here's  another example of what's called a 2D material.   Why? It's not 2D but it's called a 2D material  because it gets you like... you know more   publicity on your work. This is molybdenum--  this is molybdenum disulfide it's really cool   material. It's three atoms thick. So it's kind of  like 2D-ish, right? Yeah but see that's the model.   That's the model. This is reality. This is real--  How do you see-- How do we see atoms like this?   That's a real picture. Do we use x-rays?  No? What do we use to see atoms that well?

  Electrons. Electrons are our light, right? That's  what we're using. This is an electron picture,   electron. And if you do that you can  see individual atoms and look at that   there's there's places where atoms are missing all  over the place. That's reality. That's reality.   And those where you have one atom missing or  where you have one thing that is localized and   disruptive to the regularity of the lattice...  that's called a point defect. So let's write that   down. That's the one that we're talking

about today. So the point defect, 'point defect', is where you have a localized... localized disruption... in the regularity, 'regularity'.

The periodicity the repeating of the lattice.

And it could be on or between, we'll see this, on or between sites. Right? It could be a defect that is, like you see here, there's an actual atom missing. What could be something that maybe you've got in there in between sites? But either way it's a disruption that's localized to a point or almost a point. And so it is --Gesundheit-- that you can see that if we just make these disruptions in something. Alumina. We talk about alumina, right? Remember alumina's really strong lattice energies? So it's like sandpaper. Oh, it's also toothpaste. It's in a lot of stuff. Alumina is a great-- But look at this. That's alumina with almost no defects. It's still got some. You can never get rid of them all! But here it is when I purposely engineer the defects in alumina and I put a little titanium or iron. Or here's it when I put chromium. So you can-- There's one property where the localized disruption, and it's not a lot as we'll see, the localized disruption changes the properties. That is key. That's just color. Right? This applies to most properties of materials. And so this first one, the point defects that we're talking about today, you can kind of think of those as zero dimensional because they're they're localized. You know. They don't really go off in a line. They don't go off in a plane or a volume. And you can have defects that are that cover all of those possibilities. But these are points. Alright? This is what the word localized means here, okay? Okay. Now in this class, we're not going to cover all of them, but we will cover these two. Today: this one. On Wednesday: that one. And that'll give you enough of a sense of the role of defects and how to think about defects and crystals. Right? So this is how we think and classify defects. Okay. Now the four-- so now we're going to point defects-- now the four, there are different types of point defects that can happen. The one that you saw here is a certain one. That's called a vacancy. It's because there's an atom that's vacant. So you literally just lost an atom somewhere in there. Okay? Now that's a vacancy and that always exists. But you could also have taken something like one of the atoms that's already in there, maybe an aluminum or an oxygen that's in the lattice, and you could substitute something in place of that. That's another-- Why is that a point defect? Because I didn't like tear something out. But no, but you changed the regularity. Localized disruption and regularity. So if I put something else in for aluminum that's a point defect. Right? And again, now go back to here. You can see it here. So we classify these, right? There's a vacancy, which is an atom missing. There's what's called an interstitial, which is an atom that goes in between the other atoms. Here it's a self interstitial so it's the same type of atom. And these are-- This is where you have a different type of atom in between and this is where you have a different type of atom as well. Those are both called impurities and I

