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**MICHAEL SHORT:** Anyway, today is going to be a lot lighter than the past few days, which have been heavy on theory and new stuff. And I want to focus today on what can you do with the photon and ion interactions with matter. So we're going to go through a whole bunch of different analytical and materials characterization techniques that use the stuff that we've been learning and see what you can actually do. And I'll be drawing from examples from the open literature, from textbooks, and from my own work. So stuff I was doing here on my PhD thesis is actually a direct result of what do we do here in 22.01.

So a quick review just to get it all on the board of what we've been looking at. So I don't hit anyone on the way in. We talked about different photon interactions, which include the photoelectric effect. Let's say this will be the energy of the scattered whatever, and this will be its cross section. We talked about Compton scattering. We talked about pair production.

For the photoelectric effect, the energy of the photoelectron comes off like the energy of the gamma ray minus some very small difference, the binding energy of the electron. Let's just call it  $E_b$ . And this effect starts when you hit what's called the work function.

I'm just going to put this all up there, so when we explain the analytical techniques, we can point to different bits of this and explain why we use these different things. The cross-section, I made sure to keep this handy, so I don't want to lose it. Strongly proportional with  $z$ . So the cross-section comes out of another line.

What was it proportional to? Oh yeah, this is nuts. It's like  $z$  to the fifth over energy to the  $7/2$ , which says that for higher  $z$  materials, the photoelectron yield is much, much stronger, and it's way more likely that way lower energy. So you can imagine if you wanted to use this in an analytical technique, and you want to study which photoelectrons come from which elements, you might think to use a low energy photon to excite them, not a high energy photon, because like we had done a couple of times before, if we draw our energy versus major cross-section range, we had a graph that looks something like this, where this was the photoelectric effect.

This was Compton scattering. This is pair production.

And so by knowing what energy-- oh, I'm sorry. That's supposed to be  $z$ . And this would give you the dominant process that each the combination of energy and  $z$ . So if you know what energy photons you've got and what you're looking for, well, there you go. Let's see. What was the energy of the Compton electron? Remember the wavelength formula.

It was like  $\alpha \frac{1}{1 - \cos \theta}$  over-- let's see. Another  $1 - \cos \theta$ . In came the gamma ray energy. What was the part that came beforehand? That's why I have this here because I don't want to write anything wrong. It's good to have it all up there at once. 1. Yeah.

That's all I was missing. Cool. And the cross-section for Compton scattering scaled something like  $z$  over energy, something pretty simple, not nearly as strong as pair production or photoelectric effect, so you can think Compton scattering happens much more dominantly at low  $z$  or the other two don't really happen that much at low  $z$ , whichever way you want to think of it.

And for pair production, you get a whole mess of stuff. You get positrons coming out. You get a bunch of 511 keV gamma rays and all sorts of other things you can detect. And the cross-section, this one's got the funny scaling term. This one, yeah. It's like  $z^2 \log$ . Energy over  $m_e c^2$  squared, so some  $z^2$  kind of dependence. So let's keep those up for now.

Let's get the electron ones in.

**AUDIENCE:** [INAUDIBLE]  $m_e c^2$  squared?

**MICHAEL SHORT:** Was it  $z^2$  squared? Let me check. No, that's a  $c$ .

**AUDIENCE:** [INAUDIBLE]

**MICHAEL SHORT:** Yeah. Yeah, just make sure that's clearly a  $c^2$ . So now let's call it charged particle, or just more generally ion electron interactions. Since these are more fresh in our head, what are the three ways in which charged particles can interact with matter that we talked about? Just rattle off any one of them.

**AUDIENCE:** Bremsstrahlung?

**MICHAEL SHORT:** Yeah, Bremsstrahlung or radiative. What else?

**AUDIENCE:** [INAUDIBLE]

**MICHAEL SHORT:** Is what?

**AUDIENCE:** Ionization.

**MICHAEL SHORT:** Ionization. Which we'll call inelastic collisions. And?

**AUDIENCE:** Rutherford scattering.

**MICHAEL SHORT:** Yep, Rutherford scattering. Which are kind of elastic or hard sphere collisions. And if we had to make kind of a table of when do we care about which effect, let's say this was an ion or electron, scattering off of either electrons or nuclei, in either elastic or inelastic ways.

