Chemistry and Physics of Surfaces and Interfaces

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Lecture - 29
Ultra-violet Photo-electron Spectroscopy (UPS)

Hello everyone, welcome back to lecture 29. In this lecture, we will be looking at a new technique mainly to understand the electronic structure of the surface. So, so far what we have been looking at was the scanning tunneling microscopy and scanning tunneling spectroscopy and in this technique, we would be familiarizing something called photo-electron spectroscopy.

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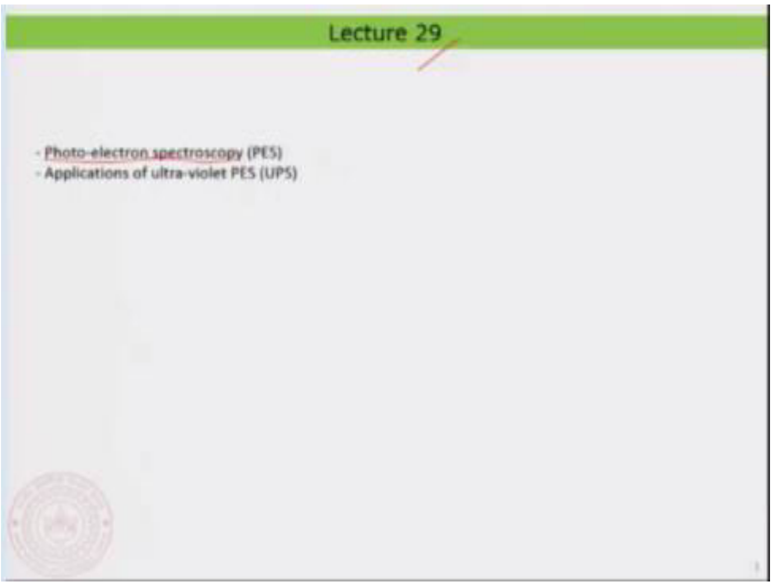

Lecture 29

- Photo-electron spectroscopy (PES)
- Applications of ultra-violet PES (UPS)

And we will also see their application of the photo-electron spectroscopy and this is a technique mainly used for understanding the electronic properties of material. So, that is something, we will basically understand and also using example, we will try to do familiarize. This technique is also a very powerful technique, which you can use for understanding the electronic structure. Good..,

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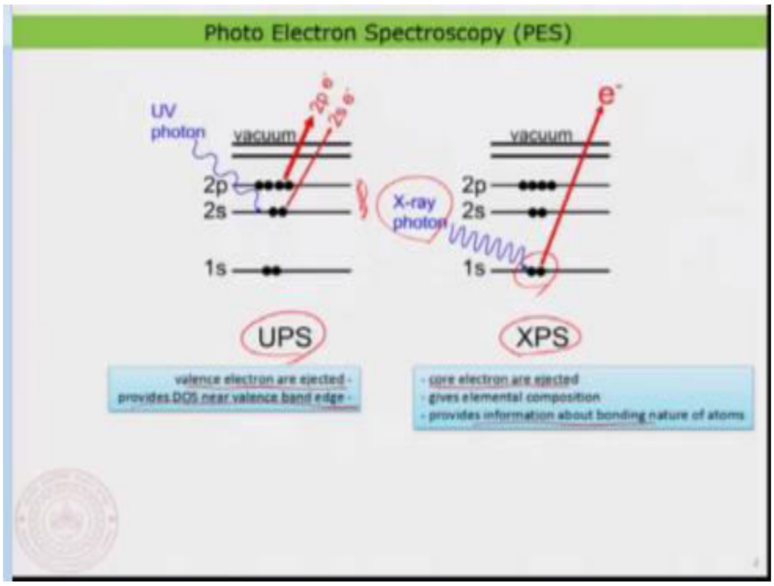

Photo Electron Spectroscopy (PES)

valence electron are ejected -
provides DOS near valence band edge -

- core electron are ejected
- gives elemental composition
- provides information about bonding nature of atoms

Now, what is the photo-electron spectroscopy? What is photo-electric effect itself? It is something, you might have studied in your fundamental classes. So, like in quantum mechanics, for example, so, photo-electric effect is actually an effect when a particular electromagnetic radiation is impacting a surface or a material, then there are electrons that are actually ejected from the material. So, this is typically known as a photo-electric effect.