will talk about those all today. We're gonna start and focus a lot of our attention on the vacancy. And that's what I want you to use this goodie bag to understand, is the vacancies. Okay. Vacancies. Why do vacancies happen? What are vacancies? To understand vacancies in crystals we have to talk about this guy. And oh... this guy was brilliant. This-- I'm sure you know his name is Svante. Yeah, it's written right there. Svante Arrhenius. Arrhenius studied in the late 1800s so many different things and made so many contributions that it's almost hard to catalog. He was brilliant. And you know he won the nobel prize in chemistry for his work on electrolytes. But he also worked on immunology. He was the very first person in the late 1800s to come up with a model for global warming and the role of $CO_2$ in the temperature change of the planet. And his predictions were actually pretty darn good. He was brilliant. And one of the things that he did is, he observed what it were called activated processes, and how they depended on temperature. And so we have this equation that I need to talk about today and it's going to come back. So we're going to talk about this equation, which is the Arrhenius equation, that relates the rate of some process to the temperature. And the activation energy for that process. So we got to talk about what all that means, alright? Now we will be using this. Today we're going to use it to think about concentrations of vacancies in a crystal which follow Arrhenius-like behavior. Right? But then we're going to come back to it when we go into reaction kinetics in a couple of weeks. Where we talk about reaction rates. So we'll be using Arrhenius multiple times throughout the rest of the semester. So what is it? So the Arrhenius-- So the general Arrhenius equation can be written like this. Arrhenius, he was not in the army but this is just the general equation. Okay. So let's put equation there. And so we have k, which is some rate, equals A. I'll talk about each of these. Times e the exponential of e to the minus Ea over RT. What are these things? So this is the general equation for the rate of some process. As we're going to see this applies to many, many processes including vacancies. Okay. But this is sort of the rate. So you can think of this as-- Okay. Let's just-- That's the rate of a process rate. The rate of some process. Okay. I mean you could think about it as the number of times something happens per second. That's a rate. Right? It doesn't have to be those units, but that's like a rate. Right? How often does this happen. The rate-- But now so that's dependent on something called the pre-exponential, that I will talk about. 'Pre-exponential-- exponential'. That is a factor that is a constant.

And here we have this exponent-- and this is such a beautiful expression. So this is the average thermal energy. 'average kinetic energy, average thermal energy' Right? It's taking temperature and it's making an energy out of it. Now remember we've already talked about this before. That you know you don't get what you get are distributions. So you know this would be T high-- remember I've drawn this exact thing and this might be T low and this might be-- You know, this might be the

you know the probability of something happening. Probability of occurring.  And then in this case we talked about this as the kinetic energy of the molecules.  That's a graph we showed already. But so the-- But this RT is an average. But so I just want  to make sure you don't forget. This is a number. This is a number. You've got at 300 degrees, at a  thousand degrees, you calculate a number here. But whenever you're talking about temperature,  you're talking about distributions. There's some average of the distribution but you're always  talking about distributions. That's important for understanding Arrhenius. Okay. Now this thing here  is called the activation energy. Activation energy. And that is the energy that you have  to get over for something to happen. For  the thing to happen. Let's take-- I love  this analogy of the bookcase. I'm going to draw  that now. So let's suppose that you have energy,  like that. Okay. So maybe this is like potential  energy. Yeah, let's go ahead and say potential  energy. Then if I've got a bookcase and it's very  very heavy. And I try-- and I want to push it over  on this hinge. So I want to rotate it and push  over. Then you could imagine that at some point  it's going to look like this. And then  at another point, it's going to look  like this. Right? So this is like step one,  and that's step two, and that's step three.  And now I'm pushing this thing over. Well this is  the activated state. Why? Because it's where I've  gotten to the highest energy, and that's where  this energy graph is important. This energy axis,  this is the activated state of the bookcase.  Right? So if I plot the the energies.

Right? You can say one, two, three. You  can think about it like that. Right?  I've literally-- So because it's a potential  energy, right? So it's like here's the  gravitational pull, here it went up a little bit. Right? So you can think about it just like that.  And here it came back down. That's why I like  this analogy because it really gives you intuitive  feeling for what's happening here. There's a  process. The process is pushing the bookcase over.  That bookcase has some energy associated  with it. Here and here. Potential energy.  And it's got some energy I gotta put into  it to activate it to go from here to here.  Right? That's why that's called the activation  energy. That's what this Ea means for the general  Arrhenius equation. You're pushing the bookcase  over. Yeah but how are you going to push it over?  Well clearly you're going to run  around the room and accidentally  knock into it because that's temperature.  Maybe that's not a good-- But if you had a  lot of people running around a bookcase maybe  once in a while they'd kind of bang into it.  Thermal energy. Right? And then maybe another  time, you increase how fast everyone's running,  and you give them more energy. So now not only  are they hitting it more frequently but they're  they're actually hitting it with more energy. They're able to give it more energy. Now you make  everyone run really fast. And the chances that this thing goes through that process are higher.  That's what that is. That's a probability,  right? This is what this exponential is. That  was the brilliance of what he did right.  So this thermal energy is like, you know,  it's how much-- It's like a probability but that's  why it goes into an exponential. Because

