SECONDARY ELECTRON EMISSION AND ENERGY LOSSES
FROM METAL SURFACES

by

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ABSTRACT

Observations of both low energy secondary electron emission and the electron energy loss spectra from clean Ni(100), W(110) and Al(100), (110) and (111) surfaces have been made to investigate the fine structure in the energy distribution of secondary electrons. It is verified that in Ni(100) and W(110) crystals, the angle-resolved secondary electron emission spectra exhibit spectral fine structure arising from variations in the final densities of states above the vacuum level. Good agreement is found between band structure calculations for Ni(100) and W(110) and the experimental fine structure, in the corresponding directions. The effect of adsorption of oxygen overlayers on Ni is to smooth out any fine structure observed in the clean material. In Al the coupling of plasmons with the conduction electrons is very strong and is reflected in the SEE spectra. The observations confirm the hypothesis of emission of secondary electrons by plasmon decay in agreement with theoretical calculations from the literature.

Energy loss spectra of diffracted beams at grazing-emergence angles are obtained which have enabled a clear identification to be made of the surface plasmon of Ni(100) at 7 eV. The position of this loss can now be considered well established.

The inelastically scattered intensity is given by the sum of the two step processes of loss before and after diffraction and it is shown that to obtain the true energy loss function at arbitrary angles of incidence the loss spectrum should be obtained under conditions for which the diffraction before loss process is dominant.
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CHAPTER 1

GENERAL INTRODUCTION

Information on the electronic structure and surfaces of a solid can be obtained by studying the scattering of electrons by the solid. In this thesis the techniques of electron energy loss and secondary electron emission are used to study Ni, W and Al single crystal surfaces, with the aim of identifying the origin of structure observed and of understanding the fundamental processes involved.

In both techniques, a low energy electron beam is incident on the sample and an energy analysis of the scattered electrons is made.

In ELS, electrons which have lost energy $\Delta E = 1-30$ eV in producing either collective or single particle excitations in the solid, are studied. Previously energy-loss spectroscopy with high energy ($\sim 10$ KeV) electrons has been used to determine the optical constants of solids. Presently the emphasis is on the use of low energy electrons which reveal much information on the surface electronic structure.

In SEE electrons which have been excited from occupied states in the solid are examined. Most of the secondary electrons once created inside the solid suffer inelastic collisions before leaving the crystal. Typical excitation depths of secondary electrons are
\( \text{\(\sim 100\,\text{\AA}\)} \) and as a result of the short inelastic mean free path \( (10\,\text{\AA}) \) a secondary electron on average is likely to suffer many inelastic collisions before being emitted. The results of such a multiple secondary scattering process is a broad smooth cascade background with a peak at very low kinetic energies. Superimposed on this cascade background there is fine structure the origin of which in different materials will be discussed in this thesis.

In Chapter 2 apparatus which was employed throughout the present work is described along with the methods of crystal preparation, mounting and cleaning. The experimental procedure for energy loss, secondary electron emission and Auger spectroscopy are described. Some spurious effects encountered when analysing low energy electrons with LEED optics together with the factors determining the energy resolution and sensitivity are discussed.

The shape of a general secondary electron energy distribution inside the metal is described using the theory of Wolff in Chapter 3. Electron escape from the solid is treated as simple refraction at a surface barrier, to give the external distribution of the secondary electrons. The relationship between the analyser collection angle and angular distribution of electrons inside the sample are also discussed.

In Chapter 4 the origin of fine structure superimposed on the secondary cascade background is considered in terms of processes leading to secondary electron emission. This is divided into two sections (a) - excitation and (b) - transport and emergence. It is shown that depending on the electronic structure of the material
considered one of the excitation mechanisms may be largely responsible for the observed fine structure in the SEE.

In Chapter 5 the experimental SEE spectra from clean and oxygen covered Ni(100), W(110) and Al(100), (110), and (111) are presented. The structure appearing in the SEE spectra of the above mentioned materials are discussed in terms of the different available theories.

In Chapter 6 the basic theory of the inelastic scattering (collective and single particle excitations) of low energy electrons from solids is presented. A description of the dielectric theory of inelastic scattering is followed by an introduction to the concept of loss functions to represent energy loss spectra.

The two-step theory of inelastic diffraction is given in Chapter 7. Angle-resolved grazing emergence results from Al are presented and it is shown how to obtain energy loss spectra free from the effects of elastic scattering.