And of course, this is one of the most important experiments that actually led also to the invention or to the beginning of quantum mechanics and so on. So, therefore, it is quite a celebrated effect that has been actually been around and popular for understanding the electronic structure of material itself. So, in photo-electron spectroscopy, what we do is we make use of this photo-electric effect and then we try to understand the electronic structure of the material itself.

So, what I am showing here is a very simple and schematic diagram of different type of electronic levels that are present in a material. So, I have basically here something called the valence band electrons and also the valence band levels. Of course, when it comes to material, you do not see any more discrete levels, it is going to be a band itself, but the band itself also has an origin in some of these atomic orbitals like the p, s, d and so on. So, here in this very simple scheme, what I am basically showing if the incoming photon energy is basically matching with the energy of the electron, then basically it can kind of remove the electron to the vacuum. So, that means, you can basically just collect them outside the material. So, that is the technique.

And then this particularly the photo-electron spectroscopy, if you are using something like an ultra violet photon, which is having a typically the energy starting from a few electron volt to something like a few tenths of electron volt, so, then what you will be typically looking for a material is the valence electrons that are ejected from the material. So, that means, typically you are looking at this region in the material, but this is quite important, because this provides the density of state, you will see in the next slide. So, that this is going to provide you quite a lot of information about the density of state near the Fermi energy and also near the valence band edge. So, that is something; quite important. Because I have already told you something near the valence band edge is quite crucial in deciding what or how is actually the electronic property of, how the reactivity of the material or their applications in electronics and so on; quite dependent on this kind of density of state near the valence band and the conduction band edge. And this actually can be understood nicely using the ultraviolet photo-electron spectroscopy. So, that is commonly known as UPS. Now, if the energy of the incoming photon is higher, so that means, if you are using something like x-ray photon or so, then you can basically kick electrons that are deep inside. So, that means you can actually just kick electrons from the core levels. In this very scheme, I am showing something like you can kick electrons from the 1s level of the material and then those electrons can be detected. But the interesting thing or the slight difference between these 2 things are basically, they are the same principle. The only difference is the energy of the incoming photon that you are using. Therefore, the type of electrons the type of levels that we are looking at.

In the case of XPS, that is the x-ray photo-electron spectroscopy commonly known as XPS, where you will be looking at the core electrons that are rejected. And but the interesting thing about the core electron is that this core electron can provide nice information about the nature of the binding or the bonding scheme within the material. How strong? And therefore, you also can understand basically the oxidation states of different elements using this particular technique. That is why these 2 techniques are applied in different regimes or different levels. And also it has different capabilities, although they are actually working with the same principle of the photo-electron effect. But now, let us look at UPS first in greater detail and then we can basically go and understand the XPS because both as I told you as a different applications and also going to use it for a different perspective basically.

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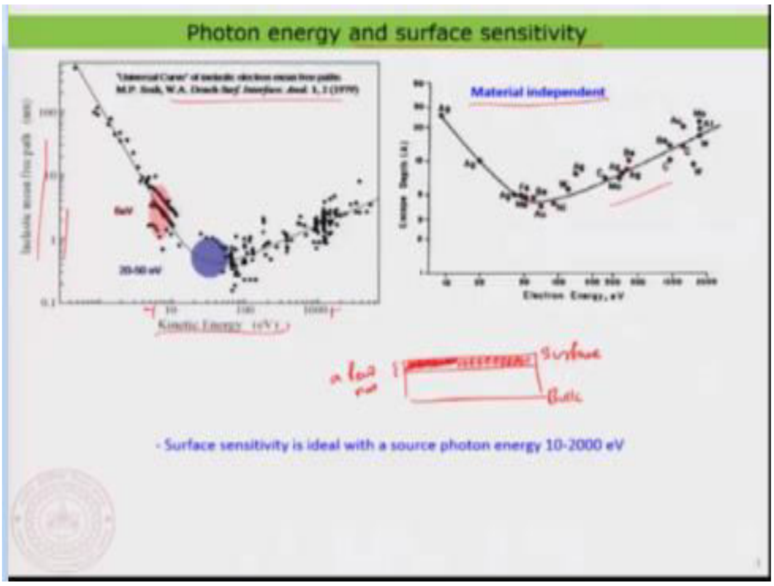

