PROFESSOR: I know I'm not Dr. Sadoway. I'm one of Dr. Sadoway's younger colleagues so-- but class is beginning, so let's get started. Dr. Sadoway, of course, would like you to know that he would very much love to be with you here today and he would probably like that very much more than what he's doing now, which is sitting in a secured area secured by the Secret Service about to meet the President. So you can ask him all about it when he comes back. Associated with that, I have one request for you. Today, when you're leaving, some of you may be used to leaving that way. Don't leave that way. Leave any other way. This way's fine. In the back is fine. Just don't leave that way. OK.

So last time, we talked about x-rays defraction and Bragg's Law. And x-ray defraction and Bragg's Law has a lot to do with perfect crystals. So perfection, right? We've been dealing with perfect crystal so far and today, we're going to be dealing with imperfections. So defects. And in the field of material science, the field that I work in along with Dr. Sadoway. there's a saying due to one of the most famous material scientists that says that crystals are like people. It's the defects that make them interesting. So now you've heard that saying and you can roll your eyes from now on every time you hear it because it's repeated it very often. So let's see.

What do we mean by defects? Well, there's two types of defects, broadly speaking, that we're going to be talking about, and we can classify those into two categories. One of them is chemical. So far, we've been dealing with chemically perfect materials. So ones that are made up of one element or ones that are made up in stoichiometric quantities of two elements, but you can also have chemical imperfections. You can have impurities. You can have alloying elements and we're also going to be talking about atomic arrangement.

And in the case of atomic arrangement, we're dealing with structure, right? Here we're dealing with chemistry. Here we're dealing with structure. You know about crystal structure so you know what perfect crystals look like, but real materials are not perfect, neither in the chemical sense nor in the structural sense. So perfect crystals don't really exist. You have always some forms of imperfections and we'll go over those today.

So in the case of chemical imperfections, we have, broadly speaking, two types. Good ones-- Dr. Sadoway labels them with a smiley face so I will do that, too. And bad ones are a sad face. So both are defects and whether they're good or bad depends on their utility. Are they useful or are they detrimental? If they are detrimental, we call them impurities. And if they are good, we call them other things. For example, dopants. We studied dopants, right? Dopants are a type of impurity, they're a kind of imperfection, but they're good. We use dopants. We use

them in semiconductors. Also, alloying elements, you can put in the elements yourself.

Those are examples of good chemical imperfections. When it comes to atomic arrangements, we're going to spend a little bit of time talking about that in more detail in just a minute. But broadly speaking, they are situations where you don't have perfect crystal in order. You have disruptions and that perfect crystal in order-- either in the form of missing atoms or extra atoms or differently oriented unit cells of the crystal and so forth. So we'll talk about that a little bit more in just a minute.

So one thing that I forgot to mention maybe is that we have a test coming up-- That is, I'm sorry. Celebration of learning, second celebration of learning. And those are your room assignments. You don't have to necessarily write them down now, but you'll see them again. So I just wanted you to see them. A through Ha in 10-250, He through Sm, 26-100, So through Z, 4-270.

OK, so let's go into the taxonomy of defects. So I mentioned that there are a number of different kinds of defects, and we can do better than to say simply, defects exist. We can actually start to classify them. So there are, broadly speaking, four types of defects, which we classify based on dimensionality.

So there's 0-dimensional defects and 0-dimensional defects are point defects or point defect clusters. It's just like in math. A point has 0 dimension, right? 1-dimensional defects or line defects, things that thread through a material like a shoestring or something, and we'll have an example of that in the form of dislocations. Then we have 2-dimensional defects. Those are interfacial defects. So if you have interfaces between two different kinds of materials or if you have two crystals that are misoriented with respect to each other, those are examples of interfacial defects. And we also have bulk defects-- 3-dimensional defects like inclusions. We'll go over some of those.

So let's start out with point defects. Point defects are those 0-dimensional defects. They're points, just like in math. And there are a number of different point defects that we can look at. We have our substitutional impurities, interstitial impurities. The general overall recurring theme in these point defects, regardless what type they are, is that they are localized disruptions. So a lattice, a crystalline lattice, is a regular arrangement of atoms, and a point defect is a very local disruption in that regular crystalline arrangement. And those disruptions can occur on lattice sites. So basically, on the positions where you would see atoms normally, they can also occur between lattice sites. So they're localized rifts, you can say, in the periodicity of a crystalline material. And here's just an illustration of the way that these different point defects play out.