A new technique in which we energy analyse diffracted beams emerging nearly parallel to the surface of the solid is presented in Chapter 8. The structure in the energy loss spectra of Ni is examined, compared to previous work and its origin is clearly identified. The effects of ordered oxygen overlayers on the loss spectra is also studied.
ELS and SEE are very sensitive both to surface contamination and the effects of electric and magnetic fields within the measuring equipment. This chapter is devoted to experimental conditions necessary for an analysis of ELS and SEE to be made.

2.1 Vacuum chamber and pumps

The vacuum apparatus used consisted of a combination of a main experimental chamber and a gas handling line - see fig. (2.1) A MD6 precision isolation valve

Figure 2.1 Schematic of the LEED/AUGER system
leak valve was fitted between the main chamber and the gas handling line to allow small, well defined, volumes of adsorbate gases into the main chamber. Research grade gases in bottles (BOC, 5N, containing 760 torr) were connected to the gas handling line by means of all-metal valves.

The main chamber was pumped by a 4" liquid nitrogen trapped diffusion pump with integral isolation valve, so that the chamber would be exposed to atmosphere without having to switch off the diffusion pump. The gas handling line could be evacuated at any time through an all-metal isolation valve by a separate 2" liquid nitrogen trapped diffusion pump; this allowed different gases to be introduced independently into the main chamber. The system was rough pumped by an Edwards ED6 oil rotary pump (fitted with a bakeable zeolite trap) which also backed the diffusion pumps.

The main chamber was equipped with a model 668 Retarding Field Analyser (RFA) - see fig.(2.2) - specially designed for LEED and AES analysis (V.G. Scientific). The analyser consisted of a spherically concave fluorescent screen and a 3 grid system with a demountable LEG 21 pentode electron gun capable of directing an electron beam through the centre of the grid system towards the specimen situated at the isocentre of the sphere and cylindrical chamber as shown in fig.(2.2.) The grid system was capable of detecting emitted electrons within a solid angle of 104° subtended from the sample in the direction of the grids.

The electron gun, which produced a parallel beam of electrons (spot diameter ~ 1 mm at specimen), had the capability of providing electron beams with energies in the range 5 eV to 5 keV with a maximum beam current of ~ 100 µA. The gun and grid connections for LEED are shown in fig.(2.3) together with the screen and grid dimensions. Electrical
Figure 2.2 Schematic diagram of the LEED/AUGER work chamber

Figure 2.3 Grid connections and LEG21 Gun (AUGER/LEED)
connections were made via feedthroughs on the mounting flange. In the Auger mode where a high beam current at \( \sim 2.5 \text{ keV} \) energy was needed A1, A3 and A4 were at earth potential and the voltage on A2 was varied for focus control. Another electron gun capable of producing a high beam current at \( 2.5 \text{ keV} \) was fitted into the chamber at an angle of 75° to the 3 grid optics. This permitted Auger spectroscopy to be performed at higher sensitivity than when using a normal incidence beam (Weber and Peria, 1967).

An additional port in the main chamber housed an Argon ion gun (Model AG2) which allowed bombardment of the sample surface with a focussed beam of \( Ar^+ \) ions in the energy range 0 eV -10 keV.

A titanium film getter could be deposited on to the large surface area in the lower half of the main chamber which was shielded from the specimen.

The pressure in the main chamber was measured with a Bayard-Alpert ionisation gauge corrected for the soft X-ray limit to read down to \( 2 \times 10^{-11} \) mbar. To achieve pressures below \( 10^{-8} \) mbar the chamber was baked using external heaters and an oven enclosure for \( \sim 8 \) hrs at 200°C. After this period, the liquid nitrogen traps were filled and the titanium sublimation pump was used allowing pressures < \( 2 \times 10^{-10} \) mbar to be maintained. A small quadropole mass spectrometer was used for detecting leaks and general vacuum diagnostics. All filaments and heater assemblies were thoroughly outgassed prior to any measurements so that the pressure could be maintained in the \( 10^{-10} \) mbar range. The gas handling line pressure, before admitting gas to it, was always < \( 10^{-8} \) mbar as read on an ionisation gauge.
For orienting the crystals in the vacuum chamber two types of manipulator were used. Earlier work employed a UMD type translator (V.G. Scientific), whilst for the later experiments on Ni(100) requiring high temperature treatment, a HPT module was used (V.G. Scientific). Both manipulators permitted x-y-z translation of several mm, rotation about a polar angle (θ) with respect to the electron beam and rotational about azimuthal angles (ϕ) and a limited degree of tilt (± 5°) about the third axis - see fig. (2.4).