First of all, when do we actually care about elastic scattering off of electrons, which would be hard sphere collisions off of electrons? To help get you going, in an elastic collision, the maximum energy transfer can be this formula  $\gamma$  times the incoming energy, where  $\gamma$  is  $4$  times the incoming mass times the mass of whatever you're hitting over  $n$  plus  $4$   $m$  squared.

Let's say if one of these masses was mass of an electron. What is  $\gamma$  approximately equal for most cases? Well, let's say this was like electrons scattering off of protons or vice versa. How much energy could an electron transfer to a proton in an elastic collision? Basically zero.

The only time which this actually matters is if it's an electron hitting another electron, in which case you can have pretty significant energy transfer. So I'd say for elastic collisions off of electrons, you only care about those for other electrons. And I'm going to put in low energy electrons.

Why do we only care about them for low energy electrons? Or in other words, what are the other methods of stopping power or interaction-- yeah, Chris.

**AUDIENCE:** [INAUDIBLE]

**MICHAEL SHORT:** Exactly. Yep. We already saw that Bremsstrahlung the radiated power scales with something like  $z$  squared over  $m$  squared. So with a really small mass and a really high  $z$  and also a higher energy, you end up radiating most of that power away as Bremsstrahlung. And there's not much of a chance of elastic collision.

So we only care about low energy electrons when it comes to elastic collisions with electrons. For inelastic collisions with electrons, well, that's the hollow cylinder derivation that we had done from before where you have some particle with a mass  $m$  and a charge  $ze$ , getting slightly deflected by feeling the pull-- depending on what charge it is, it could be towards or away-- of that electron away from some impact parameter  $B$ .

So we care about this pretty much all the time. Electrons and ions or stripped bare nuclei actually matter in this case. For elastic collisions off of nuclei, this is what Rutherford scattering is. It's a simple hard sphere collisions, so this matters pretty much all the time. What about inelastic collisions with nuclei? What does an inelastic collision actually mean with a nucleus?

So fusion could be one of them, but let's go more generally. We have some nuclear reaction, where it's the old thing that I keep drawing all the time of some little nucleus striking a large nucleus. In an inelastic collision, this is the case we haven't considered yet, but I want to show you what actually happens.

In an inelastic collision, these two nuclei join together to form what's called a compound nucleus or CN, at which point it breaks apart in some other way. So there might be some different small particle and some different large particle coming off. But in an inelastic collision, it's almost like the incoming particle is absorbed and something else is readmitted. It could be that same particle at a different energy, and it could be a different energy altogether.

So yeah, I'd say fusion is an example. It's kicked off by an inelastic collision, because you've got to have some sort of absorption event of the small nucleus by the big nucleus. And then, maybe if it fuses and just stays that way, it releases a ton of its binding energy, well, that's pretty cool. So these actually do matter, but not for all energies in all cases. So let's go back to the Janis database of cross-sections to see when inelastic scattering actually matters.

Bring us back to normal size. And we'll look at some of the cross-sections to see when do we actually care about inelastic scattering? So we haven't selected a database yet. Let's say we're firing protons at things. And pick a database that actually has some elements listed. Not a lot. But iron, that works.

So we can look at the difference between the elastic scattering cross-section and the anything cross-section. So the red curve here-- can I make it thicker easily? Probably. Yeah, I can make

it thicker pretty easily. Easier to see. Plots. Wait.

That's not what I wanted. I'm not going to mess around with this anymore. Do you guys see the two lines? OK, so this is the elastic scattering cross-section. Kind of funny to see it negative. But then there's the anything cross-section which picks up at around 3 MeV or so. And it usually takes somewhere between 1 and 10 MeV for inelastic scattering to quote unquote turn on, and that's because you have to be able to excite the nucleus to some next energy level. So sending in a proton at like 0.01 MeV is not going to excite any of the internal particles to a higher energy level.

So if you want to see some pretty interesting cases, let's go to incident neutron data where we have a ton of this data. And I'll show you some examples. We've got lots more data for neutrons. So now we can look at some of these cross-sections. Like this  $z n$  prime. Let's take a look at what that looks like. That means a neutron comes in. Different neutron comes out.

Notice that the scale only starts at 862 keV. So let's make it something else. Oh my. Look at that. Nothing going on until you reach almost 1 MeV, which means, hey, inelastic scattering doesn't really turn on until that. So I would say that this can matter, but for higher energy collisions.

So yeah, it matters pretty much all the time. But higher energy collisions. And there's actually-- yeah.