So let's start out by looking at this one. This is a substitutional impurity atom. So it's an impurity. So it's a type of chemical imperfection. You can imagine that this is, for example, some kind of FCC material like copper, for instance, and suppose that you have an impurity of some sort like iron, and it sits there and it replace one of the

copper atoms. So this is called a substitutional impurity. It substitutes for the regular atom that would have sat at that location. Substitutional impurities. There's another picture. There's your substitutional impurity up there. We'll get to the other ones in just a moment. We already talked about some substitutional impurities.

So dopants. If you have boron or phosphorus or silicon, that boron or that phosphorus replaces the silicon that would have sat at a certain lattice site. So the dopants we've studied so far are types of substitutional impurities and we call them good impurities because they give us desirable properties. They are dopants. They're good impurities.

Then we have alloying elements. I am not a very big fan of sodas, but if you were somebody else who is a big fan of sodas, then you might, for example, drink a lot of sodas out of aluminum cans. Those aluminum cans are really not pure aluminum. They're alloys. They're alloys with other metals to give them the good properties that they need in order for the forming process to occur. So if you ask yourself, how do you actually make aluminum cans? They're stamped out from sheets of aluminum, but it's not just aluminum by itself. Aluminum by itself would just tear if you do that. So if you alloy it, you give it better properties so it's ductile. You can deform it to very large strains and that's a good thing in the case of alloying elements. Another one that he showed you was nickel and gold. That's if you want to change the color of gold, if you want to be very creative when you're proposing. So that's a good kind of substitutional impurity.

There are also contaminants. Contaminants are bad kinds of impurities, but before we get to the contaminants, let me just show you what good impurities can do. So this is the Hope Diamond. It's in the American gem collection. You can actually find out more about it. I'm not a big gem expert, but anybody who looks at this Hope Diamond can immediately see that it's a really pretty diamond. But you guys are ahead of everybody, because in addition to knowing that it's a pretty diamond, the fact that it has boron impurities in it already tells you what the majority charge carrier is. So when you go to this gem collection, you can educate everybody else. So those are all good impurities.

There are also bad impurities-- contaminants. Lithium in sodium chloride is an example. So if you were using saline solution, for instance, in an IV and you had lithium in there, that is very detrimental to the person who's receiving that. That's definitely a contaminant. You don't want those. That could make you die. So let's move on to some other types of point defects.

Here's another type of point defect. So just now we talked about the substitutional impurity atom. Now we're going to talk about the interstitial. The interstitial's very different from the substitutional. In the case of the substitutional, we have a lattice site, which instead of being occupied by the regular atom that would have occupied it in a perfect crystal, is occupied by a chemically distinct atom. In the case of an interstitial impurity, that impurity can sit in the

space in between lattice sites, so-called interstitial sites. That's why we call them interstitial impurities. And interstitial impurities or interstitial atoms can be both chemical impurities, and obviously, they are rifts in the atomic arrangement so they are structural impurities as well.

Why do I say chemical? The reason is because if this is, for example, iron, if this is an iron matrix and you have a carbon atom sitting in the interstitial site which makes steel, then that's an example of a structural defect, but it's also a chemical defect. If, for example, you have, on the other hand, iron sitting in a nuclear reactor and it's getting bombarded all the time by energetic neutrons, then interstitials are being created by atoms getting knocked out of their lattice sites and they're getting put into interstitial sites. So that's creating defects that are chemically the same as the surrounding matrix material, but which are structurally distinct. So those are interstitial atoms.

So here's another picture of interstitial atoms. There it is. It's not sitting on a regular lattice site. It's sitting in between lattice sites. It's sitting in the space, in the interstitial space between atoms. And I already mentioned to you the fact that if you put carbon into iron, those atoms go into interstitial sites and there would give iron some of its beneficial properties, which we look for in steel. So some of the good mechanical properties.

Here's another example of a situation where an atom goes into a lattice and create an interstitial impurity. So lanthanum-nickel 5 is a prototype hydrogen storage material. It takes up a huge amount of hydrogen. It takes up a greater density of hydrogen than liquid hydrogen, actually, so if you expose this to hydrogen, the hydrogen just goes right in, and it sits in the lanthanum-nickel 5 lattice as an interstitial atom. So this is considered to be as a prototype hydrogen storage material. Unfortunately, it's extremely expensive so it's not being used very much these days, but on the other hand, it goes well with our gem theme in this particular lecture in terms of expensive things.