A mu metal shield lined the chamber internally. That it provided a very effective shield against external magnetic fields was evidenced by the fact that the (00) beam did not move even at the lowest energies (10 eV). A field of 1 μT will displace an electron by approximately 1 mm over a distance of 65 mm (isocentre to screen distance). A movement of the (00) beam of 1 mm

![Diagram of specimen manipulator - definition of axes](image-url)
would have been just detectable; as no such movement was discerned
1\muT can be set as an upper limit to the residual magnetic field.

2.2 The Crystal: preparation, mounting and cleaning

2.2.1 Preparation

Single crystals of Al, Ni and W (99.999% pure) were obtained from Metals
Research Ltd. (Cambridge) in the form of solid cylinders of different
sizes. Crystals were cut approximately to size (typically 5 x 10 x 1 mm)
using a spark machine and oriented using X-ray Laue back reflection
(Cullity, 1959). The final orientation was maintained by \( \pm 0.5^\circ \) by
transferring the crystal between the X-ray apparatus and the spark
machine by temporarily fixing it to a two circle goniometer, using
electrically conducting adhesive. After spark planing the crystal was
mounted in plastic (polymethylmethacrylate) and mechanically polished
using successively finer grades of carborundum paper and diamond
pastes. After mechanical polishing the plastic was dissolved using
chloroform and the crystal ultrasonically cleaned using chloroform,
acetone and ethanol.

As a final stage in the handling, the sample underwent electro-polishing
in a mixture of 80% ethanol and 20% perchloric acid. A stainless
steel beaker containing the electrolyte was used as the cathode
with the crystal forming the anode. The electrolyte was continuously
stirred by a magnetic stirrer and kept at \( T = -20^\circ C \) by liquid-solid
ethanol. A carefully controlled voltage (15 V) was applied for
approximately 10 minutes. The sides and the back of the crystal was
covered with lacomit (W. Canning & Co. Ltd., Birmingham) to prevent
the side and the back of the crystal being attacked during electro-
polishing. Having achieved a surface free from visible defects the lacomit was dissolved away using acetone. The sample was then cleaned in methanol, ethanol, washed in distilled water and dried.

2.2.2 Mounting

Various methods of crystal mounting were used depending upon the nature of the experiment. For observing diffraction patterns with the crystal at normal incidence three Al samples oriented with (111), (110) and (100) faces parallel to the surface were held in a recess in a block of Al and clamped in place by an Al top plate with the centre removed to expose the crystal - see fig.(2.5) It will be noticed, however, that whilst this geometry was suitable for normal incidence it was not possible to tilt the crystals beyond a certain angle without the top plate interfering with the diffracted beam.

Therefore, in order to observe diffraction patterns with the incidence beam set to a small or grazing angle to the crystal surface, a laser was used to spot weld the samples to an Al base plate. A disadvantage of using the resistance heating spot weld technique was its tendency
to distort the prepared surface caused by stresses at the weld and difficulties due to the high conductivity of the pure metals. The aluminium base plate had two countersunk holes drilled in it for attachment to the UMD translator. The HPT module had its own facility for holding samples, namely the SM2 specimen attachment pictured in fig.(2.6)

Using this attachment samples could be heated to 1000°C or cooled to -196°C with resistance heating or liquid nitrogen cooling attachments respectively. When the samples were mounted in the UMD translator, they could be heated only to 350°C; the heating was achieved by means of two tungsten wire heaters wound tightly on mica formers, fixed between the sample holder and the translator back plate - see fig.(2.7)
The temperature was monitored by means of a Pt/Pt-Rh(13%) thermocouple placed in close proximity to the crystal sample. Connections to the heater and thermocouple wires were made via electrical feed-throughs on the 150 mm flange supporting the manipulator. The four wires used to supply the heaters (when using the UMD translator) and monitor the temperatures were insulated from each other using alumina rods. This was a necessary precaution since rotation of the specimen might have caused the wires to short circuit during the course of an experiment. A certain amount of flexibility of movement was allowed using glass bead insulators for the last few mm between the alumina rods and electrical feed-throughs in the main flange. (An important point to consider in the use of such insulators is that charge accumulation in the field free region will distort the observed diffraction pattern, more significantly at low energies, and therefore they should not be placed in the immediate vicinity of any electron beam).

