
Appearance Potential Spectroscopy

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Appearance Potential Spectroscopy

1. Introduction

Various kinds of spectroscopic techniques are available for measuring the binding energies of core level electrons. X-Ray Photoelectron Spectroscopy is one of the modern technique in which a soft X-Ray excites the core electron and whose energy spectrum measured. A related technique is called Appearance Potential Spectroscopy (APS) was developed in the 1970's by R.L.Park and J.E Houston. This technique is based on the principle of measuring the threshold energy for the creation of inner shell excited atom. Informations about the binding energies of electrons in the core levels of surface atoms are provided by the threshold. In Appearance Potential Spectroscopy measuring the intensity of Auger or X-Ray emission as a function of the excitation threshold (E_p) can be determined using appearance potential spectroscopy. This technique also gives information about the unoccupied states of a sample. In this respect it can be termed as an inverse Auger electron Spectroscopy in which the density of occupied states are mapped. APS can be used as a tool for the investigation of electronic structure of solid surfaces. In APS we are analysing the energy of the exciting particle which is recorded and not the energy of the decay of the excited states.

2. *Theory of APS*

When a surface of a material is bombarded with an electron of energy (E_p) in the range 50-1000 eV, the atoms can be excited by the ejection of core electrons and can produce a core hole. The excited atom may relax in many ways. One way is, when an X-ray of characteristic wavelength can be emitted from an excited atom when an outer-shell (e.g. L) electron jumps in to fill an inner-shell (e.g. K) vacancy.

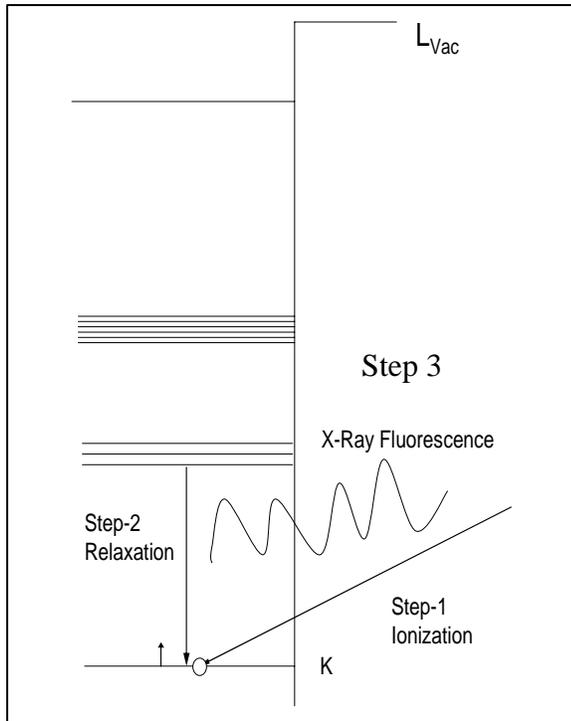


Fig: 1 – Emission of X-Ray from core level excited atom

The other method by which the excited atom can de excite by the production of Auger electron. If an inner shell electron is knocked out from an atom, the resulting inner-shell vacancy can be filled by an outer-shell electron with simultaneous emission of an electron called Auger electron. The kinetic energy of the emitted auger electron is given by

$$E_A = (E_1 - E_2) - E_3$$

E_1 =energy of atom with inner-shell vacancy,
 E_2 =energy of atom with outer-shell vacancy, and
 E_3 = kinetic energy of emitted (Auger) electron.

The emission of an auger electron is depicted in fig: 2.