Here's another example of an interstitial impurity. This one is not an alloying element. It's a contaminant. So hydrogen, but this time in iron. So hydrogen in lanthanum-nickel 5 is good. We want to store it. Hydrogen in iron is bad because it actually degrades the mechanical properties of the iron, unlike carbon, which gives us steel, which is good. You put hydrogen in, it embrittles it. So hydrogen embrittlement in steels is a big problem. And it's actually one of the challenges to a hydrogen economy. If you have steel pipelines or valves or various pieces of machinery, structural components that are made out of iron that are constantly exposed to hydrogen, over time, they're going to brittle. They're going to become very difficult to use. It's one of the challenges in that whole undertaking. OK.

So we're going fairly at a clip here through these taxonomy of point defects. So in the taxonomy of point defects, perhaps the easiest defect to understand is the vacancy. So when you think of the vacancy, think of the hole that

we talked about in the case of semiconductors. Vacancy is nothing. It's a missing atom. So if you have a crystalline lattice and it's FCC or it's BCC or it's simple cubic, whatever you like, and you know that there's supposed to be an atom at a certain lattice site and it's not there, that's a vacancy. That's a situation where you have an unoccupied lattice site and there are different ways to form these vacancies. They can be formed during crystallization. If you heat up a material, the number of vacancies decreases. So if you quench it really quickly, you can actually trap the vacancies before they can leave in service under extreme conditions.

I mentioned just a moment ago that interstitials can be created if you irradiate a material, if you bombard it with energetic particles, like neutrons for instance, you'll create interstitials, sure, by knocking atoms out of their atomic sites, but what's left behind after you knock that atom out? Vacancies. So actually, you create two defects at the same time: vacancies and interstitials. So I think we probably have a picture here of a vacancy. A vacancy is nothing. It's just empty space. That's a vacancy. There you go again. Nothing.

So we've gone through a bunch of taxonomy, right? So we know now that there are a number of different kinds of point defects in crystals. We've talked about interstitials. We talked about vacancies. We've talked about substitutionals. What can we say about these defects quantitatively? So let's take the vacancy and derive or write down what is the number of vacancies that you can expect to find in a given material at a certain temperatures? So to do that, let's be a little bit more quantitative.

Suppose that you have a crystal. I'm showing you a plane, for example, a 1 1 1 plane in an FCC material and how do you create a vacancy? You simply remove an atom. So you had an atom. Now you have no atom. You've created a vacancy. When you created that vacancy, you broke all the bonds between the atom that used to be there and the neighboring atoms. Breaking bonds costs energy. So it costs energy to create a vacancy. It costs energy to remove an atom from the place where it would have been because you're breaking bonds. So in this case, I have six bonds that I broke. If I were looking at some material, for example, placing our cubic material in 3D, I would find that I would be breaking 12 bonds to the 12 nearest neighbors, and so on for all the different crystal structures.

So we actually then take that information, the fact that we're breaking bonds, and encapsulate it in a single descriptions of how much energy it costs to create a vacancy. And we call that the vacancy formation energy. So this is an energy and so it's expressed in eV. Its units are electron volts. You can convert them to joules, anything you like. And if you wanted to then compute how many vacancies there are in a given crystal, well, first of all, it costs energy to make them, so why would you ever even have a vacancy in the material? Well, no material is perfect. We know that from studying materials, but what causes it is the fact that at finite temperature because of the Boltzmann distribution that Dr. Sadoway told you about a few lectures ago, just like in the case of intrinsic charge carrier promotion in semiconductors, you can get thermal formation of vacancies. So that Maxwell

Boltzmann distribution can actually cause there to be vacancies despite the fact that there are-- that it costs energy to do that. So how can we actually use that to express how many vacancies we have in a given material?