when you  increase temperature, again it's not just that  you're increasing how much energy over here,  Right? How this is get like kinetic energy of  some molecules. Maybe how much energy those molecules have but you're increasing how many of  them are above some threshold. So your chances  go exponentially higher. Well you think if  it was harder and harder to push. But this  is going to go the other way too. You could have  sometimes somebody might knock it the other way.  It looks kind of hard from this picture.  But there's a chance. It's just that  the activation energy going this way, right?  Going this way, the activation energy is here.  'Ea' and going this way the activation energy would be here. So this would be 'Ea'  for, let's see, three to one. And this  would be 'Ea' for one to three. Now again,  I am giving you the general Arrhenius. We will  be coming back to this when we do reaction rates.  We will be coming back to this picture, and we  will be talking about reactions, and then we'll  be using that, and going to equilibrium. Today,  I want to give you a sense for what Arrhenius is  because this is where the equation comes from. And  because if you think about now defect formation.  Defect formation is an activated-- it's a  thermally activated process. But that's exactly  the point. So that's why if we write this down--  I've said this now multiple times the vacancy...

'vacany'. No. Vacancy is  always present. Always present!

Why? Because it's thermally activated. So unless  I can get to T equals zero-- thermally activated.

There's always a chance that I  push a vacancy into the material.  There's also always a chance  that the vacancy gets pushed out.  So those are happening because of temperature.  You can think about that. It kind of makes sense,  right? Atoms are moving. Those are the people--  right-- there's the people in the room.  And now all of a sudden, something happens  somewhere that allows an atom to come out.  We'll talk about that in a second. And create  a vacancy. Now there's a chance that it can go  back too, right? And so there's at some point  there's an equilibrium concentration. Both of those are thermally activated processes that have  an Arrhenius like behavior. And so you get to...

the very nice expression for concentration.  So you can get-- can get? Yeah,  why not-- get concentration. So  the concentration at equilibrium.

Since vacancy formation is thermally activated  and it's thermally deactivated. There's some--  you know, you can say well when it's activated  and deactivated in the same rates you're in  equilibrium. That's how you get a concentration.  And I don't need you to know the math  but I need-- This is where it comes from. The  number of vacancies divided by the total number  of sites is equal to e to the minus E vacancy--  I will talk about this-- vacancy divided by,  let's use RT still. RT. Now here's the thing  about RT. Let's write this down because this  is really important, right? If-- we talked about  this

before-- if I'm using RT then it's per mole.

Per mole use RT. This is the ideal gas constant, right? That's not just used for ideal gases. This is used for a lot of things. That's the gas constant.

Gas constant. That's equal to-- let's see if i have down here-- 8.314 joules per mole Kelvin. So you see if I'm working in per mole, then I use R. This is-- the energy unit the-- those energy units have to be the same. They got to cancel. So if my activation energy is in per mole, fine, use the gas constant. If the activation energy is in per atom then we just use the Boltzmann constant: $k_BT$. Where the Boltzmann constant is something we have seen, it is equal to the ideal gas constant divided by Avogadro's number. Remember that Avogadro's number goes in and out atomic macroscopic worlds so R and kB same thing. Okay. One thing-- notice that's per Kelvin. Whenever you have equations like this that come from thermodynamics, which is where these things come from. There is only one temperature unit. There is no other. And it is Kelvin. You have to be aware of that. If you see something in Celsius, it's not going to work. It's got to be Kelvin. All of these equations have to use Kelvin. Okay. So that now-- you can see at any time, you know, any time you see an equation with an exponential. What's the first thing you want to do? I mean it's like an-- it's almost like an instinctual reaction. You see an exponential. Take a log. Don't say anything until you take a log. Right? So that's an-- so that-- so we're talking about energy of the vacancy in a minute. But if you take a log of this. Then you get that the log of what '|n(Nv)'. Well I'll talk about that. Equals log of N. Let's do it this way. Minus log of n equals E vacancy.