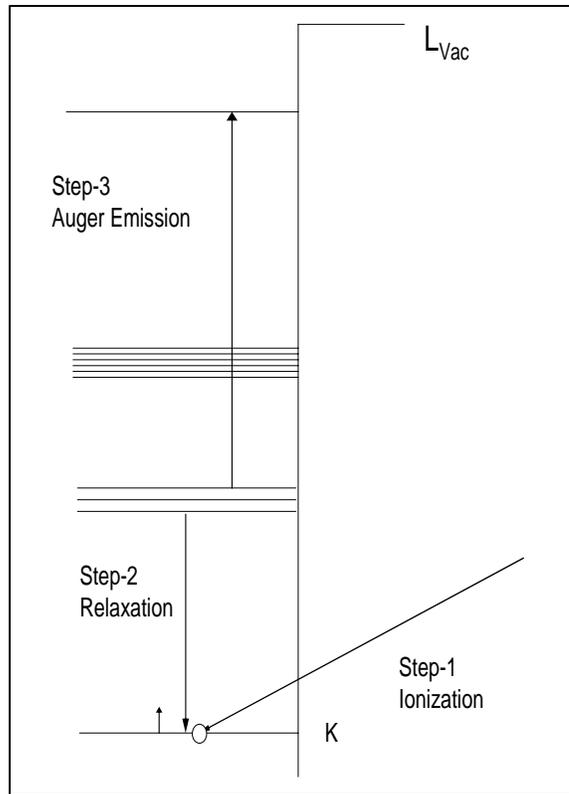


Fig : 2 – Auger emission from core level excited atom

The fluorescence yield w for a particular shell will be much less than unity for this primary energy ranges (50-1000 e V). Hence no. of X-Rays emitted per excited atom will be very less compared to the Auger electron. Relatively large no. of Auger electrons are emitted with energies characteristic of the relaxing atom may be analysed to determine the chemical constituents present in the sample surface. The characteristic X-Ray may also be used to identify the surface constituents but with less sensitivity due to small w .

APS is so called because one determines the incident energy at which the relaxation products of a certain core hole appears. The short penetration depths of electrons used makes APS highly surface sensitive.

3. Different Kinds of Appearance Potential spectroscopies

Appearance Potential Spectroscopy can be mainly classified into three. They are

- (1) Soft X-Ray Appearance Potential Spectroscopy (**SXAPS**)
- (2) Auger Electron Appearance Potential Spectroscopy (**AEAPS**)
- (3) Disappearance Potential Spectroscopy (**DAPS**)

3.1 Soft X-Ray Appearance Potential Spectroscopy (SXAPS)

This is also known as Electron excited X-ray Appearance Potential Spectroscopy (*EXAPS*). Here the core holes are generated by an electron beam incident on the surface. Here we gradually increase the energy of the incident beam. When the threshold for the production of a core hole by electron excitation or ionization is reached, soft X-ray fluorescence characteristic of the energy level concerned will suddenly appear. An electron beam having energy in the range 100-2000 eV and beam diameter 10 mm is incident approximately normal to surface of the sample. The emitted soft X-Ray photons during the relaxation are detected. The total X-Ray flux is recorded. The derivative of the soft-X Ray fluorescence is plotted as a function of the potential of incident beam. The appearance potentials correspond to the threshold energies at which core electrons can be excited to unoccupied states. The change of slope depends on the density of unoccupied states and surface concentration. Since the penetration power of electrons having energy less than 1k eV is small, SXAPS is a very surface sensitive technique. Fig: 3 represent the complete schematic diagram of a typical soft X-Ray Appearance Potential Spectrometer.

