# Appearance Potential Spectroscopy

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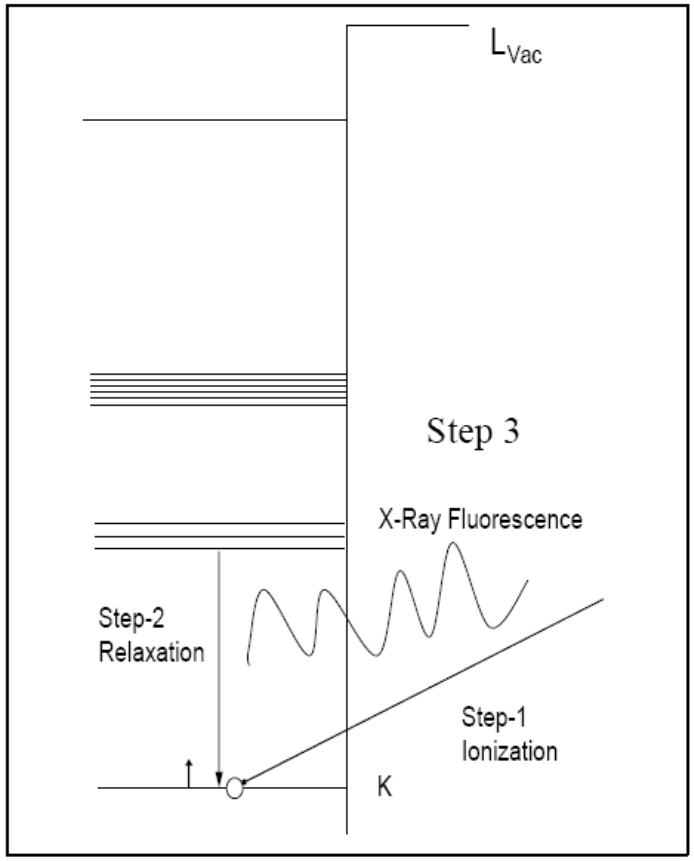
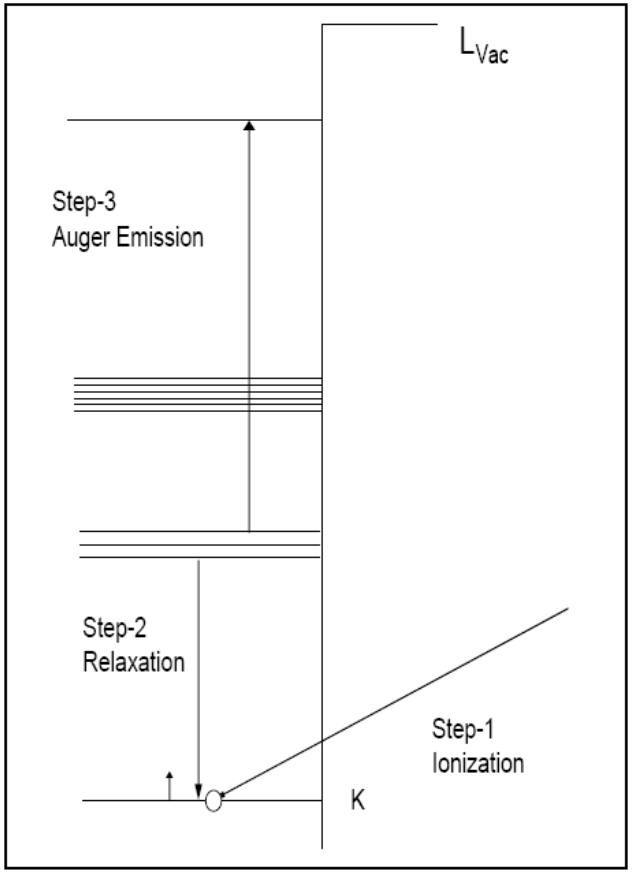
# Introduction

- Various kinds of spectroscopic techniques are available for measuring the binding energies of core level electrons.
- X-Ray Photoelectron Spectroscopy is one of the 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.
- **Appearance energy** (also known as **appearance potential**) is the minimum energy that must be supplied to a gas phase atom or molecule in order to produce an ion.
- 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 (Ep) can be determined using appearance potential spectroscopy.
- This technique also gives information about the unoccupied states of a sample.
- APS can be used as a tool for the investigation of electronic structure of solid surfaces.