Okay. Divided by RT. That's just taking an exponential, a logarithm of this equation. And now I can talk about these Nv and N. So Nv is-- this is literally a concentration. This is the concentration of vacancies that are forming in my crystal. Why did i get this expression and notice the constant cancelled. This pre-exponential factor cancelled. It canceled because I'm taking a concentration. I'm looking at the rate going one way and the rate going the other. And I get to take a ratio of those. That leads me to this expression. That's how you get from Arrhenius rates to some concentration. Okay. But you still-- but notice it's still-- we call this Arrhenius-like because it's still an exponential dependence. It's not a rate, it's a concentration. It's okay. It's a concentration in equilibrium. So this would be like the number of vacancies, number of vacancies. And this one here 'n' would be like the number of sites, number of lattice sites. So it's like you know concentration. Lattice sites. Right?

And what is this? This is exactly here, here we go. I have my crystal. Okay. Here's my crystal and here it is... I think I'll stop here. And now I did this. We're going to go graphical and this and this.

That energy is literally the energy difference. It's literally the energy difference between having a vacancy and not having a vacancy. How much energy-- Question? [STUDENT:] Isn't there supposed to be a negative sign in front of the E vacancy?

[PROFESSOR:] Yes there is. Oh yes there is. Yes there is. Thank you very much. Yes. So that's-- Okay. So now the energy difference between having a vacancy and not, is the vacancy formation energy. E vacancy. Now sometimes, and this is unfortunate, but sometimes you will see the vacancy formation energy written as the activation energy. That's fine. I mean it just it's written that way to get across the point that it's an Arrhenius-like behavior. But actually the act-- but if you're clear about it. And that's why I want to go through the bookcase example, right? The formation energy which is this energy of the vacancy forming is the difference between here and here. The activation energy is this hill that you got to get over to go back and forth. Okay? So the formation energy between having a vacancy and not is what goes into our our equation. Alright. Now we're going to use this. So we will see how this works in just a few minutes. But again there are so many processes that are thermally activated. There are so many processes that have Arrhenius-like behavior. That are Arrhenius-like. And if you go to Dartmouth then they'll give you goodie bags with live crickets. And actually I really hope not. But this is one of the labs that they have where they take crickets and they measure the number of times a cricket chirps. And they're like, well okay. Let's measure the cricket chirp over 13 seconds. We're gonna cool them down, hopefully not too cold, and then we're going to heat them up, hopefully not too hot. Because crickets are nice, right? And so then-- and they ca-- but look at that. And they count it. And then what do they do? Well they didn't know about Arrhenius yet until somebody from MIT went and visited. So the first thing they did is they plotted the data. Look at that. Chirps per 13 seconds plotted. And they're all sitting there trying to fit a straight line to it. And then someone from this class is up there visiting. They're like, you know what i think, this looks like a thermally activated process. So i think it's probably exponential. And then they fit this nice exponential and it fits the the cricket tripping beautifully. And you can go even further because you see if you got this far. Well now you see this is a line. This is a line and we're going to do that a lot when we go into reaction kinetics. If you have a exponential and you take a log, that's a line versus 1 over T. Right? That's a line versus 1 over T. And so that's another way you could look at data. They didn't do it there. But, you know, you could plot for example-- you could plot 1 over T versus the log of the number of vacancies. But the lattice-- the number of vacancies is what we want. That ratio is the concentration. That concentration is in equilibrium at some temperature. Okay. The lattice-- the number of lattice sites is simply how many lattice sites you have, in whatever volume you have, for whatever crystal structure you have, for whatever element you have. We'll see that in a few examples. So that's just a concert-- it's the

number of sites you have in the chunk of material. And then instead of-- The question this equation tells you the answer to, is how many of those have a vacancy? Because it's a thermally activated process. And if you plot that log in Nv versus temperature you get this really nice linear line. And the slope of that line is equal to minus E vacancy divided by R or it could be kB. R. Let's write this again per mole.

Or it could be kB if it's per atom. You will see both. You will see both. And this intercept-- intercept-- is equal to the-- let's see-- the intercept is equal-- what do i have here? The log of n. Did i write it right? Log of n.

Okay. Alright.