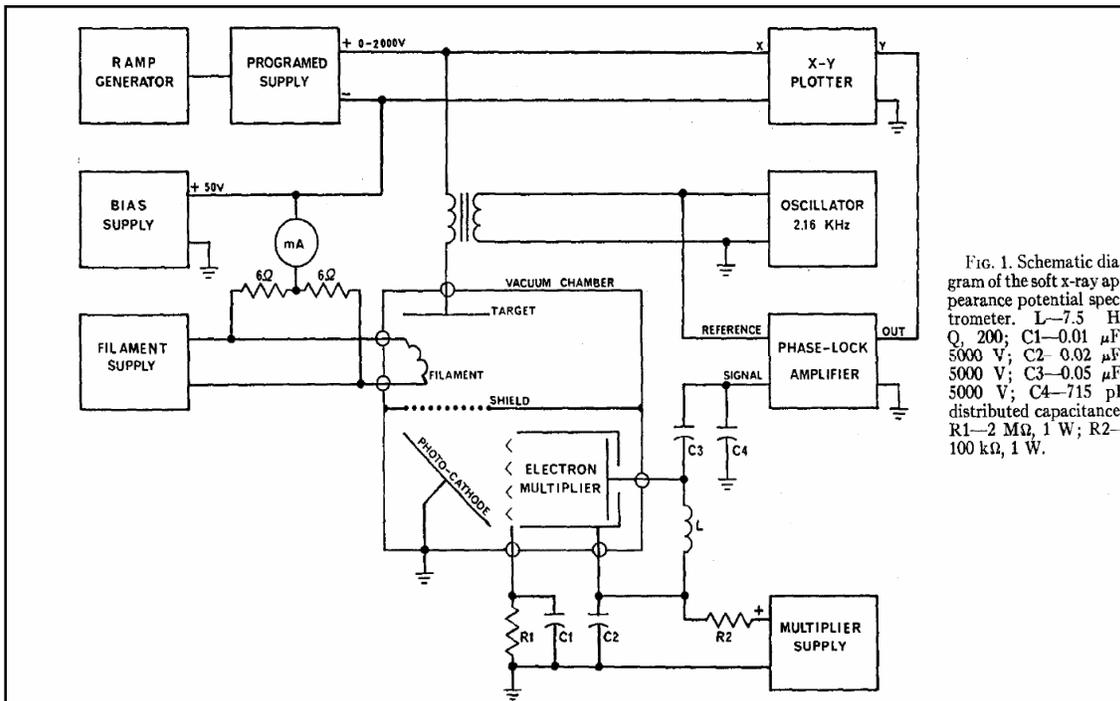


Fig:3- Schematic diagram of a typical Soft X-Ray Appearance Potential Spectrometer. Ref : *R.L.Park ,J.E.Houston &D.G.Schreiner, Rev. of Sci. Instru, 41,12,1810,1970*

The spectrometer consists of a vacuum diode and a photomultiplier. A thermionically emitted electron from a W filament is allowed to fall on the target. The soft X-Ray photons produced at the target strikes the nickel cathode biased to reject the electron. Electron multiplier amplifies that photoelectron current produced. The target potential is programmed with a linear ramp in the range from 0 to 2000 V. To get the derivative of the fluorescence produced, a small oscillation is superimposed on the target potential. The signal obtained is proportional to the multiplier current as a function of target potential. A typical Soft X-Ray appearance Spectrum of out gassed poly crystalline iron target is shown in the Fig: 4a. The sharp peak at 704 and 716V corresponds to the excitation energy of electron in Fe L_3 and L_2 levels to Fermi levels respectively. Surface contaminants like boron and carbon show much more complex spectrum

than the metal substrate. Fig: 4b.represents the carbon K shell spectrum from a contaminated Ni surface.