# Theory of APS




**ission of X-Ray from core level exited atom**




**Auger emission from core level exited**

# Different Kinds of Appearance Potential spectroscopies

- Appearance Potential Spectroscopy can be mainly classified into thee. They are

(1) Soft X-Ray Appearance Potential Spectroscopy **(SXAPS)**

(2) Auger Electron Appearance Potential Spectroscopy **(AEAPS)**

(3) Disappearance Potential Spectroscopy **(DAPS)**

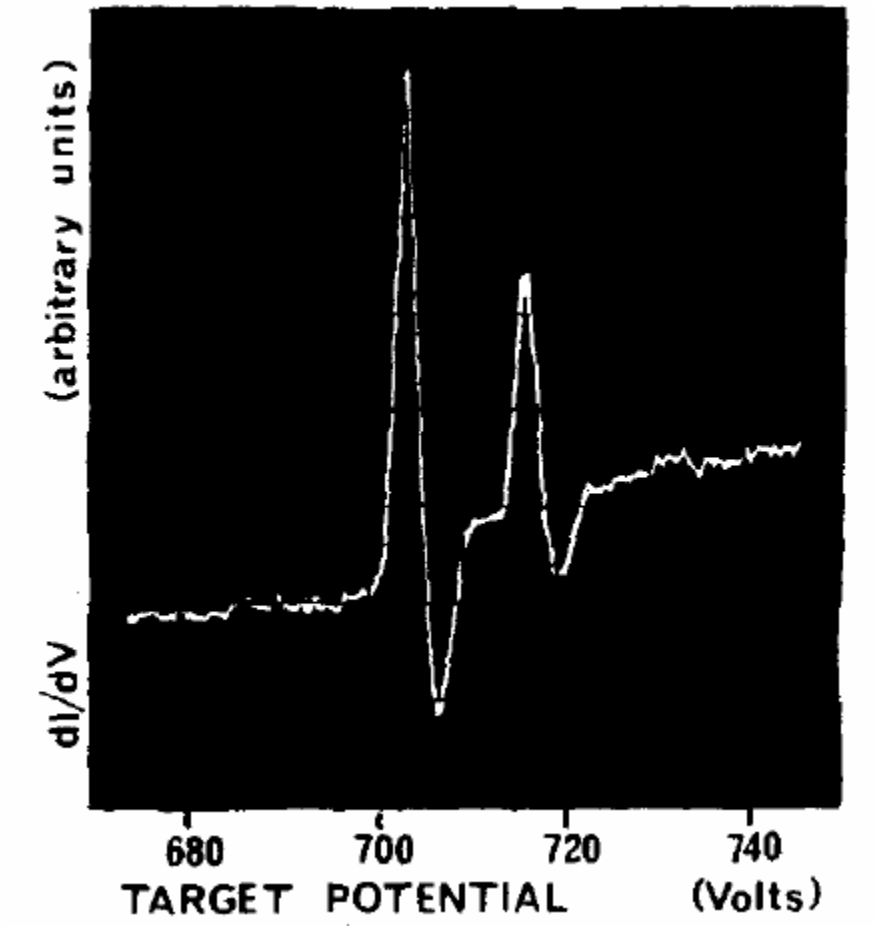
## *Soft X-Ray Appearance Potential Spectroscopy (SXAPS)*