Photon energy and surface sensitivity

- Surface sensitivity is ideal with a source photon energy 10-2000 eV

Before we go into that, I just want to also tell you that this kind of technique, both XPS and UPS are quite surface sensitive. This is the interesting aspect about it. And that is also why this is a technique which is widely used by surface scientists or people who work in surfaces interfaces and so on, because this gives you quite a lot of information about the surface. So, this can be understood using this so called Universal curve. The universal curve is actually something that you are plotting the kinetic energy of the electrons that are released from the material to the inelastic mean free path of the electron within the material. So, the interesting thing is here, if the kinetic energy of the electron itself is actually in the range of like 10 to 1000 electron volt, then what you see is that the electrons can basically just do not move along our path. So, the inelastic mean free path is actually defined like this that it is actually kind of a distance that an electron cover between 2 successive collision that means, the electron started here and it moved basically to a distance and that distance is actually is covered without any correlation. So, of course, that is strongly dependent on the kinetic energy of the electron itself. So, this is quite interesting.

If the electron energy is basically just in the order of 10 to 1000 electron volt, then what do you see is that typically, the so called inelastic mean free path is just in the order of a few nanometers. That means imagine that you have a material like this. And then; if this is the surface or this is basically the surface and this is the bulk, this is the surface and this is the bulk. And now, you can see typically that everything in this region here close to the surface. So, that is actually like a few nanometer, electrons are basically just going to be ejected only from this region here. That means all the electrons that are basically just being excited within the bulk of the material would just die out within itself. But the electrons that are ejected within a distance from the surface of about 2 to 3 nanometer or 4 or 5 nanometer is actually something that is going to be ejected out of the surface. So, that is quite interesting. So, that makes actually the so called photo-electric effect itself, very surface sensitive. And that is quite important, because this is actually therefore can be used in really understanding surfaces and interfaces. And you also see that this is quite material independent. So, this has nothing to do with a material, it is independent of the material. So, this is actually a data that is collected from many, many different measurements, but it is then collated in this paper and it shows something like a U like shape. And then also people have tried it for different material. But that also fits nicely into the shape. And that is why this kind of shape of the inelastic mean free path versus the kinetic energy is strongly material independent, but for us, it is a good message because if you would use the photo-electric effect, you clearly see that we have a very high surface sensitivity or the electrons that are rejected are actually from close to the surface. So, that is the point.

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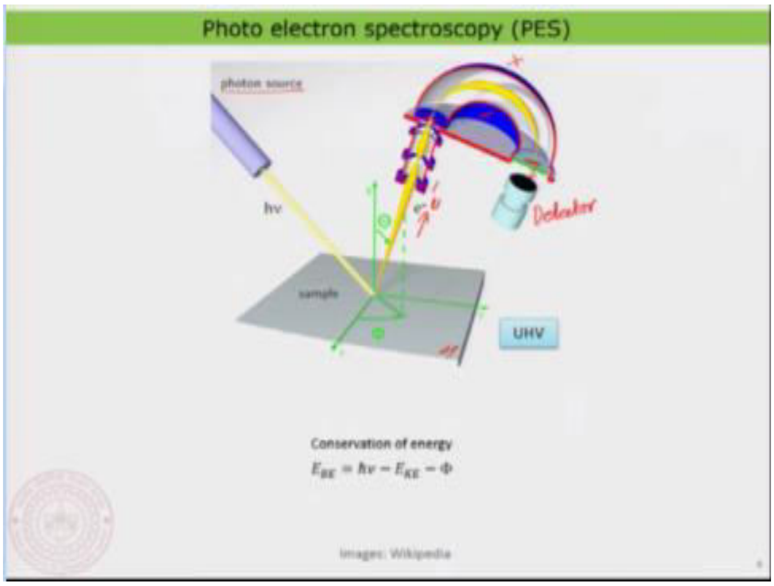

Photo electron spectroscopy (PES)

Conservation of energy

$E_{BE} = h\nu - E_{KE} - \Phi$

Images: Wikipedia

Now, this is how the whole thing looks like. It is very simple in its scheme, but of course, you need an ultra-high vacuum chamber. So, the whole setup is basically kept inside an ultra-high vacuum chamber. So, that is the interesting thing. Then you have to use a monochromatic photo source which can of course, be like a monochromatic or can also use a kind of accelerators to generate this kind of light source. And once you have the source, you impact that on the surface. This is a surface of interest and then electrons are basically ejected in many, many different directions. So, this electrons are collected by something called a particle kinetic energy analyzer. So, this is something like a generally known as a hemispherical analyzer, which has actually 2 different charges, so, there is a positive charge and a negative charge on the 2 surfaces and that makes basically the electrons to bend along the path. So, this is basically the electrons that are going inside and then the electrons would bend the path and since, you actually just use this variable potential between the top and the bottom electrode, so, what also happens is actually that the electrons would split in their energy space and then you can kind of detect it here. So, this is basically a detector. So, we are not going into the technical aspect of it.