**AUDIENCE:** What does it say in the top left box?

**MICHAEL SHORT:** Only for low energy electrons. That's the sort of compound reason that I and Chris said, one, is that you can't transfer much mass in an elastic collision, or I'm sorry, much energy in an elastic collision unless the masses are close enough to each other. And two, at higher energies, the electron radiates Bremsstrahlung much, much, much faster. As we saw at around 10 MeV, Bremsstrahlung and inelastic scattering give about equal contributions to the stopping power for high  $z$  materials like lead.

So once you're down and let's say like the keV range, yeah, electron elastic collisions might matter. So we talked about those three. Now I think we can launch into the analytical technique. So for the rest of the lecture today, it's all going to be what can you do with the stuff that we've been learning since the first exam. I know it hasn't been long since, but we've actually learned a ton. And I want to show you what's actually possible.

And this is not going to be with slides. It's all live from websites that I'd love for you guys to be able to follow along with or check out at home. So I'm going to show you an awesome resource through the MIT libraries and how to get there. If you go to [vera.mit.edu](http://vera.mit.edu), there's a great tool called the ASM Handbook. You can see I've been there before.

There's the ASM handbooks online, and this is kind of that's everything to know about material science, metallurgy, and analytical techniques, absolutely everything from corrosion to fractography, to characterization, to structure of materials to where you can find every single alloy, to binary phase diagrams of how things mix, and we're going to head to one of these handbooks.

Number nine or 10, materials characterization, because with the stuff that's on this board, you can understand how most materials characterization techniques work. And I want to show you a few of them. One of which-- no, two of which, we're going to demo out next Friday's recitation.

So I think I told you guys in the syllabus and probably in person that we're going to try out some scanning electron microscopy and some energy dispersive X-ray or EDC analysis. So with the X-ray transition stuff you've learned, you actually know how to elementally analyze different materials. And with scanning electron microscope, you can get some idea about how electrons can make images much better than optical images.

So let's head to electron optical methods, scanning electron microscopy, and show you what one of these things actually looks like. Let's take a look at an SEM, or scanning electron microscope. So up at the top, there is a device called the electron gun. For now, just imagine it's a source of electrons, but in a few minutes, we'll actually explain how it works using the principle of thermionic emission, which we talked about last Friday.

You've got some electronic lenses, some focusing coils, that caused this beam to get focused further and further. So let's say you had this electron filament giving off electrons in all directions. When you see boxes with x's like this on an electron optics diagram, it usually means this is like a focusing coil of some sort.

So that will cause the electrons to get bent and focused. There'll be another set of coils that focuses them further and some scanning coils that actually raster or xy scan this beam across the surface of a material. And so in this way, what you're actually doing is putting the electron

beam at one part of your material and then with another detector, let's call it a secondary electron detector.

Looking at the electrons produced from collisions with those other electrons that then get detected here, and the number of electrons produced at a point gives you the brightness of the image. That's kind of as simple as it is despite how complicated this diagram looks. There's an electron source. There's coils that scan it back and forth. Like has anyone ever seen the old cathode ray tube, CRT televisions?

There's going to come a day when that answer is no. And I'm kind of worried for that, because that's the day I'll officially become old. But for now, everyone's seen a CRT, and the way that actually works is there's an electron gun that fires and scans left to right and up to down our rasters and produces that electron image.

In an SEM, you use an electron gun, kind of similar, and then collect the electrons generated in the specimen, what's called secondary electrons. And the number that you see gives you the brightness of the image. The cool thing is this actually allows you to look at both secondary electron contrast and topology of a sample.

So let's say this was your secondary electron detector. And you had an electron beam scanning across your sample to some of those peaks and valleys. And I'll probably draw one right here for a good reason. Let's say the electrons hit right here, and you send out a wave of secondary electrons.

The material partly determines how many electrons come off, but also, so does the geometry. There will usually be a little cage with some sort of a positive voltage on it to attract those secondary electrons. And some of them will curve into the detector and become part of your signal, but some of them won't.

Meanwhile, if you have this beam right here producing secondary electrons, pretty much all of them go slamming into your detector. And that's what actually allows the electron microscope to get topology. That's why images in the SEM look fairly 3D. So I want to show you a few examples from my own boredom when I was doing a lot of science. There we go.

I have a whole gallery of SEM images when I was supposed to be doing something better. Oh no. 404. My website's broken. Oh yeah. This is also what you do when you're bored, right? Make your own 404 page. My SEM galleries are dead. Well, that's OK. I have other images

ready to show you guys.