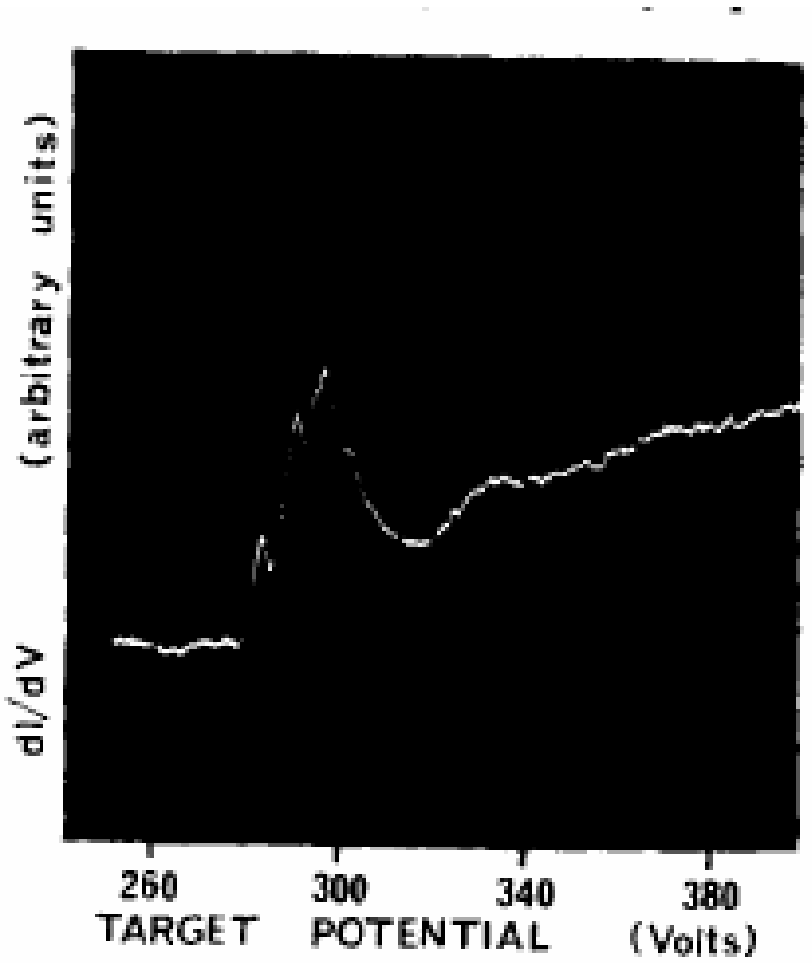
- This is also known as Electron excited X-ray Appearance Potential Spectroscopy (*EXAPS).*
- Here the core holes are generated by an electron beam incident on the surface.
- Here we gradually increase the energy of the incident beam. When the threshold for the production of a core hole by electron excitation or ionization is reached, soft X-ray fluorescence characteristic of the energy level concerned will suddenly appear.
- Incident: Variable energy electrons (100-2000 eV); beam diameter: 10 mm; angle of incidence: approx. normal to surface.

  Detected: Soft X-ray photons. (approx. 50-1000 eV. No X-ray analysis. Total X-ray flux

  Recorded. Angle of exit: almost all photons within the maximum 2π steradian are collected.

  Spectrum: Total X-ray flux vs. primary electron energy (excitation energy).



