

Ángel Rodríguez Fernández

## Summer Student Programme Report

# HAXPES



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### Abstract:

During these last 7 weeks I have been working with the group that is Assembly and Commissioning the Hard X-ray Photoelectrons Spectroscopy system in the beamline 09 of Petra III. My supervisor has been Sebastian Thiess. In this report describe the work that I have realized as well as everything what I have learned about the spectroscopy.

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## **1.- Introduction.**

This report describes the work I have carried out during my stay as summer student in Hasylab. During these eight weeks, besides attending all the lectures, I have been employed with the group of Wolfgang Drube on a subject in the field of X-ray photoelectron spectroscopy (XPS) at beamline P09 at the Petra III storage ring. My supervisor during all this time has been Sebastian Thiess. With him I have learned about spectroscopy of materials, and I believe that it has been the reading that I have understood better, maybe for the support (books, Internet..) that I have used to understand more on the above mentioned matter.

The time dedicated to my different

work during these eight weeks depended on my availability, if not tape-worm neither morning lectures nor German classes were taking more time to work with my supervisor. As well as also several my dedication. During the first two weeks I devoted myself especially to the reading of texts on XPS and to the construction of the system together with Andrei, postdoc at beamline P09. Later I devoted myself more to the comprehension of the programming language Python, this was due to a break caused by malfunctioning of the detector of the XPS system at which I was employed, the repair of which took at least two weeks, in which it was not possible to be employed at all at the system. During this time my supervisor proposed me to create a program for analysing XPS spectra: that on having introduced the position of a peak in terms of a electron binding energy / kinetic

energy was returning the possible elements and the transition to which they belong.

During the last weeks, after solving the problem, we continue with the construction and adjustment of the system. We place the system in position and began the last adjustments. During this time I had a break of one week, since during this week I performed, at the beamline B1 of Doris III, my exercises week in which I joined a group of 4 students for measuring certain samples with anomalous small-angle S-ray scattering (SAXS). The two last weeks I was helping again my supervisor and I improved the program that I had written. Last Friday I finally measured XPS from to system of three samples, which later I analyzed with the program that I have been developping.

In the following I will summarise everything what I have realized in this time. Later I will give a more detailed explanation on my different tasks during this program.

## **2.- Theory.**

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra high vacuum (UHV) conditions.

XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its "as received" state, or after some treatment, for example: fracturing, cutting or scraping in air or UHV to expose the bulk chemistry, ion beam etching to clean off some of the surface contamination, exposure to heat to study the changes due to heating, exposure to reactive

gases or solutions, exposure to ion beam implant, exposure to ultraviolet light.

- XPS is also known as ESCA, an abbreviation for Electron Spectroscopy for Chemical Analysis.
- XPS detects all elements with an atomic number ( $Z$ ) of 3 (lithium) and above. It can not detect hydrogen ( $Z = 1$ ) or helium ( $Z = 2$ ).
- Detection limits for most of the elements are in the parts per thousand range. Detections limits of parts per million (ppm) are possible, but require special conditions: concentration at top surface or very long collection time (overnight).
- XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, etc.

Because the energy of a particular X-ray wavelength is known, the electron binding energy (BE) of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford (1914):

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$$

where  $E_{\text{binding}}$  is the binding energy of the electron,  $E_{\text{photon}}$  is the energy of the X-ray photons being used,  $E_{\text{kinetic}}$  is the kinetic energy of the electron as measured by the instrument and  $\phi$  is the work function of the spectrometer (not the material).

A typical XPS spectrum is a plot of the number of electrons detected versus the binding energy of the electrons detected. Each element produces a characteristic set of XPS peaks at characteristic binding energy values that directly identify each element that exist in or on the surface of the material being analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The number of detected electrons in each of the characteristic peaks is directly related to

the amount of element within the area irradiated.

It is important to note that XPS detects only those electrons that have actually escaped into the vacuum of the instrument. The photo-emitted electrons that have escaped into the vacuum of the instrument are those that originated from within the top 10 to 12 nm of the material. All of the deeper photo-emitted electrons, which were generated as the X-rays penetrated 1–5 micrometers of the material, are either recaptured or trapped in various excited states within the material. For most applications, it is, in effect, a non-destructive technique that measures the surface chemistry of any material.