2.2.3 Cleaning

Both Al and Ni crystals were cleaned in situ by applying cycles of argon ion bombardment at 5 \times 10^{-5} \text{ mbar} with ion gun settings of 4-5 kV and \sim 12 \mu A, for various times (10-30 mins), and then the Al crystals were annealed at 350°C and the Ni crystal annealed at 750°C. The cleaning procedure is repeated until the Auger spectra showed no impurities within the detection of AES with signal averaged multiple scans. The typical background pressure was 10^{-10} \text{ mbar} after the annealing procedure.

2.3 Experimental procedure

For energy loss, secondary electron emission and Auger spectroscopy,
the retarding field analyser was used in conjunction with the necessary circuitry for phase sensitive detection and signal averaging in any one of three modes:

(i) Angle-resolved mode to perform ELS and SEE (using fundamental $\omega$)
(ii) Angle-integrated mode to perform ELS and SEE (using fundamental $\omega$)
(iii) Angle-integrated mode to perform AES (using first harmonic $2\omega$)

2.3.1. Angle-resolved ELS and SEE measurements

In the angle-resolved mode the relevant apparatus was connected as shown in fig. (2.8). With a primary electron beam of energy in the range

![Figure 2.8 Schematic representation of angle-resolved ELS and SEE experiments](image-url)
5-300 eV incident on the sample, a diffraction pattern in the form of bright spots appeared on the fluorescent screen. The light emitted from any particular spot or area on the screen was then focused through a lens system on to the plane of a circular aperture $C$ (of variable diameter $D$) positioned in front of a photomultiplier, fig.(2.9). The photomultiplier photocurrent was resistively converted to a voltage, and fed into the input of the lock-in amplifier. The DC ramp voltage applied to the grids $G_2$ and $G_3$ was modulated using a low distortion signal generator in conjunction with a low distortion audio transformer. A modulation frequency of 270 Hz was used, to be away from mains noise and its harmonics. The photomultiplier was attached to a precise x-y

![Diagram of photometer arrangements](image-url)
motion drive. The arrangement was such that the whole screen could be scanned in the vertical and the horizontal planes. Fixed image and object distances of 600 and 225 mm were kept throughout the course of this work. Thus light from a circular region of diameter 2.66D on the screen was collected. The range of angular resolution was due to a small variation between the centre and the edge of the screen. Slightly poorer angular resolution is obtained for spots nearer the edges of the LEED screen.

Spectra were obtained by ramping the DC voltage applied to \( G2/G3 \) and the \( X \) channel of the signal averager in synchronism and applying the output from the lock-in amplifier to the \( Y \) channel of the signal averager.

2.3.2 Angle-integrated ELS and SEE measurements

A schematic drawing of the experimental arrangement is shown in fig. (2.10). The total current induced by the scattered electrons was collected on the positively biased (250 V) screen. \( G4 \) was connected to earth. The DC ramp voltage applied to the grids \( G2 \) and \( G3 \) was modulated using a low distortion signal generator. A modulating frequency of 4701 Hz was used. The collected current was fed into a frequency sensitive preamplifier and then into the lock-in amplifier, where the fundamental frequency was detected. In the Auger mode the arrangement was the same as above with a modulating frequency of 2350 Hz and the first harmonic component in the lock-in amplifier was detected. The stray capacitance between the grid \( G2 \) and the collector was neutralized by using a capacitance bridge network which was fixed on the LEED optics flange. The output was recorded on a signal averager.
Figure 2.10  Circuitry and connections for angle-integrated ELS and AES
2.4 Instrumental effects

Some spurious effects encountered when analysing SEE and ELS with the retarding field type LEED apparatus and the factors determining the energy resolution and sensitivity are discussed below.