Now, okay. Oh yeah. What else can you do? Well before we go on to the defects, this explains the doping. I kept calling the doping in semiconductors a thermally activated process. But look at what happens. This is the carrier concentration in that conduction band. The thing you've been you've been learning about, right? And thinking about. But look at it now versus temperature. It's a straight line. It's a straight line. This is-- this is experimentally what you observe. And the reason is because it's a thermally activated process. And in fact, in this case, what is the activation energy? Right? The activation energy for getting an electron into the conduction band is the gap. Right? And so now you say germanium has a smaller gap than silicon, which has a smaller gap than gallium arsenide. The slopes are different. The slopes are different because the energy that it takes in that activated process is the gap. That's why the slopes are different. Right? Okay. Alright. Now on to-- oh no i didn't-- I did want to mention this because it's so cool. Where are these vacancies going? Did you actually just take an atom from the middle of a crystal and remove it? No. Because that would cost way too much energy, right? And so instead they have to-- you call out to the surface. It's a call out to the surface. Or, you know, maybe the surface calls in. It all has to happen on the surface. So what ends up happening is a surface atom may go away and then another one may take its place, right? And then the next one, and then the next one, and that's literally how you can rip an atom out from somewhere inside. But by the same-- that's literally pushing the bookcase over. Right? And now you can push it the other way and the surface atom could go in to the crystal so that some atom inside is able to fill a vacancy. It all comes to the surface. This is a beautiful paper, where they're showing how you get these rings. This was published almost 20 years ago now. But how-- they're studying how do vacancies actually pull atoms from the surface specifically. And what they did is they change the temperature and they see islands growing and shrinking. Where are those islands going and where are they coming from? Vacancies. It's all about the vacancies, right? And one of the things I

loved about this, is this is the abstract of this paper. Look at this. Here we show the vacancy generation and annihilation, right? Both ways on the 1-1-0 surface of an ordered nickel aluminum inter-metallic alloy. Oh, I love reading that because you guys all are experts in this now. You know what that means. You know what that means. Where do vacancies come from? Okay. And now we got to make vacancies. Right? And so this is the kind of problem you might get. How many vacancies are in a centimeter cubed of copper? How many vacancies are in a centimeter cubed of copper? Well, now you know how to do it. You're just going to apply this Arrhenius-like behavior. You're going to apply this equation to figure that out. And i won't go through all the math but i do want to just give you a sense of the types of questions that you can now answer; that you know how to think about vacancy formation. So for example, in this one you've got step one. Step one: you would find N.

Step one: you'd find N. How many sites do I have? Because remember this equation is about a concentration between the number of vacancies and the number of available sites for vacancies. And so step one-- well-- so step one you'd say N equals Avogadro's number times 8.4 grams per mole. Right? Divided by all this-- is such old-school stuff right now, right? Grams per mole. Then you look that up in the periodic table and it's 8 times 10 to the 22nd sites per centimeter cubed.

Why am I using centimeter cubed? Well because that's what i was given the density in. So I'm just leaving it in those units for now. Right? And then step two you can find Nv. So now we can apply our our equation. Nv equals N, I won't repeat it, times e. Now I've got my kB instead of R. So it's 9.9 electron volts divided by and then this is kBT. Now I get-- so I'm given that it's a thousand-- wait a second. What's the term, oh a thousand degrees. So do I put T equals a thousand. No! No! You never use-- you only use Kelvin. 1273, right? T is always in Kelvin for any of these thermodynamic equations. And I won't go through the math but it goes something like 2.2 times 10 to the 19th vacancies. I'll write the units here just for completeness. Vacancies per centimeter cubed. Now that seems like a lot but it's actually not. You say it's like one in a thousand or one in ten thousand atoms are missing and I'm at a really high temperature. If I were at-- then this is the power of what Arrhenius gave us. If-- Because it's exponential. It's all about probabilities and sampling and how many times did i bump into that bookcase. If I'm down at room temperature I've got so much less energy, and so many more chances-- so many fewer chances to deliver that energy. Right? Where the surface is taking atoms in and out to create vacancies. That at room temperature the number of vacancies is 10 to the seventh instead of 10 to the 19th. Right? So that's the power of that exponential. That's the power of the exponential. You might also be asked questions like this one. Right? So --oh no like-- let me do this one. Then I'll talk about your goodie bag. Where instead of