So I'm going to write down an expression for how many vacancies you can expect to find at a given temperature on the basis of their formation energy, OK? So let's do that. This is going to be the fraction of vacant sites. So if you have a given material-- FCC, BCC, whatever you like-- you know that there's a certain number of lattice sites per unit volume, and you learn how to calculate those things. And to quantify the number of vacancies, you have to basically say, what fraction of those sites does not contain an atom? Is that 1/100 of a percent or is it 1% or how many? So this is actually going to be expressed as a ratio, which I'm going to call this. This is the number of vacancies per unit volume and this is the number of atomic sites, also per unit volume, OK.

So this is the definition of the fraction of vacant sites. And how do we express it? Well, we express it using a very simple formula. This formula contains a factor here which is experimentally determined. This is an empirical factor and then an exponential. So the exponent we take here, the vacancy formation energy, and we divide it by the thermal energy at the given temperature of interest.

So this is actually telling you that to form vacancies, you actually have two competing factors. On the one hand, you have the bonding energy that makes the difficult-to-form vacancies because you're breaking bonds, you're taking it an atom out. On the other hand, you have this thermal energy, Boltzmann constant times the temperature, and the thermal energy is competing with that bonding energy. And when that thermal energy is high enough, you can actually start knocking atoms out despite the fact that it costs you some energy, and obviously when this ratio is very large, that means that the bonding predominates, and when it gets smaller, that means the thermal energy is more and more sufficient to actually knock atoms out of their positions and cause there to be vacancies. So when you do these calculations, make sure to use the absolute temperature in Kelvin, and dimensional analysis will tell you the units of the Boltzmann constant have to be energy units per degrees. So eV's per Kelvin, for instance. So this is the absolute temperature. This is the vacancy formation energy and this is the Boltzmann constant. So what that means is that at any given temperature, you'll actually expect to see some fraction of vacancies. So let's actually try to do a calculation with an actual vacancy formation energy and see how many vacancies we get at a given temperature.

So to do that, we've been provided with what is the common currency in science, which is published experimental data, which we find from published journals which we find online through, for example, Web of Science. And from this journal, we find that for copper, the vacancy formation energy is 1.03 electron volts. Furthermore, in the same journal in the abstract there, you'll find the magnitude of this constant A, which as I told you is experimentally determined. This quantity A we call the entropy factor. And even though there's no way to very easily derive it-- I can't tell you what's the entropy factor for iron and you can't really tell me just by thinking about it-- nevertheless, it

turns out that this factor usually fall within a certain range. It's usually between 0.1 and 10. That's usually the range and what you find As. And in the case of copper, it's very much in that range. It's just 1.1.

So let's use this information to actually figure out how many vacancies we expect to see in copper at the given temperature. OK. So here's my fraction of vacancies and we know that it is going to be expressed as 1.1 times exponent minus the formation energy, which is 1.03 eV, and then we'll put in Boltzmann's constant, and then let's pick a temperature. For the moment, let's just take room temperature. So T, room temperature, and room temperature's about 300 K. So when we put in all these numbers, it's just a matter of calculating. This is on your sheet of constants. This is the temperature which we choose at room temperature. Let's actually write down T, room temperature, is about 300 K, and we find a certain number of vacancies. And the number of vacancies that we find is 2.19 times 10 to the minus 18 vacancies. So this is the fraction of vacant sites.

Well, is that a lot? Is that a little? How can we determine whether this is a lot or a little? We compare it to the number of atoms that there actually are, and in the case of solid materials, we expect there to be something on the order-- this has to be compared to something on the order of Avogadro's number, but we can actually calculate more explicitly that this turns out to be something like 10 to the 5th vacancies per centimeter cubed. And if in a real material, a solid material like silicon, for instance, or boron or whatever you're interested in, your number of atoms is something like 10 to the 23rd, Avogadro's number, right, then this is actually a very tiny number. Compare 10 to the 5th to 10 to the 23rd. The number of atoms that are missing at room temperature is very low in copper. We can compute that using this expression. However, even though it's low, it's not zero. And if we continue going down in temperature, we'll find that the number is lower and lower and lower, but it never really goes to zero because we have this expression which gives us the total number.

So let's do another one and this time, let's take a different temperature. Let's take the melting temperature of copper. The melting temperature of copper is considerably higher. It's about 1085 degrees Celsius and we can go through exactly the same calculation. 1.1 times all these quantities here times melting temperature, OK? And when we do this, we get a vacant site fraction which is 1.67 times 10 to the minus 4 and that corresponds to 1.41 times 10 to the 19th vacancies per centimeter cubed.