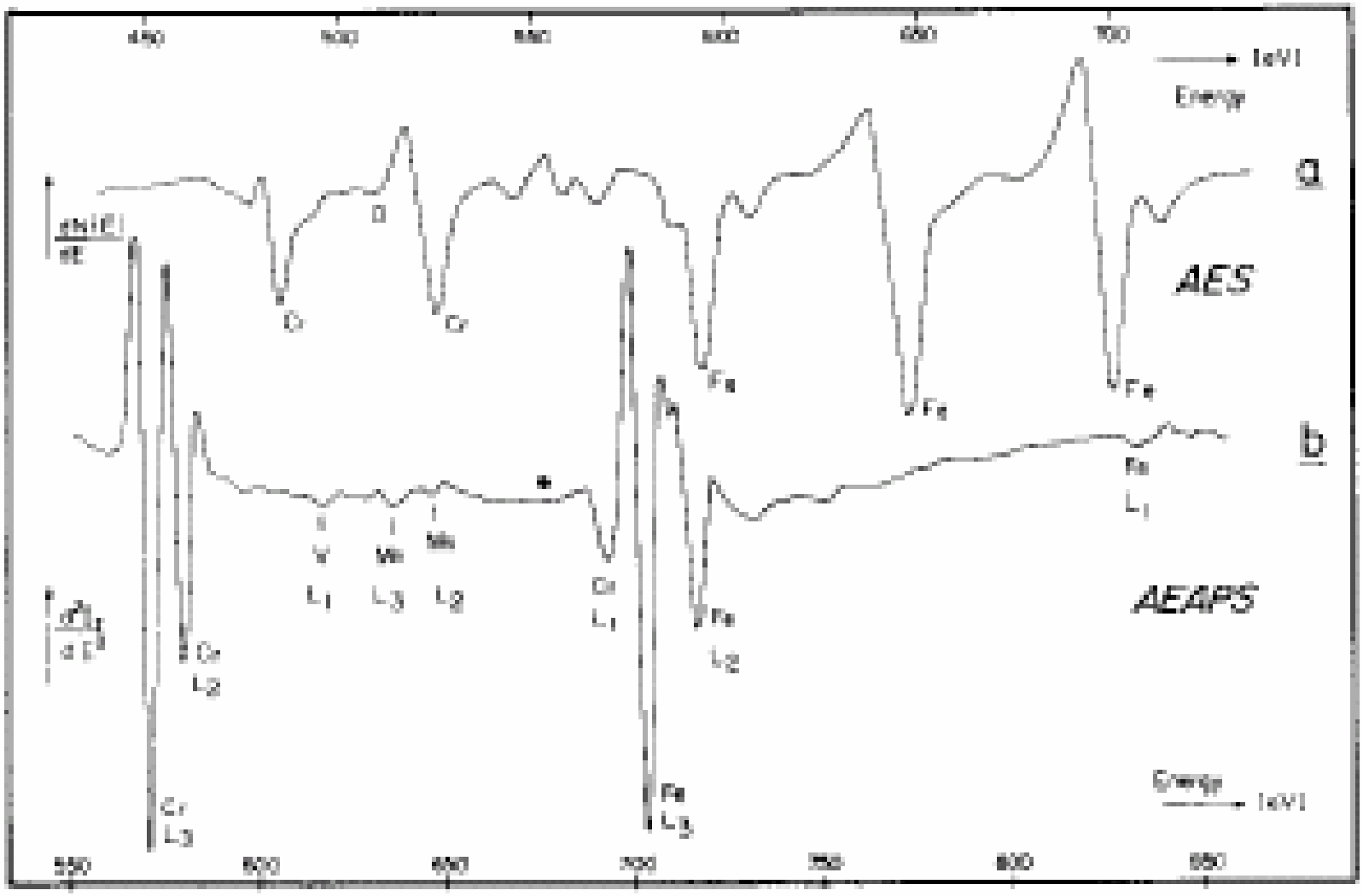

A typical Soft X-Ray appearance Spectrum of polycrystalline Fe target (b) The carbon K shell
spectrum from a contaminated Ni surface.

# 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 occurs.
- 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.
- Incident: Variable energy photons (100-2000 eV); beam diameter: 10 mm; angle of incidence: approx. normal to surface.

  Detected: Secondary Auger electrons (50-1400 eV); angle of exit: usually 2π steradian.

  Spectrum: Auger electron current vs. primary electron energy (excitation energy).




Typical AEPS Spectrum of stainless steel alloycontainingFe(63.7%),Cr(22%),Ni(12.8%),&Mn(1.45). (a) AES (b) AEAPS