Not only there are studied the electrons due to the excitation provoked by the incidental bundle. But also secondary electrons named Auger can arise. These electrons are owed to one series of reactions that take place on the first electron having been excited, when a hollow stays inside the structure, one can give that an electron of a top cap goes down to the above mentioned position to minimize its energy, on this process having been realized there is emitted a photon that can be observed as fluorescence or is able to excite one second electron of the material, this with the above mentioned energy it was escaping of the atom and it will be gathered by the detector.

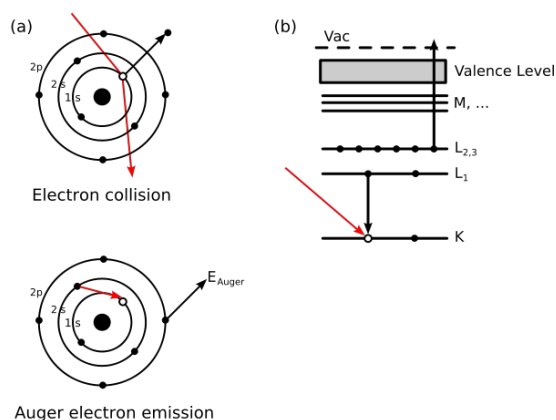


Image 2.1.- Possible effects that take place in the electronic structure of an atom when a photon

affects.

An emitted electron will have a kinetic energy of:

$$E_{kin} = E_{Core\ State} - E_B - E_C'$$

where  $E_{Core\ State}$ ,  $E_B$ ,  $E_C'$  are respectively the core level, first outer shell, and second outer shell electron energies, measured from the vacuum level. The apostrophe (tic) denotes a slight modification to the binding energy of the outer shell electrons due to the ionized nature of the atom; often however, this energy modification is ignored in order to ease calculations. Since orbital energies are unique to an atom of a specific element, analysis of the ejected electrons can yield information about the chemical composition of a surface.

### 3.- Work at beamline 09 in Petra III.

#### 3.1.- Assambly of the Hard X-Ray Photoemission Spectroscopy (HAXPES) system.

From the first day on I joined my working group, I had made diverse tasks. During the first two weeks I installed diverse devices at the beamline 09 of Petra III., with is currently beging prepared to become operational soon. The equipment available comprises a hemispherical photoelectron analyser, a UHV chamber and an W- ray source. Beginning for a computer to control the power supplies and the detector of the spectrometer up to the installation of a transfer system for the introduction of the samples, passing for diverse types of small devices like Shutters or mounting a source of radiation with changeable anode of Cu and Mg.

Of among these tasks, which more time I take to myself was the installation of a small shutter. The shutter was a device that must place between the sample and the lens of the

detector without interfering with any other piece of equipment placed inside the ultra high vacuum (UHV) chamber. The shutter carried slit system designed to perform an angular calibration of the spectrometer. The slits define ranges of angles of incidence for the photoelectrons. These packages of electrons are related to the reciprocal space of the sample, with what doing the analysis with the help of the shutter we are obtaining information it brings over of the internal structure of the sample.

Another installation was that of the Cu and Mg anode X-ray source. This one needed a water cooling system, a whole of 4 connections (two entered and two gone out), placed in the head and the body of the source.

One of the days that was more exciting for my, was in that we move the anti-vibratory table to hutch-3 of the line 09. This anti-vibratory table was divided in two pieces of great weight that it was necessary to displace for quite Petra III by means of the utilization of the derrick of the installation. After realizing this transport, we prepared to place the UHV equipment on the table, for it we had to divide it in two parts, since but it was traversing the risk of splitting the detector with the UHV chamber. With the help of the internal derrick of the hatch, we raise every part and we arranged it on the table, aligning and fitting every part on the table with supreme care. As soon as both parts, cavity and detector, were placed well on the table, we joined them together and later we moved the table to the ideal position for the installation of the beamline where will guide the photon beam coming from the synchrotron.

Later, we reinstall all the circuits of cooling, pumping and electronics to control the sources. From this moment we begin to do measures of control to know if everything was continuing in order. I returned to try to install the shutter with slits but due to a problem with a manipulator that was going incorporated we

had to withdraw it and installed it to a later time.

Finally, my last contribution to the system, was the installation of the magnetic transfer rods for the introduction and extraction of the samples to measuring. This installation was realized on September 3, and with it we began the study of a series of samples which we had. These three samples belonged to my supervisor, and he had already been measured in other equipments, with what we were prepared to know if the system was working correctly. Unfortunately only we were capable of using the Mg anode, since the photoelectron CCD detector was not ready for detecting photoelectrons with high kinetic energies excited by radiation from the Cu anode, on not having been able to use the system with alone Mg were capable of doing spectroscopy to low energies.