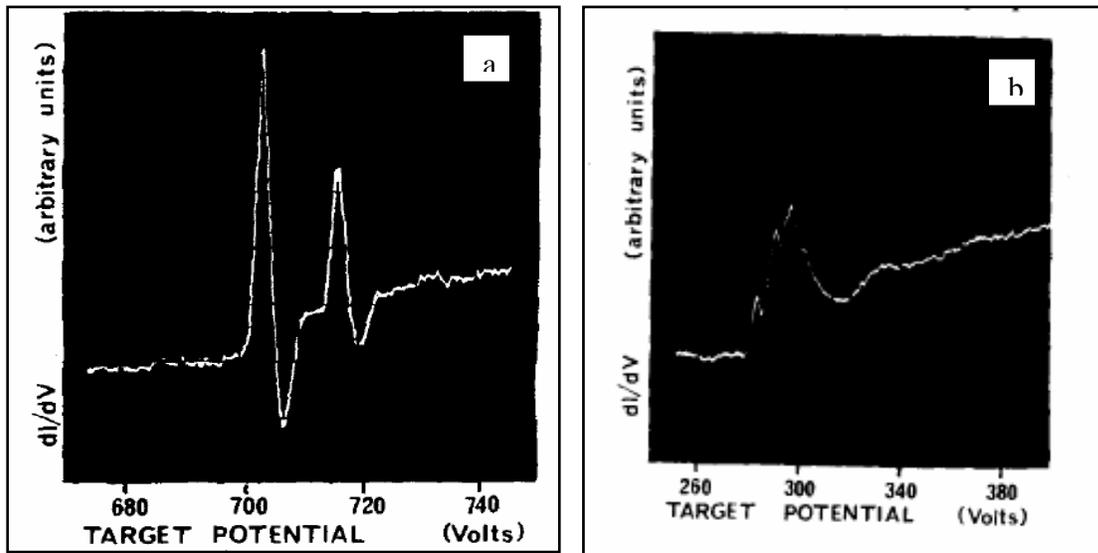


Fig : 4- (a) The Fe, L₃ and L₂ spectrum from a polycrystalline Fe target (b) The carbon K shell spectrum from a contaminated Ni surface. Ref : *R.LPark ,J.E Houston &D.G .Schreiner, Rev. of Sci. Instru, 41,12,1810,1970*

3.2 Auger-electron appearance potential spectroscopy (AEAPS)

This is also known as Electron-Excited Auger-Electron Appearance Potential Spectroscopy (*EAAPS*) or Incident Energy Modulation Method Spectroscopy (*IEMM*). As in *SXAPS*, core holes are produced by an electron beam incident on the surface. When the energy of this electron beam is increased to the threshold for producing a core hole by electron excitation or ionization, a sudden 'appearance' or increase in both the X-ray fluorescence yield and secondary electron current will occur. These soft X-ray photons and Auger electrons can produce further secondary electrons. So the secondary electron current is greater after the threshold than before it.

An electron beam having energy in the range 100-2000 e V and beam diameter 10 mm is incident approximately normal to surface of the sample. The emitted secondary auger electrons during the relaxation are detected. The Auger electron current is recorded. The second derivative of the auger electron current is plotted as a function of the potential of incident beam. The appearance potentials correspond to the threshold energies at which core electrons can be excited to unoccupied states.

