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3.091SC Introduction to Solid State Chemistry, Fall 2010
Transcript – Exam 2 Problem 3

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OK we're going to do problem 3 now on exam 2 from the fall 2009 class. Let's talk a little bit about what the problem concept is. This is doping. We're going to talk all about doping semiconductors. As we say chemistry, where doping is legal.

So we're going to look at the things we should probably know before attempting the problem. You want to review your doping principles. How does doping work. What are the mechanisms, your conduction mechanisms? So why does the material conduct? What's actually happening? Your donor and acceptor levels, understanding which is which. And your p versus your n type doping. What those mean. So look at those real quick and do the problem. Let's go on.

I wrote down the information that we're given in the problem. The problem part a asks us to find specifically how much gallium is needed to reach a certain carrier concentration in our germanium. So we're doping gallium into germanium. We're given the fact that the germanium band gap is 0.7 electron volts. We know that we want to achieve a carrier concentration of 3.091×10^{17} carriers per centimeter cubed. And we're working with 1 kilogram of germanium. So we need to achieve this density or this carrier concentration in one kilogram of germanium.

I've drawn schematically-- now remember the germanium crystals are in 3-D so the bonds don't actually look 90 degrees like this-- but I've drawn just for visual a germanium crystal. So this is what a pure germanium crystal would look like. I'm going to draw the band structure for the pure germanium crystal now as well. When you see a problem that gives you your band gap and it tells you this is about doping, the first thing you want to do is just get some points. Put some stuff on the paper that you know to be true. So let's draw the band structure.

I'm going to abbreviate conduction band with cb and valence band with vb. So here's my conduction band, here's my valence band. We're told that this is here. We know our band gap energy is 0.7. OK and I'm going to use this blue to show where electrons are. This just shows that there's electrons in the valence band going all the way up to the top of the valence band. That's how the valence band level is defined. So this easy points. You've got this on the paper, we're good to go.

Now what we're talking about is putting gallium into germanium. So let's do that. Let's take out this germanium. And let's put a gallium in its place. We'll put it in red. OK so this isn't exactly correct yet. Germanium makes 4 bonds. If you look at the periodic table you'll see that it has 4 valence electrons to make bonds. But gallium does not. Gallium only has 3. So what that means is that one of these bonds can't exist like this anymore. So the way I like to draw it, is we still have an electron from this germanium but we're missing one for this gallium. And this is what a hole

basically is, schematically, in doping. So we're going to write this as hole plus. And the reason it has a positive charge associated with it is because in our neutral crystal with no charges you having an electron there. And you've just removed an electron and now it's positively charged. You have a positive charge in this region of the crystal, which corresponds to a missing electron.

So we just created a hole. We have a hole here and then it's going to result in what we call-- I'll use red again-- an acceptor level. And remember this band diagram is an analogy for, these are the energy levels where your electrons can exist. So we have these energy levels and the valence band and we've got energy levels up in the conduction band. What's just happened is that this dopant has created an energy level slightly above the valence band.

If you have a donor level from a different type of doping-- which we'll talk about in a second-- you'll create a level right below the conduction bands. So we've got some points. We understand the system now. It's just going well. So let's try to do a.

So a, as I said before is asking us to figure out the actual amount. We're looking for grams. This is what we're looking for. Grams of gallium. That we need to put into a kilogram of germanium to create a carrier concentration of 3.091×10^{17} carriers per centimeter cubed. Not too bad of a problem. This is basically just stoichiometry. Dimensional analysis.

Here's how I did it and many people did it this way. I start off. 10^{17} . And I always keep my units. That's really important. So we're going to write this as carriers per centimeter cubed. Now we're also told in the problem, we have the additional information that the temperature is high enough that all of the sites are ionized. What that means is that-- let's take a look at this band diagram-- we have electrons existing in the valence bands up to that level. We've doped and now the temperature's high enough that these electrons can be excited, one of them in this case can be excited to this level here, the acceptor level, creating, of course, a hole in the valence band. That's what it means that it can be fully ionized.