### **3.2.- XPS measurements.**

During the 3rd and 4th of September we recorded data with the system of spectroscopy with Mg anode, this indicates that the energies of excitation that we use were low, since the Cu is not sufficient to excite the atoms in high energies.

The first sample that we studied, a fluorescent crystal, we realized it study to calibrate the system like already I have mentioned, but we also used these measures to realize a study of it composition. In the crystal we were supposed to find Y, O, Al and Ce. The study of other samples was only in order to see the material that were in the spectra. Both samples have the same composition but, since one will see in the spectra, the disposition and the deep of the layers were not the same with what we could have different results.

There was studied a whole of three samples. It was giving priority to a crystal of unknown chemical composition doped in such a way that it had a tonality in the middle of

yellow and green. The study of this sample also had the purpose of seeing with the fluorescence of the above mentioned sample the X-ray beam position in order to help aligning the sample which they were doing impress the X-rays and of this form to calibrate the position on that it is necessary to place the samples. Other two samples were thin multilayers of different (unknown) chemical composition deposited onto Si single crystal substrates on which certain elements grew bolder.

During the get of data, several repetitions were realized, since in the experimental system the instantaneous average is realized by each of the repetitions. This mitigates the noise in the spectra. These values were saved in a file that afterwards is the agreement. In certain zones, where the peaks are not observed correctly in the scale to which the spectrum is done, particular studies are realized to improve the resolution, this realizes also in zones where, for the composition that we hoped has the sample, it is possible that there are double peaks.

Once realized the measures to work with them is indispensable to import the data. We did it in files with the extension ".txt".

## **4.- Data analysis: Programming.**

Along my stay at HASYLAB being employed with my supervisor, I have dedicated most of the time to the programming of elements capable of 09 of Petra III helping the future users of the Beamline. Of this effort there have gone out 4 programs capable of giving the first idea to the possible elements which the sample could contain that he will study with the experimental HAXPES's system.

### **4.1.- Python, learning a new**

### **language.**

Since the whole beginning is the most difficult thing and even knowing other languages of programming to begin to write code in Python, for that one that does not know it, Python is the official language of Petra III due to being a free and very comfortable language (as soon as one begins to know it different ways), it turned out to be to me hard enough. First I studied held up the manuals that I was in the official pages, and later, began to wander for the forums observing like the people were employed at Python with real examples. Of these long days sailing along the forums there arose four programs that later I detail.

### **4.2.- The program PeakAnalyzer.**

It was the first one of the four. Its task is simple, the user introduces the kinetic energy at which one XPS/Auger peak occurs and the program returns the possible elements that have transitions of the first electrons with this value of energy and also the possible elements that have peaks from Auger's electrons of importance in this value of kinetic energy. The most arduous of this program was to construct the tables that it uses to compare the kinetic energy introduced with that of every element, since the tables include all the elements between the Li and U. The tables contain the energy, the element and the transition for every element, both for primary electrons and for electrons Auger. These values were acquired of the sources:

- Table of binding energy : [http://xdb.lbl.gov/Section1/Sec\\_1-1.html](http://xdb.lbl.gov/Section1/Sec_1-1.html)
- Table of Auger's electrons: F. P. LARKINS: "Semiempirical Auger-Electron Energies for Elements  $10 < Z < 100$ ", Clayton (Australia), Atomic data and nuclear data tables 20, 311-387 (1977)

This program is designed to work with information proceeding from any spectrometer, due to the fact that it has two special commands related to the energy of the incidental beam  $E_0$  and the work function  $W$ . These two variables are stored in a few files in such a way that always it reminds the used one during the last session.

On having returned the values, which it prints for screen, not only it gives the most nearby value, but also it print the adjacent values on the above mentioned value, in order that the user could be able select the one that seems to him to be more correct or awaited, since there are times in which if it is a question of samples as insulating, due to the photo current ionization of the sample on having lost electrons, the values of kinetic energy are not the ones tabulated for free atoms: Charging effects will lead to spectra being shifted on the energy axis.

#### **4.3.- SpecBreak, PeaksAnalyzer and PeakGenerator.**

The following programs I realized it after having the information obtained during the calibration of three samples, the purpose of these programs is to help the users, facilitating the treatment of the information to them.

The first one is SpecBreak this program divides the file obtained of the program that controls the detector. In order that it works adequately it is necessary to export the values obtained with the extension .xy and later change this extension to .txt.