So, that itself is a lecture or a course to conduct. But we are not going into the details of that, but we are actually just assuming that we are basically able to measure the kinetic energy of the electrons that are emitted from the surface or from the material in general. But, of course, you know that it is coming out of the surface. Now, we will try to understand this a little bit more in detail. So, to understand, how we can basically just make use of this kinetic energy that you detect in understanding the density of state of the material. So, that is what we are going to do.

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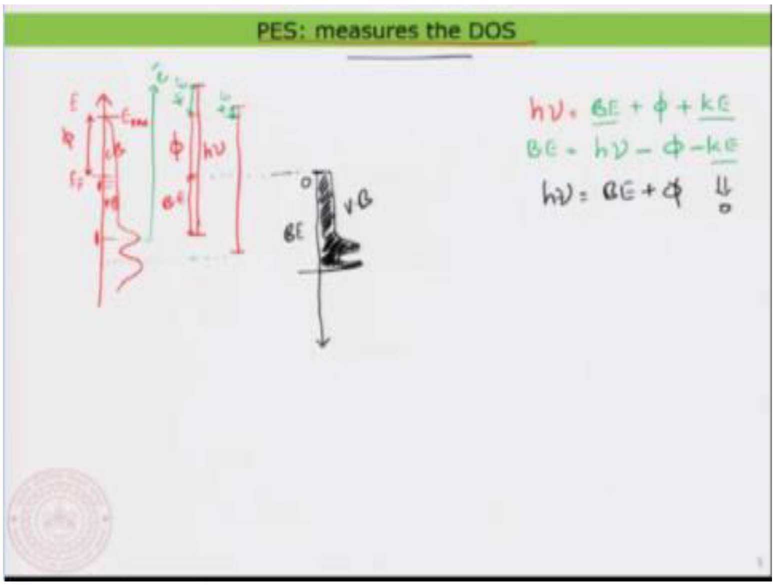

PES: measures the DOS

$h\nu = BE + \phi + KE$

$BE = h\nu - \phi - KE$

$h\nu = BE + \phi$

So, the UPS itself is a measure or in general, the photo-electric electron spectroscopy is a measure of the density of states. So, you remember, we talked about this density of state that is actually something that we are going to measure. So, let me just start explaining it to us like, imagine, I am going to take actually an arbitrary density of states. So, this is not something scaled to any material. So, this is quite arbitrary.

So, I have here a Fermi level and this is basically the energy of the electron so, the electronic levels and then I am going to just basically plot something like a simple density of states. So, this is just the density of state, kind of flat near the Fermi level and here, it is kind of increasing like that. So, this is just to understand it carefully. So, like I have just made some peeks inside. So, this shows that there is a nice constant density around the Fermi level.

But as you go deeper in energy, then you see basically, that the density is actually very so, that is something we have also looked at in the case of Nobel metal, we also told that around the Fermi energy, we can have actually something like a flat density of state. Now, below the Fermi energy, so, this is something you call it as the valence band. And this is something you call it as the conduction band basically. So, this is the density of state of the material. Now, what we are going to do is we are going to take this material and shine photon onto this material and try to eject basically the electrons. And before that, we also need to define something called E vacuum. So, that is something I have also told you, E vac and this energy is basically representing the work function of the material. The vacuum energy is basically representing the energy about which you can basically remove the electrons from the material itself. So, that work function is therefore an indicator of the minimum energy required to remove an electron from the material. So, that is something also, you might have studied in the photo-electric effect itself now. Now, what we are going to do is we are going to basically just shine this material with a photon having an energy, let us assume an energy of this magnitude. So, this is just to a depiction.

So, an energy of this magnitude, so something like this and now, this is actually the incoming photon energy. So, I have something like now h nu is basically just given to the material. Now, you see that this part here is nothing but the work function. This is the work function. And this part is actually corresponding to the binding energy of the electron that you will be kicking because this is the electron that you are basically just going to remove from the material.