So what do we know by-- what can we see now by comparing these two quantities? Number of vacancies, add room temperature, number of vacancies at melting temperature. How many orders of magnitude do they differ by? Huge difference in the number of vacancies that we find at two different temperatures. And why do we see such a huge difference? Let's actually write down what that difference is.

Let's write down the ratio. The fraction of vacant sites at melting temperature divided by fraction of vacant sites at room temperature is something like 7.6 times 10 to the 13th. That's the difference in number of vacancies you get

just by increasing the temperature from room temperature to melting temperature. Why is that? Well, one way to look at that is just from the expression that we have to calculate the number. Here's where the temperatures go. So any difference in temperature if it's a factor of two or if it's a factor of three or if it's a factor of four, it's going to go into the exponential. So that exponential is actually making a huge difference as a function of temperature in terms of number of defects that you get. The higher you go up in temperature, you don't get just-- you go up a factor of four in temperature, you don't just get a factor of four increase in the number of defects. You get that in the exponential. So the factor of four is hugely magnified by the exponential.

So that means that at any given temperature, even the lowest temperatures, you expect to see some defects, but if you increase the temperature, you see a hugely larger number of defects. And you can use this sort of expression for any kind of defect. So I talked about vacancies right now and vacancies have a specific formation energy, but interstitials also have formation energies, substitutionals also have formation energies. So you can use this expression to determine the fraction of defects per lattice site for any kind of defect so long as you have the formation energy of that defect.

So just to show you how difficult it is actually to remove defects, if you have a crystalline material, defects want to stay even at the lowest temperatures. I have this interesting little piece of art to show you. This particular piece of art was actually discovered, I guess, by some scientist at the University of Toronto where Dr. Sadoway went to school, and this particular-- what do they call it? They call it The Atomix. Let me write down the name of it in case you want to look it up because I think they sold a lot more of these to material scientists than they sold to anybody else.

And all this is two plastic plates, two PMMA plates, polymethyl methacrylates, or plexiglass. And in between them, there's a little hole that's cut, a gap, and in that gap are a number of ball bearings. And the ball bearings are kind of like atom, right, so they move around. And here we're going to the document camera right now. So if you shake these things around and the ball bearings are moving around, that's like introducing temperature. That's like taking a crystal, melting it, all the atoms are bouncing around. You will even see some vapor atoms when these sort of leave the surface and fly through the air, but then if you stop, that's like quenching. That's like suddenly I've taken this crystal, which was originally molten, and I've dropped the temperature. Here's what I see. So can you see that? How to use this thing-- there we go. So you can actually see a lot of the defects that we were talking about just a moment ago.

Here you can see areas of perfect crystalline order. Here's another area of perfect crystalline order. So you have many, many crystals that are adjacent to each other. They're oriented differently. So they're forming misorientation defects between themselves. So for example, here's a grain boundary. This is a crystalline grain. And inside this crystal, you see a vacancy. It's right there, So here's another instance of the vacancy. There's

another vacancy. And what happens if I try to remove some of the disorder? By the way, interesting thing is that some of the vapor is also left here. So there's the vapor.

If I then try to remove some of these defects, I can just tap on this. If I just continue to tap on it, I'm removing defects. The whole thing is crystallizing more and more and more so now I put it down again. OK. You still see the vapor phase. Now you see a big huge crystal right here with some grain boundaries around it. Here's another big huge crystal. Here's another crystal. There's a smaller crystal. Each one of them is bounded by grain boundaries, but what do you see in each of these crystals? There's a vacancy. There's a vacancy. There's a vacancy. And you can actually sit here-- well, not here. Maybe later, but if you want to take a look at one of these things, you can probably go to Dr. Sadoway's office and pick it up and he'll let you play with it for a little while.

You can try to get all these vacancies out. You can try to get all the defects out. No matter how hard you try, if you spent hours, you'll get things to be more and more and more perfect by tapping on it, but there's always going to be a vacancy. Always. And even if you are extremely patient, you get things down to just one vacancy and you think that all you have to do now is just give it a little bit more of a tap to remove that one vacancy, well, more often than not, you'll find that with that tap you'll remove the vacancy, but create another vacancy somewhere else. So you'll always find these vacancies in these crystalline materials.