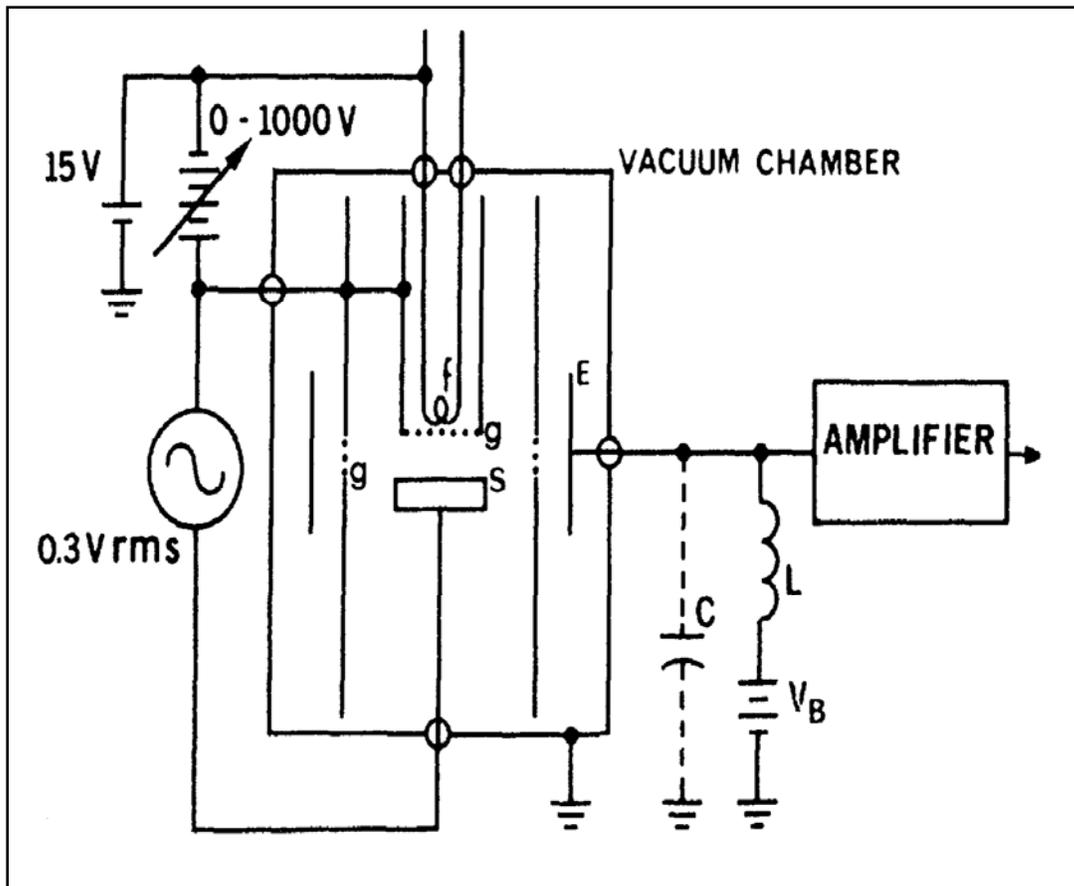


Fig: 5 -The schematic diagram of AEAP Spectrometer. Ref : R..L Park, J.E Houston *Phy. Rev. B* , 5,10,1972

Fig: 5 is the schematic diagram of AEAP Spectrometer. In the figure, "f" is a W filament and grid g maintains a field free region around the sample S. The secondary electrons emitted are collected by the electrode E. To get the derivative of collector current, a small oscillation is superimposed on the sample

potential. The Bias voltage V_n (~200V) is reversed while we are measuring the soft- X-Ray. Figure 6 shows the AEAP spectrum of stainless steel alloy. From the spectrum we can analyse the various elements present in the alloy using their characteristic peaks. The main advantage of threshold spectroscopies are the smaller no of lines and the more sharpness of the lines compared to AES. In the spectrum given below, it is not clear in AES spectrum whether Mn is present or not. But in AEAPS we can easily identify the presence of Mn. In AES it is difficult to identify elements with concentrations less than 10 % which is easy in the case of AEAPS.

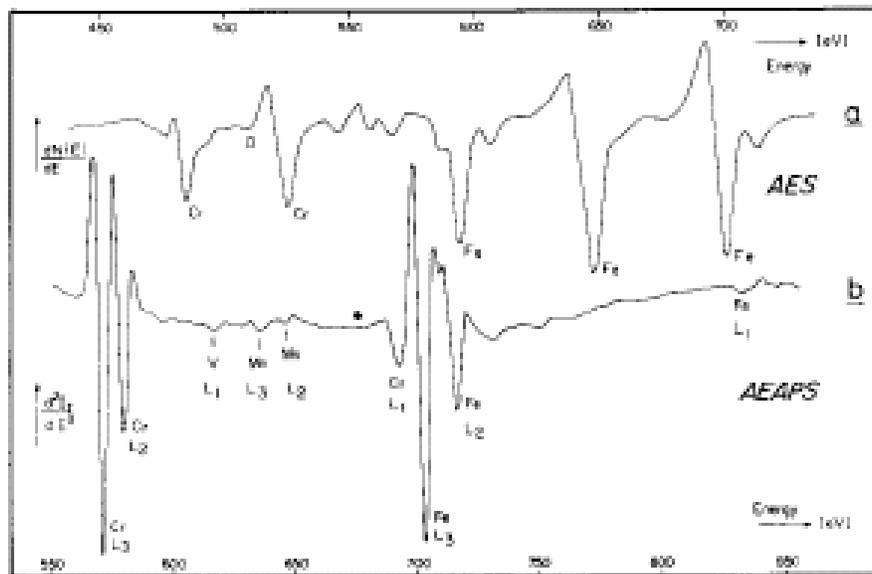


Fig: 6 Typical AEPS Spectrum of stainless steel alloy containing Fe(63.7%),Cr(22%),Ni(12.8%),&Mn(1.45). (a) AES (b) AEAPS Ref: *J.Krischner,W.Losch J.Vac. Sci.Technol,14,5,1977*

3.3 Disappearance Potential Spectroscopy (DAPS)

As with SXAPS and AEAPS core holes are created by a variable energy electron beam. Whenever the primary electron energy slightly exceeds the threshold energy, an incident electron can transmit its energy to the core electron so that both electrons move to the states above the Fermi level E_F . At this threshold of excitation the electrons in the primary beam, which create the core hole, **disappear** from the beam. In DAPS it is the attenuation of the primary

beam which is studied. As secondary processes do not contribute to this attenuation DAPS observes the excitation directly without any interference from the decay processes. The attenuation of the primary beam is small (~ 1 in 10^3). Using DAPS; one can find additional information on the chemical bond origin and on the density of unoccupied states in the surface region.