2.4.1 Spurious structure in SEE

As outlined in Chapter 3, it is a general property of materials that they produce secondary electrons, when bombarded by a primary beam of electrons. The electrons reflected from the crystal will produce tertiary electrons from the grids of the analyser. This effect has been studied by Wei et al (1969) and Cross (1973) in the low energy region. They both applied a bias voltage to $G4$ (both positive and negative) which shifts the spurious peak by an amount equal to the applied voltage and showed that the true secondary peak from the crystal can be masked by the large peak of tertiary electrons emitted by $G4$. Wei et al attributed this spurious peak to field penetration effects, causing electrons from the scattering region to reach the collector. Cross, after analysing this spurious peak, suggested that it is unlikely that field penetration is responsible and attributes it to the tertiary electrons produced at the first two grids by the secondaries from the target. Using estimates for the transmission of the grids and of the tertiary yield, Cross calculated that a spurious peak of the order of 30% of the size of the true peak was quite reasonable. In general the relative sizes of the two peaks will depend on the yield of the tertiaries from the first grid and their subsequent path to the collector. Cross also indicated that the field penetration from the collector could influence the size of the spurious peak by pulling tertiary electrons scattered back towards the crystal into the optics but he thought that this was unlikely through three grids. The tertiary electrons created at the retarding grids is negligible since the negative bias on the grids
will reduce the number of electron collisions. Any tertiaries produced will not have passed through any modulating grids and therefore not be recorded as a signal. Another contribution to the above observed secondary peak comes from secondary electrons produced within the gun collimator.

In conclusion it is necessary to know what percentage of the low energy peak really represents the true secondary electrons from the sample, what percentage is due to secondary emission from the grids and how much is due to electrostatic field penetration. For an accurate measurement of the true SEE the spurious secondary peak must be separated from the true one. This can be achieved by applying a potential difference of around $15 \, V$ to the grid $G4$, and the target at the expense of a decrease in the resolution of the system.

In this work no attempt was made to separate the spurious peaks from the true one; therefore any structure near zero retard volts was disregarded as it could have been due to such artifacts as mentioned above. Features above $2 \, eV$ are regarded as reliable.

2.4.2 Spurious structure in ELS

Avery (1976) reported on instrumental effects in electron energy loss spectra from surfaces due to the use of LEED optics. He found that the loss spectra in the region within $10 \, eV$ from the elastic peak, changed with the beam energy and he concluded that this was due to transmission effects at the retarding grids. By using an electron gun at the centre of the grids as an electron source he demonstrated that the "loss" spectra depended upon the path of the monoenergetic beam through the grids, and hence small
numbers of intense LEED beams could produce much the same effect. Thus for a characteristic loss spectra due solely to the crystal, a beam energy low enough to exclude all LEED beams from the analyser (about 35 eV for most LEED optics) should be used.

Avery did not check whether or not the energy distribution of electrons from his electron gun was dependent on focus conditions. Demuth and Rhodin (1974) presented very good evidence that backscattered elastic electrons had different elastic energy distribution half widths for the two modes of operation of the electron gun, demonstrating that although a monoenergetic incidence beam is desired, magnetic fields and the optics of the electron source limit the degree to which this objective can be achieved – see fig. (2.11) So some care must be exercised in drawing too many conclusions from Avery's works. Experiments carried out in this laboratory to check for this effect have been rather inconclusive.

2.4.3 Factors affecting the energy resolution

Factors listed below would have an effect on the energy resolution:

(1) Due to the physical geometry of the retarding grids the assumption that they represent an equipotential surface is an oversimplification. In practice there is a potential gradient from a point in the center of the grid aperture to the grid wires themselves. A better approximation to an equipotential surface can be achieved by the use of a finer mesh or by the use of two grids separated by a small distance. The system described in this thesis employs a double retarding grid.
Figure 2.11  Electron energy distribution for 20 eV incident electrons

(1) the "normal" mode
(2) the "low" mode
(3) for untrimmed fields the low mode
(2) Since it is the velocity component of the electron beam perpendicular to the equipotential surface which is measured by the retarding field analyser (Simpson, 1961), any change in direction of the electrons due to the focussing effects of the grids as they enter the retarding field region will give rise to a reduction in the resolution of the system. It is easily shown that for an angle of deviation \( \theta \) the change is given by

\[
\frac{\Delta V}{V_0} = \frac{\Delta E}{E} = \sin^2 \theta
\]  

(2.1)

It is therefore important to have an idea of the value of \( \theta \) in order to know the limit of resolution due to this effect. A good estimate of \( \theta \) is given by the expression,

\[
tan \theta = \frac{r}{q} \left( \frac{E' - E}{V_o} \right)
\]  

(Klemperer, 1953)  

(2.2)

where \( r \) is the radius of the aperture with different fields \( E' \) and \( E \) on either side. \( E = eV_o \) is the energy of the electrons. A minimum value of \( \theta \) occurs when both \( r \) and \( E' \) are as small as practically possible. The typical value of \( \frac{\Delta E}{E} = 10^{-4} \) with \( r = 0.25 \text{ mm} \) can be obtained which is a small effect and negligible for the work reported here.