So this is a neat-- this is a paper that I published out of my PhD work that shows the real difference between optical and electron microscopy. Part of it is the limit of your resolution depends on the wavelength or de Broglie wavelength of the thing you're using to make the image.

So an optical microscope, in this case, you can't get better resolution than about half a micron, because even the blue wavelengths of light are getting down into about the 450 nanometer regime. And it's very difficult without interference techniques or other fancy things to beat that diffraction limit, to beat the sort of wavelength limit of optical microscopy.

So this is a 500x optical microscope image, and you can see these little fingers-- in this case, it's liquid lead bismuth penetrating into a stainless steel that we were doing corrosion experiments on. And that's as good as the image can get in an optical microscope. Switch down to an SEM, and then all of a sudden the picture becomes much, much, much more clear.

You can start to see things-- the best SEM we have in our lab has an ultimate resolution of about 1 nanometer. Now, resolution is kind of a funny thing. It's neat to tell you what that means. It doesn't mean that if you have a pattern of lines that are exactly one nanometer thick, that you will see them as lines 1 nanometer thick. It means that if you then plot, let's say, your signal or your brightness versus  $x$ , you'll have some barely distinguishable and fuzzy lines, just enough for you to say those are two optically distinct features.

So what you'll actually see in a 1 nanometer microscope is maybe something like this. That's technically resolved at the level of 1 nanometer. So the best you can do for crisp objects in this thing is about 20 nanometers. Not bad. It's like something that's a few thousand atoms on a side. Pretty cool.

And so what you can see in here is liquid lead bismuth penetrating into this stainless steel, and you notice a few different things. This image was taken in backscatter electron mode. Back scattering is-- we've talked about this before. When you have a scattering event where  $\theta$  equals  $\pi$ , we call that backscatter.

Let's kind of split this into regular and backscatter. For a backscattering, the cross-section for this is proportional to  $z^2$ , another one of those extremely  $z$  dependent cross-sections,



which means that the larger the  $z$ , the higher the atomic number the more backscatter contrast you get, so if you want to figure out where the little lead whiskers are penetrating into the stainless steel, since lead has a  $z$  of like 82, and iron has a  $z$  of like 26, it shows up like night and day.

Do you have a question, Julia? OK. Yeah, so this is something we'll actually be able to do. So for the two folks I asked to bring in samples, if you want to bring in something with very different elements in it, we should be able to see it in backscatter contrast very, very clearly. And in the image of the SEM, I'll go back to that-- which one of these pages is it?

Notice here that there is a backscatter detector. So it will detect which of those electrons scatter back at almost 180 degrees. And that's at about  $z^2$  proportionality, super useful tool, because if you want to see, for example, where the circuit board traces are, and you want to look at aluminum versus oxygen contrast, that'll help you really well.

If you want to see where is lead penetrating into stainless steel, it shines up clear as day, which is pretty fun. The other thing the electrons will do when they enter into a material is excite lots of things. So anything from X-rays to Auger electrons. So now I'd like to bring up Auger electron spectroscopy.

Electron or X-ray spectroscopic methods. Auger electron spectroscopy, it's not just a thing to trip you up on the exam or a little minutia from radioactive decay. It's actually incredibly useful, because of where the Auger electrons are generated and what they tell you about the material. So as a quick refresher, normally you could have, let's say, if a photon comes in and injects a photo electron as another electron comes to fill that hole, either an X-ray will be emitted or an Auger electron will be emitted.

And it's those Auger electrons, they're outer binding energy electrons. They have very low binding energy, which means-- let's see. I keep running out of room. You know, I'm not going to draw it. I'm going to show you, because I know there is a diagram of what I want to show you here.

If you want to see where the Auger electrons are actually produced in the material-- here we go. Since they're such low energy, the only Auger electrons that actually get out would be in this outer few mono layers. In fact, there's some Auger electron energies that can only get out one or two atomic mono layers from a material.

So it's one of the best surface analysis techniques that we have. You can both use Auger electrons to make an electron image, like any other SEM. And you can collect them and measure their energy to figure out which elements they came from. And this kind of teardrop shape is a-- one, it's a great synthesis of all the information you need to know in the SEM that we'll see on Friday.

And two, it's why people screw up SEM analysis a lot. A lot of the X-ray excitation happens down here. Why do you think that the X-ray excitation would happen near the end of the path of the electron beam from what you know about stopping power?