So, that means, I am basically just going to remove this particular electron from here and it will be basically placed here. So, this is the electron now that is ejected from the surface. Now, you can see that this extra energy, so, this extra energy is nothing but the kinetic energy of the electron that is now coming out, because you have given a magnitude of amount of energy.

And of course, that energy is actually nothing but the sum of the binding energy of the material. So, the photon energy is basically just the sum of the binding energy plus phi plus kinetic energy of the electron that is emitted. So, that is actually something nicely matching. So, that means, you need to definitely give a photon energy which is more than phi, therefore, that is definitely a requirement that if it is more than phi or the work function, then you can basically eject an electron. So, that means the electron that is coming out now, having a kinetic energy like this. Now, you can also just imagine a situation where you actually can using the same photon energy, you can also kind of excite another electron that is somewhere here. This is also possible. What I have done is actually I have just drawn the diagram slightly different. And then now, you can see that this is basically the electron that I am going to eject.

So, the difference now is that the kinetic energy of the new electron that is actually deep inside is slightly smaller. So, the magnitude of the kinetic energy is now smaller. So, that means, when the binding energy of the material or the electron that you are rejecting is actually increasing, then the kinetic energy of that particular electron will be smaller. So, that means, if you would measure basically the kinetic energy, you can measure the binding energy of the material, because, what I am interested is the binding energy of the material.

So, the binding energy is directly related to h nu – phi – kinetic energy. So, if I measure the kinetic energy, then I can clearly measure the binding energy of the material. Now, you also see something interesting. So, depending on which electron you are rejecting whether you are rejecting an electron from here or you are ejecting an electron from here or you are rejecting an electron from here, that electron density also matters.

Because you clearly see that at this region. The density of state or that itself means the number of electrons that would come out at that particular binding energy or that particular kinetic energy is much more than the binding energy or the density of this electrons which are close to the Fermi energy in this particular case. That would means, if you would have basically made a plot of the binding energy.

So, now, what I am just drawing is basically the binding energy, sorry the binding energy axis should go down because binding energy is basically increasing and this, I am calling it a 0, the zero would correspond to the Fermi level. You can see here this actually correspond to the Fermi level. So, this is the binding energy. So, this is basically our Fermi level 0 and then from there, you know that a certain density is there. So, now, the density is basically increasing and when it reached close to this particular point, the density increases, again the density increases and but the interesting thing is that we cannot basically just continue drawing it as we want. It will basically come and stop at one point where the photon energy is actually finished because there is also a magnitude for the photon energy that you supplied.

That also means that when the photon energy is actually matching with that binding energy maximum value that means, the binding energy when it is reaching h nu plus sorry, h nu is equal to binding energy plus phi and if kinetic energy is actually equal to 0, so, this magnitude is basically zero. So, that means, then there is no electrons is actually a emitting from the material. So, that is how the spectrum is going to look like. So, that means, what you have eventually done is a measure of the density of state of the material of the valence band as a function of binding energy of the electrons. So, now, you clearly see that I can measure the density. So, this is low here and as the binding energy increases, the density increases. And somewhere here, I stopped the process because I do not have sufficient photon energy to excite anything below this particular binding energy. So, that is the point here. So, now, this is quite interesting. So, you are basically able to measure the density of state of the material as a function of the binding energy. So, this is quite beautiful. So, now, that is what we are going to do. So, when we actually look at a few spectrum, so you will clearly understand what we are measuring. And then we can make sense of this. So, that is basically what I want to tell in this case.

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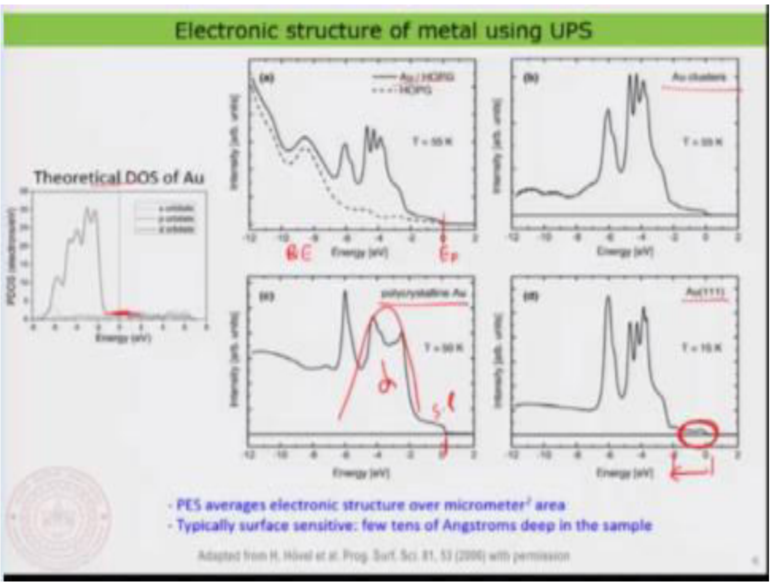