So basically every gallium atom that we put into our material creates a carrier. And why do I say that? Because conduction is either, the movement of electrons in the conduction bands, which we don't have. Or it's the movement of holes in the valence band, which we now have. So we're talking about conduction. And so for every gallium atom we put in, we're creating an acceptor level, which takes an electron up, which creates some conduction in the valence band. Now if we add lots and lots of gallium atoms-- there's a lot more gallium atoms in here-- we're going to actually see many more of these levels showing up. And you're going to get what almost looks like very thin bands, an acceptor band or acceptor level there.

So we start off like this. And I went into that's digression because now I'm just going to say that for every atom we put in we get 1 carrier. And then we're going to say-- I want to be sure I get this right-- we have 6.02×10^{23} atoms per mole. That's right. And then we have 1 mole. And notice how I'm being very careful about the dimensional analysis here. Because if you put something in the wrong top or bottom you're off by 46 powers. So don't make that mistake. We saw that a lot on the exam. So we're good here.

Let's do our dimensional analysis. We start off, we're looking for this particular concentration carriers per centimeter cubed. We have 1 atom creates 1 carrier. 1

mole has this many atoms. And one mole of-- we're talking about in this case-- gallium. I'll put Gallium here to be clear. 1 mole of gallium has this much mass. And you're left with something like this. You're left with 3.58 times 10 to the negative 5 grams per centimeter. Grams gallium per centimeter cubed.

So we're looking good. We're pretty close to the answer but we don't actually have the answer yet. Remember we're looking for total grams of gallium. Not how many grams per centimeter cubed. That's pretty easy because we're told the we have 1 kilogram of germanium and we know the density of germanium from our periodic table. So looking at our periodic table we can look up germanium's density and we can then back out how many centimeters cubed of germanium we have. We'll do that right here. So 1 kilogram of germanium is 1,000 grams, times-- we have the density, which is going to be times 1 over the density, rather-- grams per centimeter cubed. And that's going to give us 187 centimeters cubed. And now we're good. Because we know here we have 3.58 times 10 to the negative 5 grams of gallium per centimeter cubed of germanium. We have this many centimeters cubed of germanium. Multiply them together and you get the answer, which is 6.69 times 10 to the negative 3 grams of gallium.

So that's part a. Just dimensional analysis and stoichiometry. But I stress, be careful about the way these things are. Even I pause to make sure they're correct because if you get this wrong, the whole problem's wrong. You're off orders of 46. You're off by orders of 1,000 here, so just be careful.

Part b. We've actually already answered when we drew it up, we threw down the things we knew. We knew that we were creating a hole. And a hole corresponds to p type doping. How do I remember p and n? It's easy. p means positive. We've created a hole, which has a positive charge. n, I think of as negative. So if you had put something else in there like arsenic, arsenic would've had an extra electron compared to germanium, which means you have a negative charge. So n negative. So we have p type doping. We're done with part b. Easy.

Part c. I'm just going to erase some of this stuff here and we're going to draw a couple more of these band diagrams. So basically what we're asked to do now is to think about, what does this band diagram look like at different temperatures? Because it actually looks slightly different. I've drawn it here schematically. But let's actually think about what it looks like in real life.

So let's do 2 more of these. And we'll use that one as well for part c. OK so I'm drawing my conduction bands. These are my conduction bands. These are my valence bands. I have the same band gap for all of them. So you know band gap here, here's the band gap. It's always worth putting down. If you know it's true, put it down. And we know that in both cases-- let me just get rid of this thing here; we're going to start from the beginning; put our electron back-- we've created all these acceptor levels. Because we've doped with more than one gallium atom. We have many, many, 10 to the 17 gallium atoms. Which sounds like a lot, but in a mole we have 10 to the 23 spots in a mole of material. So it's 6 orders of magnitude less.

So we have these systems and we're asked to do them at-- I'm going to keep going back and forth-- 300 k, 4.2 k and 1200 k. That's Kelvin. Let's go with the extremes first. And we'll do the middle one, 300 k, once we have an idea of what's happening. So basically, in the very beginning when we to dope in a material, time t equals 0 and no electrons have had a chance to move around. You have all your electrons in

the valence band, you have these open holes in your acceptor levels. And the reason that electrons would move between levels is if they have some energy associated with them. Now why would something have energy in a crystal? Well that's because of thermal vibrations. It's a thermal energy they have. So it's completely based on the temperature at which the crystal exists. So at a very low temperature-- let me write that up there for you, this is our basic equation-- at a very low temperature we have a very low thermal energy. $k_B T$: this is the Boltzmann's Constant. At a very high temperature, we have a very high thermal energy, which means that these electrons have the ability to move between levels more easily.