Or, if I asked you to draw a graph of let's say energy versus stopping power for ionization, what would it look like? Yeah.

**AUDIENCE:** It comes up like a peak at low energy.

**MICHAEL SHORT:** Yeah.

**AUDIENCE:** And then drops back down.

**MICHAEL SHORT:** Yeah.

**AUDIENCE:** And as the energy goes out, it sort of flattens out.

**MICHAEL SHORT:** Yep, sort of flattens out, and then eventually starts picking up again but not very much. So as the energy of whatever you're going into-- I'm sorry, whatever particle you're sending in it gets lower, it's stopping power increases, and you have a much higher chance of this ionization happening, especially in the case of electrons.

They usually come in at between 10 and 40 kV. And so near the end of their range is where they produce a lot of the X-rays. Now there's a lot of other nuances to say, well, which X-rays were produced here and what elements are they from. Let's say you had the same material here or here.

Fewer X-rays will get out of the bottom region than they will from the top region. So if you happen to be analyzing something that has a gradient in composition or a change in composition from the top to the bottom, you might be like, oh, well, I have a few nanometers of oxygen on silicon. Why aren't I seeing any oxygen X-rays?

Because you're probably generating them down here. That's one of those things to note. So

sometimes you'll see and elect an elemental map of things that shows X-rays of certain element coming from somewhere, and you can't see it at all in the image. That's because they might be underneath what you can see in the image. It's kind of tricky like that.

I'll show you some examples of what those maps look like also from this paper. So from the electron image, we sort of concluded, all right, lead is probably penetrating into the stainless steel. How do we know for sure? You can make EDX or elemental dispersive-- I'm sorry, energy dispersive X-ray maps by focusing the electron beam at one point, collecting all the different X-rays and then moving from one point to another to see when do you get characteristic X-rays from each of those elements.

So you can actually prove to say, yes, those little fingers are indeed bismuth and lead, and you can see that, in this case, where the lead in bismuth is, the iron is not. But the curious thing we found is that in this whole band right here, most of the chromium disappeared. So it turns out that the corrosion mechanism was chromium dissolution. And we would not have been able to know that without this EDX mapping, and without understanding how the EDX maps are made from the electrons interacting with matter and producing characteristic X-rays, wouldn't have been able to prove this.

Yet another example where the basic stuff you're learning in 22.01 is the theoretical underpinning of the techniques that we use all the time in material science, which I thought was pretty cool. I've got more examples of that that are even more striking, because I let it collect for a little longer. You can actually see right here that where the bismuth is, the iron isn't, but the iron's not dissolving. The chromium is.

It's just the lead and bismuth are kind of sucking the chromium out of the metal right there, and that's what making the stainless steel less stainless. It's pretty neat. Then on to EDX analysis, what sort of information are we looking at every one of these pixels?

I have a couple of other example X-ray spectra. So now we're in a position to understand why one of these X-ray spectra looks the way it does. In this case, we're firing electrons at a material. Let's see. Where is our material we're firing at? Right here. So we're firing in electrons. And in some cases, let's say we had an iron atom.

That electron can eject another electron. And then one of those other electrons will fall down in that shell, giving off a characteristic X-ray. In this case, since it's from the third to the second shell, that would be what we call an L X-ray or a something to level two transition. And every

element has got its characteristic X-ray transitions, like we saw on the NIST X-ray transition database.

And since we know what all of those are, we know where to expect them. So we know where we expect to see chromium's X-rays and iron's X-rays. Gold's kind of an interesting one. There's two things about doing analysis with gold. A lot of times you have to coat your materials in gold to boost their secondary electron contrast.

But also gold, I think it's its L line or M line, I forget which one, is the same as argon's K line. And we have an expression in the electron microscopy world, the probability of finding argon in your sample decreases with experience. Takes a second to parse that.

Chances are, if you're looking at a solid material. You don't have argon in it. But there are extra lines that overlap with each other, like the L line for gold and the K line for argon are at pretty much the same energy, certainly similar enough that it's within the resolution or like full width of half maximum of these two peaks.

So remember how we were analyzing the uncertainty of our banana spectra with the FWHM or full width at half maximum? Same thing here, and you can really see that the energy resolution of this detector is not the best. So if you see a peak, it might be due to two or more peaks crowding in that right there.

And with a lot of correction factors that I won't get into, you can then use this information to integrate the area under these peaks and get elemental analysis. You can say how much chromium or how much iron and silicon is in one of these samples.