now-- Okay. What-- Example two. What is the vacancy formation energy in aluminum? And now notice, instead of giving you the vacancy formation energy per atom, I'm giving you other stuff. I'm actually giving you how many vacancies you got, at some temperature. Well that's-- This just going in a different direction but it's using the same math. So you can go in different ways, arrive at the same kinds of equations, and get all of these things, and I won't go through the details. But in this case you get that Ea equals minus $k_BT$. I'm using $k_B$ because look at that... the formation energy I'm asking is what is the vacancy formation energy-- Okay, well actually look at that. No, I just want to do it per atom. It didn't say per atom but if I wanted to do a per atom, I'd use $k_BT$ times log $N_v$ over N. And so you see 0.75 eV per atom. Now what's interesting, copper was-- copper was 0.9, aluminum .75. You're going to have a lot more vacancies because it's exponential. This seems like-- 0.9, .75 is kind of the same. No. It's going into an exponential, so it has a really big difference on how many vacancies you have at any given temperature. Aluminum is going to have a lot more because it's easier to get them in there. Right? Notice I did the thing that I said other people do and I don't really like. That's the energy of the vacancy. The vacancy formation.

People call it activation energy all over the place. Okay. Now this is your goodie bag. Now why am I giving to you? Because first of all, this is the most sophisticated vacancy generation machine you'll ever find. There are exactly 500 beads in this. Exactly. There are not 501. There are not 499. And you know why? Because Laura has spent 7,000 hours counting beads in every single one of these. So you have exactly the right number. Then there's precision tape and polycarbonate films maybe. And what you guys can do is build your own crystal. It's a 2d crystal. Here's what's so cool about this. Try to get those vacancies out. Look at this! Dude-- None of you can see what I'm talking about. [LAUGHTER]

There's a big vacancy there, I've literally made this right in front of me. This is here. And now I'm gonna say-- okay, I'll use temperature.

There's so many more. There's so many more because I use temperature. This is temperature. You are temperature. And you can run around, and you can shake it, and all you bring it to the dance floor, and on. Then you're like how can I get-- Whoa, wait a second. I'll just quietly go down in temperature and I'll get rid of them. Yeah, tell that to your friends down the street. See how long they go until they stop trying because you guys know not to try because you'll never get rid of them. You'll never get rid of them. You'll always have vacancies and this is proof that you will always have vacancies. You can try to tap it like that. See if you can get rid of the defects. You can't. Luckily that's a good thing because defects are what make everything interesting. Everything. This is your goodie

bag. So you can touch and feel-- Oh, but we got to cover the other case. Because-- See I could have had not just a metal, where every atom is the same, but i could have had an ionic solid. You can make point defects in ionic solids as well. Right? So yeah. So if I had a defect in an ionic solid-- well now you got to consider the charge. I can't just keep pulling-- If this is sodium chloride, I can't just keep pulling out like one type of atom. If I take a sodium atom out. Like imagine that's a plus, minus, plus, minus. Right? The size-- if I take a sodium atom out then it becomes charged. Because remember the ionic bond is one of them, grabbed it and it has it. And so if I take one out, I've charged the crystal. You can't do that. It won't let you. So if I take a sodium atom out, a chlorine is going to come too. It's got to come too. You got to keep it charged neutral, if it starts charging neutral. So these have special names because of that. And there are two types of defects in ionic point defects. We're still with point defects. Local disruption in the regularity. One is called the shocky defect, right? So in the shocky defect you got both an anion and a cation are removed. Cation. Now here's the thing- I should have put 's' because you may need to take more than one out. Alright? Removed-- and because you got to ensure-- ensure charge neutrality. Charge neutrality. So like you know-- If I had so inquiry that's fine. But what if I had you know something else. What if I had instead of sodium chloride. What if I had like calcium chloride. So now what if I had calcium chloride. Well that looks like that. Because calcium goes to two plus. We know this. Right? But chlorine is only minus one so that ionic crystal is different. And what it means is that if I remove-- if I remove a calcium it's going to come out as Ca2 plus but that means i need to remove two Cl minus atoms.