An electron beam having energy in the range 50-2000 e V and beam diameter 2-10 mm is incident approximately normal to surface of the sample. The Attenuation of primary electron beam during the relaxation is detected. A spectrum is plotted between electron current at sample (target current) and primary electron energy (excitation energy). However, DAPS is not widely used now, and there is insufficient number of papers dealing with this technique. This is due to some disadvantages of DAPS. Particularly, the DAPS signal intensity significantly depends on the nature and chemical state of the element being studied. Also the attendant diffraction background will hinder the desired spectra features. However, sensitivity of the DAP spectra features to the origin of surrounding surface species and to the presence of impurities or adsorbed residual gases make the technique very promising for studying adsorption and catalysis

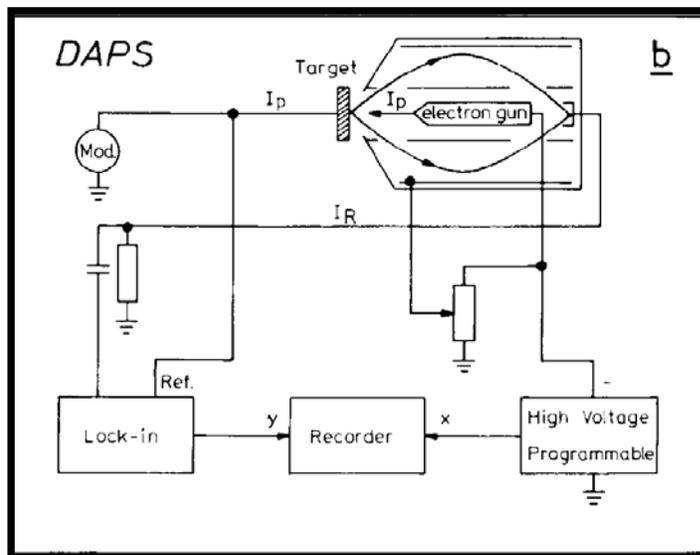


Fig : 7 - Experimental setup of DAPS. Ref: *J.Krischner,W.Losch J.Vac. Sci.Technol,14,5,1977*

The experimental set up is very much similar to the other appearance potential spectroscopies. The only difference is in the analyser. In DAPS the analyser is used to separate the quasielastically scattered electron from secondary and inelastically scattered electrons. In this mode modulation is applied directly to the target. So the electron energy is modulated with respect to the target but not with respect to the analyser. Thus ac component of the multiplier output is a measure of the derivatives of the elastic reflection coefficient as a function of primary energy