It's just a consequence of the fact that when you're agitating a material like you're doing here-- you're shaking it-- that's the same thing that happens if you have some finite temperatures, some non-zero temperature in the material, you're always going to be creating some defect. So that's exactly what this expression is giving you. It's telling you that there's going to be defects at any temperature, but their number goes up dramatically as you increase the temperature.

So let's go back to the slides real quick now. OK. So everything I've told you so far is concerned with defects in crystals that are of one type, so that are made up of a single element. But in the case of, for example, things like ionic crystals, and ionic crystals are made up of multiple elements with multiple charge states, you can get new kinds of point defects that you can't see in a single element material. So we'll talk a little bit about those and when it comes to those defects in ionic materials, we have to expand the taxonomy a little bit. The taxonomy is now going to include defects called Schottky imperfections, Frenkel imperfections, and F-centers. So let's go to a visualization of what these are.

Here you see an ionic crystal. So you have alternating types of atoms. You have these big ones, which are presumably the negatively charge ones, and then you have the small positively charged ones, and here you have an example of a Schottky imperfection. So a Schottky imperfection, it's kind of like a vacancy. It's missing atoms. The main difference between a Schottky imperfection and a vacancy by itself is the fact that in a material that

involves charged atoms-- ions, right-- in an ionic crystal, when you take atoms out, you have to make sure to maintain charge neutrality. So these materials are charge neutral. They have equal numbers of positive and negative ions, but you want to make sure that you take these out in equal numbers. So in the Schottky defect, you take out one negative and one positive ion, or basically one unit, one stoichiometric unit. If you add zirconium oxide, which is ZrO_2, you would have to take out three atoms to maintain charge neutrality. That would be the Schottky defect.

So here is another example, another visualization of a Schottky defect. So when you take these two atoms out, nothing says that they have to be taken out from right next to each other. You can take out one here. You can take out one there. It's good both ways because in the end, it's just about charge neutrality. It's about maintaining a charge neutral material. So we can actually write down reactions to describe the formation of these Schottky defects. So let's do that. When we write down reactions to describe the formation of Schottky defects, we first recognize the fact that we're dealing with empty sites. We're dealing with void. We want to see how this void, or in scientific parlance, null, is decomposed into two vacant sites in the particular ionic crystal that we're dealing with.

So let's-- to make things specific, deal with sodium chloride. So sodium chloride, we have two type of atoms. Sodium and chloride. And to maintain charge neutrality, we have to remove one of each. So this is actually-- this null space is actually going to be composed of two vacancies: a vacant site on a sodium lattice where a sodium atom would have been sitting and a vacant site where a chlorine would have been sitting. And because this entire process takes place in the presence of materials that are composed of ions-- so ionic solids-- these two vacancies, in fact, have some charge them.

So when we think about the charge of these vacancies, what we actually have to think of, it's a little bit counterintuitive. The sodium in a sodium chloride crystal is charge positive, but what does that make the vacancy? So if you have a lattice of atoms that are charge positive like the sodium atoms and you remove one of them, what is the effective charge of that vacancy? You have nothing, as Dr. Sadoway would say, in the land of plus. So the charge of this vacancy, the effective charge of this vacancy, is going to be negative. And we mark that with this little thing right there. So void or nothing in land of plus is negative. We mark that with one of these apostrophes.

So what about this vacancy? That vacancy is created on a lattice of sites which are usually charge negative. So if you have these chlorine atoms that are charged negative and you remove one of them, now you have void in a land of plus. So this is going to be effectively charge positive and so we have this void in land of minus. It is positive. And we do it-- we annotate it with one of these dots.

We can do the same thing for other kinds of crystals. So I mentioned that in this case, a Schottky defect would just be composed of these two atoms, because these two atoms constitute the structural unit for this crystal. But if we

had some other, more complicated crystal, like, for examples, zirconium oxide, then we would still write down a similar reaction. So we could put a Schottky defect into zirconium oxide. OK.