Electronic structure of metal using UPS

- PES averages electronic structure over micrometer² area
- Typically surface sensitive: few tens of Angstroms deep in the sample

Adapted from H. Hövel et al. Prog. Surf. Sci. 81, 53 (2006) with permission

Now, let us have a look at a particular example. This is gold. So, I have gold in different forms. I have here. So, I have basically gold, which is deposited on HOPG. So, that is the kind of synthetic graphite. And then I have a gold cluster. So, that is actually a collection of atoms and forming some kind of particles or clusters of gold. Then I have polycrystalline gold. And then I also have the gold 111 surface. So, that is actually something you clearly know. So, we have actually just studied. In all the cases, if you look, what you are plotting is basically the binding energy. So, please just notice this, this is always the binding energy and the binding energy is going to the negative direction is indicating that the energy is actually increasing in this direction. And this would represent always the Fermi level of the material. Because you see that below the Fermi level or higher than the Fermi level, there is no density. So, that is the indicator basically, because you are not expecting because you need to remove electrons using photo-electric effect. So, that means you need to hit the valence band. And that is the reason why you can see, always there is a step here.

Now, that is the indicator of the Fermi energy and it basically increasing so nice. So, what you clearly see in all the cases is that, that in the beginning, there is so you can see it clearly here. So, in the beginning, there is a constant density. So, that is like we have expected and then after a while around 2 electron volts, you can basically see that the density is basically coming up large. And this is exactly what I was also telling you that near the Fermi energy in that range of 2 electron volt, the density is quite flat, that is actually due to the fact that it comes from the S and P band. So, I also have a theoretical calculation done here, for a comparison, where you can also just calculate the density in a very special way called the projected density of state and then, you can clearly see that near the Fermi energy, you clearly see that the density is looking more or less flat. But then around 2 electron volts, you see the density is basically increasing. And that is exactly what you are seeing for all the different type of gold that you are looking at. But of course, there are small differences and that differences coming is due to the fact that basically the way that gold atoms are arranged in these cases. So, one is kind of a thin film and another one is a cluster. And another one is a polycrystalline gold, but in all the cases, you have this nice plateau here, that is actually the SP band here and this here is basically the D band. So, that is beautiful. So, that is quite reproducible in all the cases. So, what I want to show you here is that we can measure clearly the density of state without any issue. So, we can understand everything in greater detail.

But now something interesting, I want to show you is actually in the case of this one here. So, that is basically the gold 111 surface, you see something special there. In all the cases, you can see that the density is somewhat flat around that region, but only for the gold 111 surface, you see that there is some kind of a step like feature just in that density of state in that particularly the SP band.

But what is that?
That is an interesting question that we can actually just see, if you would zoom a little bit into this part. So, now we are actually just zooming inside that region. So, that we can clearly see what is going on in this small region here. So, let us do that.
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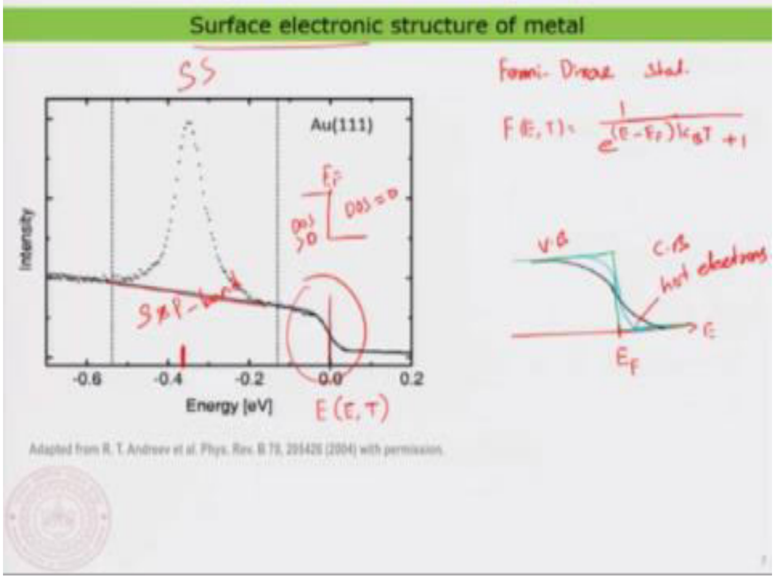
Surface electronic structure of metal