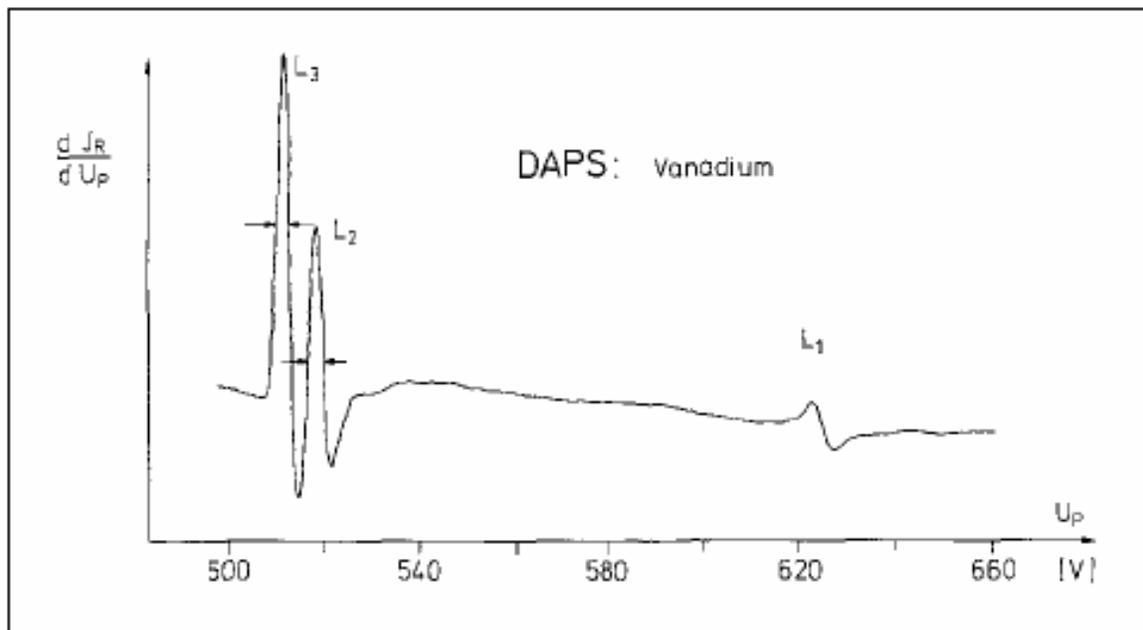


Fig: 8- DAPS-spectrum of clean vanadium in the region of the L-shell. Ref: *J. Kirschner and P. Staib, Appl. Phys. 6, 99--109 (1975)*

4. Some Related techniques

4.1 X-ray excited electron appearance potential spectroscopy (XEAPS)

It is a variable photon energy photoelectron spectroscopy. Monochromatic synchrotron radiation is incident on the surface and the photoelectron yield is recorded as a function of varying frequency of the incident photon. The XEAP spectrum shows distinct threshold peaks for core ionization processes. A synchrotron radiation having energy in the range 100-1000 e V having medium to

low flux. The emitted electrons during the relaxation are detected. The total X-Ray flux is recorded. The spectrum is a plot of Photoelectron current (total yield) vs. photon energy

4.2 Extended (electron) appearance potential fine-structure analysis (EAPFS)

This technique is based on the analysis of the fine structure close to the threshold for the excitation of a core electron by a variable energy electron beam. Thus, in terms of experimental technique EAPFS is similar to AEAPS and DAPS. An electron beam having energy in the range 200-2000 eV is incident approximately normal to surface of the sample. The emitted secondary elastically scattered electrons are detected. The Auger electron current is recorded. The spectrum is drawn with the second derivative of the elastic electron current with respect to the incident electron energy vs. incident electron energy.

5. Summary

In the APS spectrum, from the peak positions elements can be identified. From The threshold used for the excitation we can calculate the Binding Energy. The chemical shift correlates to changes in the chemical bonding and the signal strength is proportional to the Unoccupied Density of States at the Fermi Level. So APS reveals the Total DOS. Being an extremely Surface sensitive tool, it can be used for the investigation of electronic structure of solid surface and surface compositions. Widely used for the study of 3d transition metals and their alloys Compared to AES, it has only low sensitivity towards surface contaminants. So the spectrum will be simple and can be easily interpreted. Compared to other techniques the instrumentation is very simple making it a valuable tool for surface analysis. The sensitivity limit of the technique for the identification of surface impurities is unknown. It is a simpler technique for the determination of core electron binding energies at solid surfaces.

1) Why gamma rays and UV rays are not used in appearance potential spectroscopy?

In this spectroscopy we are not using Gamma rays and UV rays because of the difficulty to produce varying energy gamma or UV radiations. For the production of a core hole, continuously varying excitation energy is needed. In the case of X-ray because of the bremsstrahlung continuous emission we can produce X-Rays of varying energies. So normally this spectroscopy deals with this region.

2) Comparison between XPS and APS

Usually the binding energy measured by XPS and APS differ slightly from each other. Binding energies obtained from APS are usually less than that measured by XPS. Park and Houston attributed this to a higher degree of surface sensitivity for APS. They suggested that reduced coordinations of the surface atoms would lead to a relaxation in their energy states and accordingly to low binding energies observed. The resolution of the instrument was determined from the broadening of the Fermi level. Because of the sharpness of the Fermi level, effects due to the core-level width may be expected to dominate the low energy part of APS threshold and XPS spectrum. But the spectra differ markedly at high energies when final state effects become more significant. The "surface effect" or surface shift as predicted by Park and Houston would give rise to broadening of the observed core level width if sufficient surface atoms contribute. A surface shift would not displace the XPS peak but would broaden it. A similar effect would displace the onset of APS threshold to lower binding energies.

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