And so now we have to figure out how this reaction plays out. We have to create vacancies. Here's our vacancy on the zirconium. And because the structural unit contains two oxygens, we have to create two oxygen vacancies. And now we have to think about how do we maintain charge neutralities? What is the effective charge on all of these atoms? So the zirconium sites are usually the positively charged atoms, so when we remove one of them, that's removing something, that's putting void basically into the land of plus. So we have now a negatively charged vacancy, and this negatively charged vacancy has four negative charges, an effective minus 4 negative charge. And the oxygens are the negatively charged ions, and so when we create voids there, these two vacancies have an effective positive charge, and because the charges have to balance, we know that this has to be effectively two negative charges and there are two vacancies. So we have charge neutrality. So that's how the Schottky defects work. OK. So let's move on to Frenkel defects. In the case of Frenkel defects, it's really not so different from Schottky defects in some sense, except now instead of dealing with a situation where we maintain charge neutrality by removing two atoms, we actually displace one atom from its initial location to a different part of the crystal. So we're creating actually a vacancy right there, and this atom, which was originally sitting on a lattice site, is now displaced to an interstitial location. So that's an interstitial. So a Frenkel defect is a vacancy and an interstitial.

And here's another view of a Frenkel defect. Here, I've removed an atom from one of the lattice sites and moved it over to here. So that's my Frenkel defect. And in the case of Frenkel defects I can also write down reactions for Frenkel defects. Let's do that. OK. So Frenkel defects usually occur in crystals with widely differing atomic radii, and in ionic crystals, the radius of whatever is positively charged would have to be much, much less than whatever the radius of whatever's negatively charged occasionally, or very rarely, but I suppose it's still possible, you would have to have basically a very big difference in radius between these two cases.

An example of one of these situations is, for example, silver bromide, where here the silver's positively charged and the bromide ion is negatively charged. And we can write down a reaction to describe the Frenkel defect formation just like we did in the case of the Schottky defect formation. So in the case of a Frenkel defect formation, how do we actually go about this? We have, for example, can start out with a silver atom site and we're going to displace that silver atom away from its original site so it now sits in an interstitial position and we're going to leave behind a vacancy. So let's do that. OK. So we're going to have silver interstitial site and let's just be clear-- say that this is on a regular silver site. And then we have a vacancy left over on the silver site and this is the reaction for the formation of our Frenkel defect.

Frenkel defects, just like Schottky defects, preserve charge neutrality. So how do we actually mark down charge

neutrality in this case? Well, there's no change in charges in the original state so we'll just mark that with an X. And the vacancy is sitting in a place that used to be positive so it's a hole in the land of positive so we know that this one's going to be negative. And this silver ion, which was displaced from its original lattice site, is now going to be sitting in an interstitial site which was originally a land of zero. So this one's going to be charged positive. And now we've balanced, once again, this reaction. We have charge neutrality. We've created a defect and this is defect, just like in the case of vacancies, costs us energy to make. So we can actually write down a formation energy for Frenkel defects. And this formation energy is usually a little bit higher than the formation energy of vacancies so it's going to be something more perhaps on the order of 2 eV. OK.

So we have gone through-- before I go to this one, let me just mention one last defect that you might run into if you're working in ionically bonded materials. An F-center is a situation where you have a vacancy with a bound electron inside of it. And F-centers have the property that they give ceramics a tint, a hue. They actually scatter light in the visible range so you can see them.

So with a very short amount of time left, I wanted to tell you about a couple of the other defects that you will encounter in crystals and one of the most interesting ones to me is the dislocation and dislocations are line defects. They're 1D defects.

So if you look in, for example, a corn ear right here, you can see dislocations as the termination of a single atomic plane. So here's a picture of what a dislocation looks like in a crystal. You have these atomic planes and here you have one that just ends. That's a dislocation.

Some of you probably have dislocations in your fingerprints. So after the class is over, you can look for dislocations in your fingerprints. They're line defects. So here's another example of that. You see that there's an extraatomic plane which ends. That's a dislocation. We mark it with one of these Ts. Here's a picture of a dislocation. Dislocations actually help materials to deform easily without having to shear off.

Here's a little picture of mine which I really like. This is the only way that people really had to study dislocations before computers existed. So now we can study, for example, dislocation by simulating them in real crystals. And this is a mid-20th century computer. It's a raft of bubbles. It's just a bunch of bubbles that somebody blew on the surface, soap bubbles, and you can deform them. You can deform this raft of bubbles by shearing it and here you see-- what's wrong? Why isn't it going? There it is. There's your dislocation running through and you see lots of dislocations running through this crystal. This was, by the way, done by Lawrence Bragg, who you heard about in connection with x-ray scattering. You'll hear about Bragg again when we get to DNA. So keep him in mind.