That's the thing about shocking defects. You got to keep the charge balanced. So now you-- It's not just a one for one. This could actually be a way to take atoms out. Or if I want to take chlorine out of this, we'll take some calcium out. Chlorine will come out too. Right? Could be a way to engineer it.

So that's a that's a shocking defect. But the simpler thing that could have happened is just that one of these atoms kind of moved over. So now I didn't remove it from the crystal but it just kind of wandered over into some site. So like you know... here's BCC. I can have like an atom-- so this doesn't look like an ionic solid but suppose-- it doesn't matter. I could have an atom leave a site and go-- Notice that there are these voids, right? They're these spaces in between other atoms. Well those spaces are places where atoms can go. They're not-- It's not part of the regular lattice but it's just-- it's like a hole, right? Remember the packing fractions. We never got above about three quarters. We never got about three-- that means there's still a bunch of volume in there that's free volume. Right? Where is it? Well this kind of defect will find it. Right? So you could have the smaller ion migrate over, create a vacancy, and it's going to find a place where it likes to go. Ah. Okay. Yeah,

we'll do this. And so-- so that's called a Frenkel defect.

So Frenkel defect is the other kind of special name we give to a vacancy in an ionic solid, and it's where one ion-- right-- anion or cation. Anion or cation. Moves to some open space. Open space in the lattice. And you can already kind of feel where this might be kind of common. It might be common in situations where you've got a big size difference, right? So like the silver halides are a good example. Like silver chloride, silver bromide, silver iodide. Those are all good examples because what happens there is this ionic structure has a very big mismatch between the atom sizes. And so you can see. Let's blow up a picture of this is silver iodide, a cartoon. Look at that. So those are the silver atoms and what you see is because there's such a big difference in size, you're going to have these pretty big voids. And one of the atoms is small enough that it actually doesn't mind-- it's actually pretty easy to move it. Ah now, if you think about it. Well if you have enough vacancies in there, then maybe those ions can actually move really freely. Because they're so small and the voids are all kind of nearby. And you actually can get a conductor, a good conductor, this way. You're creating vacancies on purpose so that one of the ions can move around. The smaller one, right? That's what we do. We make these solid-state ionic conductors. You need the vacancies. You need the vacancies. Okay. Now, I told you that we got this map here. We've talked about literally just one. Luckily I don't have nearly the same amount of material to talk about these others. The vacancy is clearly the one that I'm very interested in. The substi-- the self-interstitial is actually pretty easy to understand. The self-interstitial is actually pretty easy to understand because it simply doesn't really happen much. And the reason is, if you look at this. Here's a picture of is basically what i drew on the board, right? But now I've put-- so these are-- this is not a vacancy, right? This is a kind of point defect but it's not a vacancy. I've actually added an atom into the lattice and I've squeezed it in between all the others. You can just feel how much energy, how much strain, those other atoms are gonna have to make and how much energy that's going to cost. Those are high energy defect. So a self-interstitial-- a self-interstitial-- self just means it's the same atom as the rest of them, is very infrequent. Is very infrequent. The self-interstitial-- let's see-- I'll just use this one again. The self-interstitial has an energy of formation of something like you know five electron volts. And you think but-- five electron volts.

Self-interstitial. Self-interstitial.

It went in between, so it's not substitutional it's interstitial and itself because it's the same atom type. The energy energy of formation is 5ev. I think 5ev doesn't even sound that much higher than like the one ev you had for copper, right? 0.9 ev. But it goes into the exponential, right? So it's like

one per centimeter cubed.   Literally. You get like one of these happening  per centimeter cubed instead of 10 to the 20th,   or 10 to the 10th, or you know many many orders  of magnitude higher. So the self-interstitial is   actually not very interesting. It's actually  not very interesting. Now because we have   like half a minute left, I'm not gonna  talk about these. We'll have a very brief   discussion about these last two types of  point defects and then we're gonna make   line defects on Wednesday. And my why this  matters, I'll give you on Wednesday for this.