So here's our very low temperature. At a very low temperature we can actually calculate the energy. We'll find that the energy here is about-- just so you have a scale-- it's about 0.00036 electron volts. Now you say to yourself, wow that is a lot less than 0.7 electron volts, which is the energy of this gap. So there's no way these electrons here can even make it up to this acceptor level. That's not exactly true.

This is best thought of as an average thermal energy that an electron will have. It's based off of a distribution, if you will. So most electrons will have around this energy. But some will have a little bit more and some will have a little bit less. And very, very, very few at the tail of that distribution will have enough energy to actually make it up to one of these levels.

So the way to do this problem, to be actually fully correct, is to say that and explain it. I actually, when I did this problem on the answer key, I have an electron, one electron going up into one of these spots and the rest are all empty. I denote that with a little bit of blue here. But everything else is empty. We've got a hole here. So there is a finite, very small, amount of conduction. But it's extremely small. And it's extremely unlikely to have electrons moving around but probabilistically it will happen. That's 4.2 Kelvin. Very, very low.

Let's go to very, very high. Starting at the beginning again, we know all of our electrons are in the valence bands. At 1,200 we have an energy of about 0.1 eV. Still less than 0.7. We have a significantly larger proportion electrons in that distribution, which are at 0.7. So we actually do have electrons that will move up into the spots. And even many that'll move up here as well. Because they can overcome this 0.7 eV. So we've got some electrons, they're going to move here, they're going to fill up most of these. Because this delta here, the difference between our acceptor level and our valence band, is actually quite small. It's extremely small. That's another reason why we have an electron moving up at 4.2. I should have mentioned that.

This is very small. This gets pretty much completely filled. And I'll denote that with a blue line here. And we have some electrons, even going up into here. What that means, that that has to correspond to electrons being depleted out of the valence band. This is the way you would draw this picture. So we lose these electrons from the valence band. Some jump up to the acceptor levels and the rest will go up to the conduction band. So this is 1,200. We have more than enough energy to reach this acceptor level and we have probabilistically some electrons will make it up to the conduction bands. That's the best way to think about it.

Now let's go back to our middle temperature. I think the best way to do this one is to just go somewhere in the middle. That's the safest play, right? So we're at a temperature which corresponds to about 0.025 eV. Now that is obviously smaller than the gap. Probabilistically we'll still get some electrons in the gap. Diminishingly

small. But we'll put one up there. OK maybe one goes up there. And it's still much bigger than the delta here between the acceptor level and the valence band top. So these electrons will still pretty easily make their way into the acceptor level. Now I'll put a little bit here. We're going to lose electrons very slightly.

That's how I would have done that problem. It sort of looks like that on the answer key. Now I want to emphasize that, what is what's the importance of this? Well when you dope, you're creating conduction. Why is that? Because the more we dope, the more holes we have that can be played around with. So we have more and more of these acceptor level energy levels. And what happens is these electrons at finite temperatures-- temperatures above 0 Kelvin-- will move into those levels. And they will cause conduction in the valence band. And you know at high temperatures, back over here, we have electrons moving to the conduction band, which is traditionally what we think of when we think of conduction, electrons moving around. So we have in this case conduction in the conductor band as well as in the valence band.

So that's this problem. This problem was generally pretty easy; many students got it right. The learning goals and objectives we had from this problem were, number 1, to understand doping principles. What it means to n and p type dope. Holes versus electrons and how you get them. So if you have germanium or silicon, those are very common examples and you dope things into them. So gallium or arsenic or aluminum, for example. We talked about conduction mechanisms-- just like here-- and we also talked about the donor and acceptor levels. So the donor levels are just slightly below the conduction band and are full of electrons. And the acceptor levels are just slightly above the valence band and initially holes. So that's problem 3 and I hope you had good luck at it.

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