Once the program reads the file is capable of counting the number of spectra that it has and the length of each one, in addition it extracts the work function and the beam energy which it was employed at each of the spectra. Once it has all this information generates files in different folders that contain

the energy of every spectrum, the intensity of every spectrum, the beam energy, the work function and what turns out to be more important a file with the energy and the intensity that can be read by a support as Origin and with it fit all the peaks of every spectrum. As soon as we have the values of the energy of the peaks and the intensity we can use PeakAnalyzer.

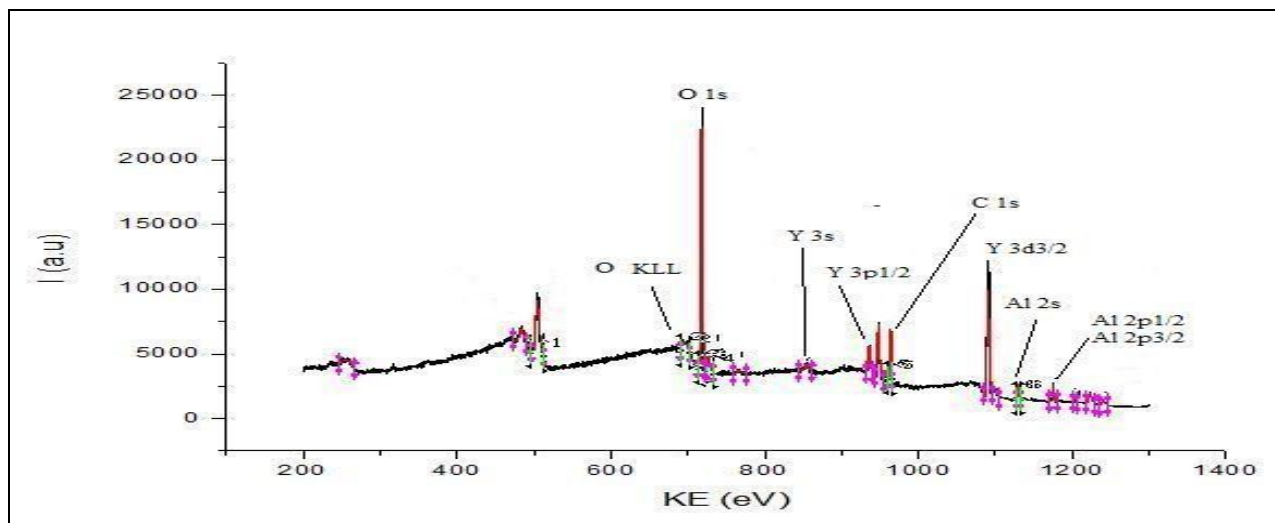
But since it is very tired one introduces to one the peaks, I decided to do a program that was constructing a list with the energies (PeakGenerator) and later other one who was reading these lists (PeaksAnalyzer). The functioning of the first one is a very simple alone keeper in a list the values that the user introduces for the keyboard and finally it guards them in a file determined by the name that the user gives to the sample to which the peaks belong.

In case of the second one it is a basic improvement of the first program that instead of the keeper stamps for screen the information on a ready variable and finally it introduces the data in a file, this file is easy to concern a program as it can be Excel, and from there is necessary to compare the values of the elements obtained with the awaited ones.