# 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 *EF.*
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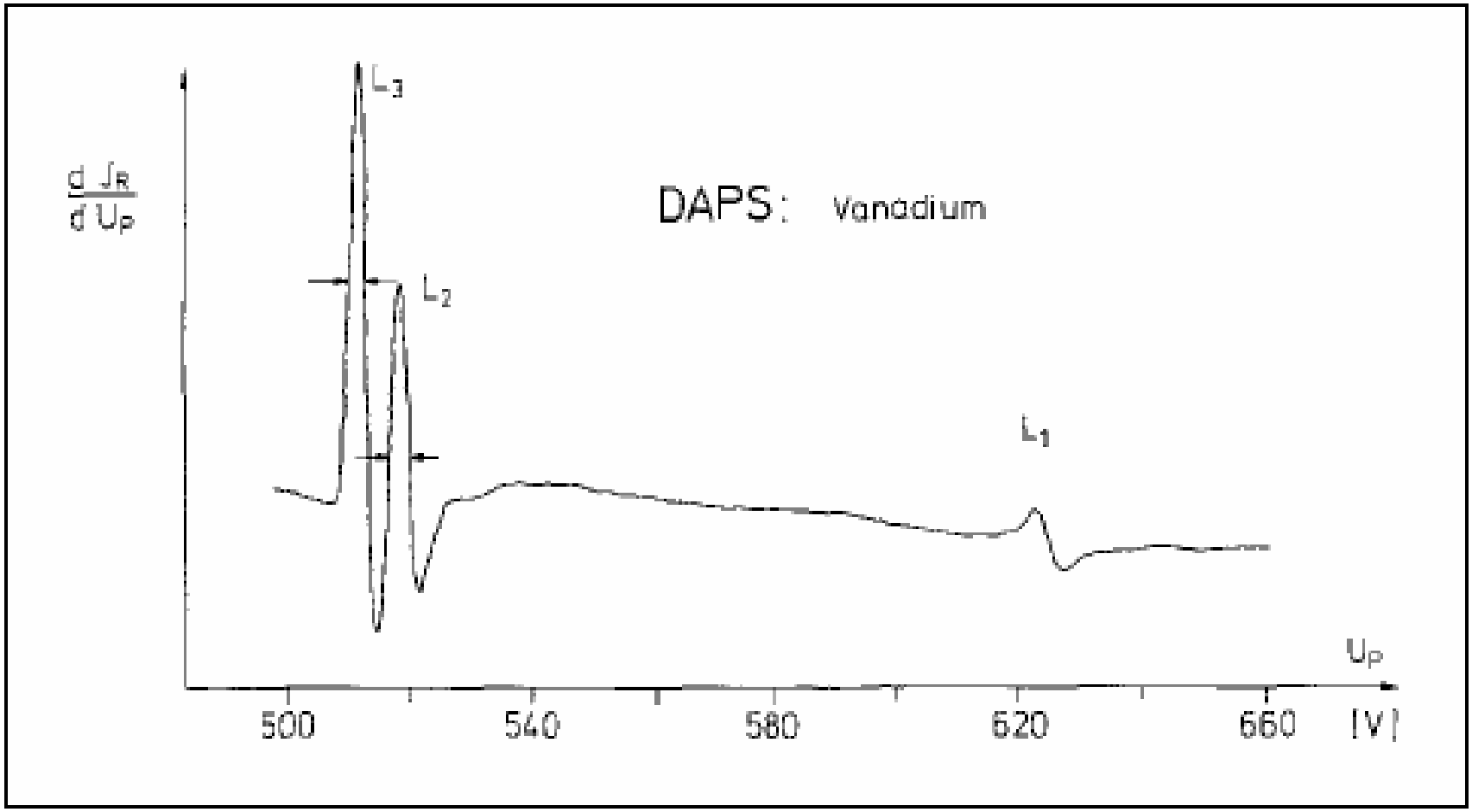
- In DAPS it is the attenuation of the primary beam which is studied.
- As secondary processes do not contribute to this attenuation DAPS observes the excitation directly without any interference from the decay processes.
- Using DAPS; one can find additional information on the chemical bond origin and on the density of unoccupied states in the surface region.
- Incident: Variable energy electrons (50-2000 eV, modulated with 0.1-1.0 volt a.c. at 6-10 Hz); beam diameter: 2-10 mm; angle of incidence: approx. normal to surface.

  Detected: Attenuation of primary electron beam .

  Spectrum: Electron current at sample (target current) vs.




DAPS-spectrum of clean vanadium in the region of the L-shell.

# Some Related techniques

- **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 Xray flux is recorded. The spectrum is a plot of Photoelectron current (total yield) vs. photon energy
- Incident: Variable energy photons (100-1000 eV, synchrotron radiation); flux: medium to low; angle of incidence: not critical.

  Detected: Electrons (approx. 0 eV to within a few eV of photon energy).

  Spectrum: Photoelectron current (total yield) vs. photon energy.

- ***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.
- Incident: Variable energy electrons (0-1 eV) temperature: ≈1 K.

  Detected: Tunnelling current.

  Spectrum: Second derivative of tunnelling current with respect to applied junction voltage vs. junction voltage.

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

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 Xray 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 co ordinations of the surface atoms would lead to a relaxation in their energy states and accordingly to low binding energies observed. The resolution if 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

# Applications

- 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.
- It is a simpler technique for the determination of core electron binding energies at solid surfaces.