What's this stuff here on the bottom? Anyone tell me? That continuum of observed X-ray energies?

**AUDIENCE:** Compton.

**MICHAEL SHORT:** Compton scattering is a photon effect, so that would be-- if this were a photon analysis spectrum, then you would see something like this but of a different shape. You'd have that Compton bowl with an edge. But this is, in this case, electrons interacting with material. What do you think is causing that broad background?

Well, what are the different ways in which electrons can interact with matter? You're seeing the ionizations here. We're not really seeing Rutherford scattering. What's left?

**AUDIENCE:** Bremsstrahlung?

**MICHAEL SHORT:** Bremsstrahlung. Yep, that's exactly it. So the observed Bremsstrahlung spectrum follows this sort of characteristic peak early and then tail off curve. What's the actual Bremsstrahlung spectrum that we're not sensing? What would it look like?

Always running out of room. If this is what we're actually observing, let's say we have a few peaks, that would be intensity, and that would be energy, what's really going on physically that we're not seeing? Yeah.

**AUDIENCE:** Isn't it sort of like almost like exponential decay. So it starts out with very high intensity and goes down.

**MICHAEL SHORT:** That's right. You actually should get more low energy Bremsstrahlung. One of some of the reasons you don't is that the lower energy, those X-rays come out, the more they get self-absorbed in the material in the few gas molecules in the SEM and in the window of the detector. So just because this is what you see doesn't mean this is what's actually going on in your material.

If we think back then to where the electrons and X-rays are generated, the X-rays that are generated down here, the lower energy ones are going to be shielded more. And this kind of messes up your elemental analysis, because if the X-rays produced here, proportionally more of the low energy ones will get out than the ones produced here.

So as you change your-- as you change your electron beam energy, you might see your elemental composition appear to change when you know it's really not. And that's because where the X-rays are being generated change, and proportionately, more of the low energy ones get self shielded by your material.

So you actually have to correct for that and input your beam energy into the EDX analyzer so it knows how to correct for this. But with the understanding I've been giving you guys in this class you can understand like well, why can you get screwed up? Why do we have to have all these correction factors? I think it's pretty neat.

Then let's get on to some of the other methods, like X-ray photo electron spectroscopy or XPS. This is something I hinted to a little bit earlier that actually uses the photoelectric effect, because it's a photo electron spectroscopy method.

This one's incredibly useful because not only does it tell you what elements are there, but in what binding state they are, because photo electron spectrometers can be incredibly precise. The energy equation should look pretty familiar to you it's whatever photo electron you get is the gamma ray energy that comes in minus the binding energy of that electron and the work function.

And so you can very, very simply figure out for a given element and a given electron shell what photo electron energy's do you expect. So you can collect them. So I'll show you another example from this paper, where we started to do that. We wanted to answer the question, what are the oxides forming on the stainless steel when lead corrodes it?

And just telling you which elements are there and in what proportion doesn't give the answer, because what if there's multiple phases of each oxide? Like, for example, iron can take forms like FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, and this FeO can actually have a range of stoichiometries. So how do you know? You don't know. There could be like scores of phases of this iron oxide.

The question is how you know which ones are there. The photo electrons will tell you. So what you can do first is fire monochromatic X-rays, so single energy X-rays, in this case from aluminum at your material and see which photo electrons of which energy come off. And you can tell which atomic shell they're from and which elements they should be to a very high precision.

In this case, this is done to 100 milli MeV or 0.1 MeV precision, 0.1 eV precision. So we can tell not only what elements are there, but what shells they came from. Then you can get even crazier. You can scan very slowly over one of these peaks with 0.001 eV precision and start to see something pretty cool.

If you look at the carbon 1s electrons, you can see that there are actually three of them only a couple eV apart, and this corresponds to different binding states of molecules with that carbon. For an even more subtle example, but ended up being incredibly important for us, here's one of the chromium 2p shell peaks.

You can actually see there's three of them superimposed give that funny looking peak shape right there. What that actually tells us is that there's chromium in three different binding states in that oxide. And the ones we figured out must be there, we saw the ones corresponding to Cr<sub>2</sub>O<sub>3</sub>, FeCr<sub>2</sub>O<sub>4</sub>, and I forget which other one, but we have them tabulated.