### **5.- Study of the unknown samples.**

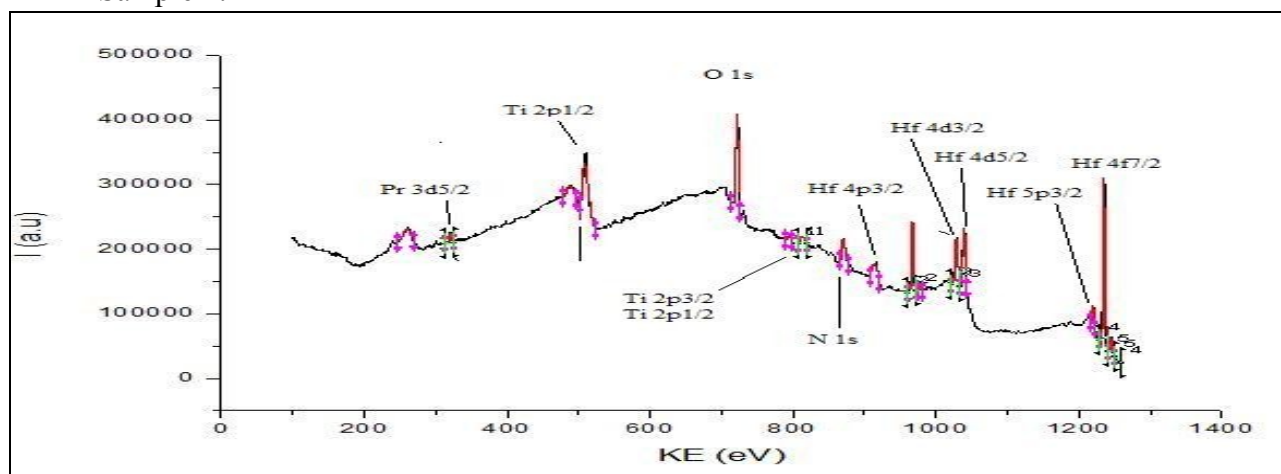
The data recorder from the samples studied with the experimental equipment were treated by the written programs, in them there were detected the elements that were looked but not always of the wished form. Later I show the spectra that were obtained by the opposing peaks:

Fluorescence sample:



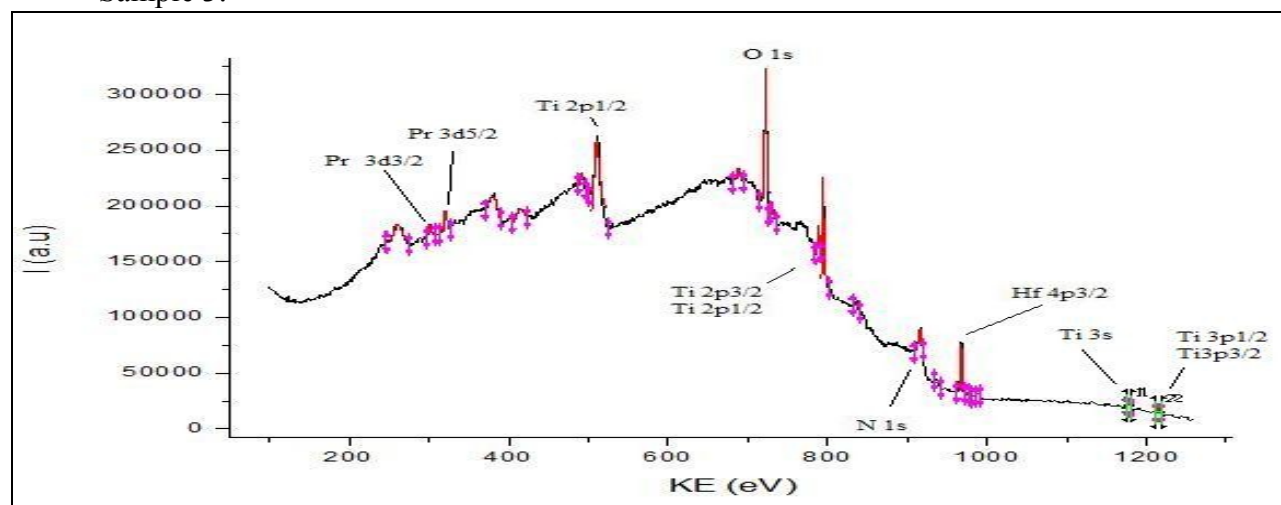
Figs.1: XPS survey spectrum recorded from the fluorescence crystal at an exciting photon energy of 1253 eV.

Sample 2:



Figs.2: XPS survey spectrum recorded from the multilayer sample 2 at an exciting photon energy of 1253 eV.