Adapted from R. T. Andreev et al. Phys. Rev. B 70, 205426 (2004) with permission.

When we do that, what you clearly see is that around 400 milli electron volts, you have a peak. Well, what is this peak supposed to be? Interesting thing is that you have not seen that kind of a peak or that step like feature for the polycrystalline gold or for the thin film of gold. It is only observed when you do the experiment with the gold 111 surface. Why is that? Well, it is nothing but the surface electronics structure or it is nothing but the surface state of the gold 111 surface.

So, if you recollect it that we have already discussed that for every surface, you are expecting to see something like a surface state and that is the reason why you see basically this kind of a surface state. Otherwise, the density should have gone just like that, because that is the expected bulk density of state of the gold which is actually coming from the S and p band. So, that is what you were expecting. So, therefore, this is particularly the surface state of the material, but now, you can also clearly see the Fermi level. So, the Fermi level is looking kind of not really like an expected step like function because you would assume that Fermi level is a particular energy so, then I know that basically that when I hit that particular energy, then I should be able to basically just see the energy. So, instead of observing from the theoretical expected step like function because everything below here is actually like the density of state is actually equal to 0 and here the density of state is greater than equal to 0. So, that is basically it. So, therefore, what you would have expected is basically a step like function near the Fermi level, but instead, you see here that there is a kind of smeared density of state or smeared step at the Fermi level.

So, what is it? Why do we see that? That is actually something I have also told you previously that everything is controlled by something called as Fermi Dirac statistics and this is basically a statistic that Fermi Dirac statistics. so, this is something that controls basically the density of state. With this, we can basically clearly understand the density of state of the material as a function of temperature. Otherwise, it is not possible. So, normally the Fermi Dirac function is actually a function of energy and temperature. So, this is written like this 1 by e raised to energy – E f by k bT + 1. So, this is basically the Fermi Dirac function and this function if you would plot as a function of energy. So, this is let us say energy again so, the same electron energy and if I would mark here as the Fermi level so, let us say like this is the Fermi level and this is the energy axis.

Then at 0 Kelvin, you can definitely plug here the temperature is actually equal to 0, then you would find that everything is just going to look like this. So, the density would just be like a step function. But as soon as you have a temperature dependence like when the temperature is increasing, then what happens is that there is actually a smearing out of the function and the function would start to appear like this. So, the function started to appear like this. And if you increase the temperature further, then what happens is that the function would smear out much bigger and then there will be an appearance like that. So, the smearing is quite symmetric with respect to the Fermi level, but that smearing is actually something which is due to the fact that you basically see that the Fermi level that we are measuring here is not looking really like a step function. It is looking like a smeared Fermi function. So, now, you can see that the experiment is done at 55 Kelvin as you have seen in the previous slide and you see clearly that there is a smearing out and that is because the density of state is always a function of temperature. The density of state is not a function of temperature, but you have to take the density of state and the Fermi Dirac statistics to completely understand the density of state or the electronic structure of the material. And due to that fact you basically see that there is a smearing out of the density near the Fermi energy. So, this is a truly therefore, a function that is dependent on the energy of the electron and the temperature. So, normally the density of state as you measure has no temperature dependence, but the Fermi Dirac statistics controls basically how the electron population or the whole population within the material. So, this actually indicates that even about the Fermi level so, this actually known as hot electrons. It is actually due to the fact that only when you increase the temperature, electrons are also populated in the conduction band and that the valence band will start to get empty a little bit. So, this is what the Fermi Dirac statistics does to it and that is the reason why we see this.

Well in the next class, we will look at a few more examples and application of ultra violet photo-electron spectroscopy and with this, I would like to conclude the lecture. Thank you.