There we go. Oh wow. Fe 2.4 Cr 0.64, known crystallographic phases of these oxides. So you can look at the peaks found to have resolution of like 100th of an electron volt, compared to reference values taken on pure compounds and materials to figure out what actual oxides do you have. That can help tell you things like how protective are they, how fast are they going to grow, and are they going to be a problem if you want to use this new stainless steel that we developed in a lead bismuth reactor.

The biggest problem with lead bismuth reactors is lead corrodes like everything. And so the whole point of my graduate studies was design an alloy that doesn't corrode and lead and make an alloy composite out of it. But you can't prove that it works unless you not only know how fast it corrodes, but how it corrodes, which oxides form, and in what order.

That's the last part I haven't told you about yet is what order. So I want to switch to another technique called secondary ion mass spectroscopy or SIMS. In this case, you start off with firing ions at a material, which will then eject or sputter away secondary ions. In this case, this process of sputtering-- let's say this is your material here.

You send in something like oxygen ions, which might be like O<sub>2</sub> minus with a mass of 32, and then you blast off or sputter away. A few atoms at a time from that surface, and they'll come off the various masses and charges, and in this case, the sputtering could be due to Rutherford scattering, because you might directly ballistically slam an ion out of the surface.

Then every one of these ions has a different mass and a different charge. And by sending it through a mass spectrometer, something that separates these materials by their mass to charge ratio, because the higher the charge, the more deflected an ion will be. But the higher the mass, the less deflected it will be. That should sound really familiar.

In our idea here where how these ionization collisions happen, if you remember the higher the charge, the stronger the Coulomb force-- that  $q_1, q_2$  over  $r$  squared. I think there was a constant in there. So the higher the charge, the higher those  $q$ 's, and the stronger the Coulomb forces. But the larger the masses, the less momentum it can impart. And so the deflection will be weaker.

Exact same thing's happening here. And you can separate out atoms not only by their charge and their mass, but specifically by their isotope. So this is one of those ways that you can figure out and make an isotopic map of a material in three dimensions. You can scan your ion

beam across the material and collect the ions at every point.

And as you sputter, you slowly wear away layers of this material. And so you can actually reconstruct a 3D map with almost nanometer precision of every single isotope that was at every location, which is quite cool. As you can see, these master charge ratios can depend on which isotope of silicon you have, what sort of cluster, what molecule, what charge you have.

And you can do some pretty crazy analysis of things to even figure out what sort of compounds exist on surfaces, because sometimes you sputter off whole molecules. They're going to have their own mass to charge ratio. And that's what we did for this lead bismuth work. Lots of XPS spectra to jump through.

We wanted to find out which oxides were forming and in what order. Which one's the best one I want to show? Think it's this one. So in this case, we used ion sputtering to sputter away surface layers to a depth of a few hundred nanometers, and we're actually able to show that the chromium oxide, right here, was on the outside of the sample, followed by silicon oxide, followed by iron metal.

So in this way, we were able to figure out using XPS, the nature of the oxides and using SIMS, the order of the oxides, so not only how fast were they growing to nanometer precision, but in what order did they form. And that helped us figure out this sort of synergistic chromium and silicon oxidation mechanism that helps really protect the layers of the stainless steel and explain why it's corrosion resistant lead bismuth, all using principles from 22.01.

So it's about two of five of. So I wanted to stop and see if you guys have any questions on these analytical techniques, knowing that we're actually going to go do a couple of these next Friday. Has anyone used any of these before? Yeah, which ones have you used?

**AUDIENCE:** SEM and XPS, XPS [INAUDIBLE]

**MICHAEL SHORT:** SEM and XPS? OK, cool. Yeah, we've got all these instruments I think except for SIMS here at MIT. Yeah. Yeah.

**AUDIENCE:** Sorry, what is that second equation on the energy for Compton scattering?

**MICHAEL SHORT:** This would be the energy of the Compton electron that comes out when a photon scatters off of it. So the photon will end up losing some energy, and the Compton electron will pick up that energy.



**AUDIENCE:** [INAUDIBLE]

**MICHAEL SHORT:** Sorry?

**AUDIENCE:** What's the denominator of that?

**MICHAEL SHORT:** It's a 1 plus alpha times 1 minus cosine theta, where alpha-- I'll mention what alpha is. It's a ratio of the photon energy to the electron rest mass energy. This is kind of a nice-- on these two boards right here, it's kind of a nice summary of the stuff we've been doing over the last three weeks or so, and then all the stuff I showed you today is what you can do with it.