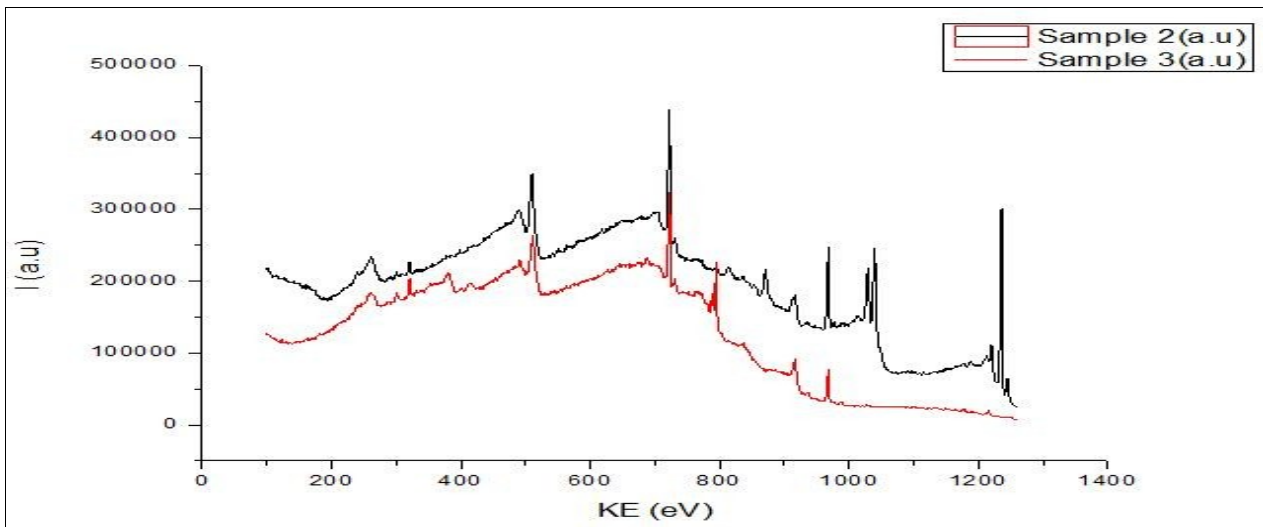
Sample 3:



Figs.3: XPS survey spectrum recorded from the multilayer sample 3 at an exciting photon energy of 1253 eV.

Comparison sample 2 vs sample 3:





Figs.4: XPS survey spectrum recorded from the multilayer sample 2 and the multilayer sample 3 to compare their peaks that are seen.

In the first figure (Fig.1) we see the spectrum related to the fluorescent crystal. We can observe peaks of Al, Y and O, but from Ce. This should be because this element is inside the structure as dope element. The concentration of this element is so low that it generates small peaks and due to its condition, the Ce suffers different interactions depending on the position where it has placed, with what its chemical interaction will be different and with it the energy that the electrons suffer, this generates peaks furthermore small and elongated peaks.

In case of the sample 2 (Fig 2) we can observe like there are detected all the elements that were waited. These are Ti, Hf, O and N, since the layers are of Hafnium oxide and titanium nitride. Though the Silicon is not observed. On the other hand, there are peaks of this Pr do not explain unless you know that the company that realized the samples had studied the same structures with Pr instead of Hf.

In case of the sample 3 (Fig 3) it is possible to observe that Hf's peaks disappear. This can be due to the fact that there is no Hf or to that the Hf is now in a more deep zone where the resolution of our system does not allow to work.

In the figure 4 we can compare the spectra of the multilayer samples. We can observe how in sample 3 the peaks from Ti are more higher and the peaks from Hf have almost banish. We can explain that since the point that the layers have been change between them so in sample 3 we have the layer of Ti upper that Hf one. And in the sample 2 what we see is high peaks from Hf and small peaks from Ti, and this make sense what we have argue before.

During the get of data we could estimate since no Si's peak were seen, for what we can venture that the large caps were overcoming in it set than 100 Å of thickness. This is due to the fact that to the energy at which we are employed, the photons only enter the material, in a sufficient quantity as to provide sign to the detector with the excited electrons, less the above mentioned distance.

## **6.- Summary.**

In the study of the samples it was shown that the programme proves useful to identify XPS and Auger electron signals in experimentally recorded spectra. However, the programme has also some limitations, the occurrence of chemical shifts has not been

taken into consideration so far. So to have the programme working correctly every user should improve in the table the energy of the peaks he is waiting to be in the sample.

Furthermore, the spectra could be displayed by the programme in order to possible to see as the program not this one completely finished, this is due to the existence of chemical shift that generate diversions in the values of the kinetic energies of the peaks. This estimates all the graphs since the elements that my supervisor knew about their existence had light diversions in their values in such a way that for the program it was turning out to be not too trivial to find the above mentioned elements, but it was meeting as more possible different elements on energies of binding more nearby to found in the spectra.

In future work, the programme could be extended such that the programme will be ready to al al the work without using other external support like Origin to find the peaks.

Finally I want to thanks to DESY and to my supervisor for been so good with me, I have learn a lot of them, and It has been one of my greatest time. Now is really difficult to return to our place one you have seen how is the life in one facility as DESY.

THANKS TO ALL THE PEOPLE THAT  
WORKS IN DESY.