(3) Improper positioning of the sample also causes the beams to enter the retarding field region in an off-normal direction which gives rise to a shift in the measured energy of monoenergetic electrons. A typical value of \( \frac{\Delta E}{E} = 3.10^{-4} \) could be obtained in angle-integrated spectra with a position of a sample 2 mm off the centre of the curvature of the grids at \( E = 100 \text{ eV} \). In angle-resolved spectra the energy spread will again be negligible.
(4) The finite cross sectional area of the electron beam means that some electrons enter the retarding field region at an angle $\theta$ to the normal of the equipotential surface. The effect of this has already been discussed.

(5) A further contribution to a reduction in the resolution of the energy spectrum is due to the energy spread of the primary beam. The smallest distribution in energy that can be expected is given by the Maxwell equation for thermionic emission. Therefore this spread in beam energies can be reduced by the use of cathodes which operate at lower temperatures. The type of cathode used in the apparatus described here was lanthanum hexaboride one which has an energy spread of 0.5 eV at 1300 C°. The Boerch effect due to lateral spreading of the beam in space charge regions of the electron gun could also give a small additional contribution to the energy spread.

(6) Variation in the work function $\phi$, over the retarding grids is also a source of error in the measurement of electron energies. It has been pointed out however (Hughes, 1982) that there is a contribution to the error only if a variation in $\phi$ over an area greater than or equal to the area of a single mesh occurs. Otherwise the grid can be considered as having an effective work function. It has been reported that a gross variation of $\leq 0.2$ eV in the work function for a Ni plated tungsten grid can be expected. Variations in work function will occur through contamination of the grids and consequently they are always shielded from the sample during ion bombardment.
(7) In the event of imperfection in the manufacture of the grids, non-radial fields between the grids can occur in the region of the defect. This will cause the electrons to travel in non-radial paths and hence a reduced retarding field will be necessary to produce the cut-off. The effect of a number of imperfections for angle-integrated spectra will be to cause a minor degradation of the energy resolution of the system. For angle-resolved work, because only a small region of the grid/screen is sampled, minor imperfections can have a less predictable effect. If the imperfection is of the order of or greater than the sampled area it will uniformly shift the spectrum to lower energies, whereas if it is smaller, it will again degrade (i.e. broaden) the spectrum.

2.4.4 The differential technique for recording $N(E)$

As the RFA is a high pass filter device only electrons of energy greater than the applied retarding voltage reach the collector. Therefore, the induced collector current $I(V)$ is related to the number density of electrons with energy $E$ by

$$I(V) \propto \int_{E}^{E_{max}} N(E) dE$$

(2.3)

The usual method of differentiating the collector current is to modulate the retarding grids with a small sinusoidal voltage and using phase sensitive detection techniques to detect the dominant harmonics corresponding to the successive differentials of the collector signal (Taylor 1969). It has been shown by Taylor that by modulating the retarding grids with a sinusoidal voltage of amplitude $k$ and frequency $\omega$ and using phase sensitive detection with a reference frequency $\omega$, the signal produced will be proportional to
\( \kappa I'(V) \)  

(2.4)

\( \text{i.e. } N(E) \propto \kappa I'(V) \)

As the amplitude of the modulation increases, the higher harmonics begin to contribute significantly to the differential and hence the proportionality begins to suffer. This manifests itself in the recorded data as a distortion of the true spectra so the smallest possible modulation consistent with sufficient signal to noise performance is necessary. Taylor has suggested that the peak to peak modulation amplitude should be less than one half of the full width half maximum of the peak under the analysis. In the present work a modulation amplitude of 0.5 to 1V peak to peak was used.
REFERENCES


CHAPTER 3
SECONDARY ELECTRON EMISSION

3.1 Introduction

The phenomenon of secondary electron emission was discovered in 1902 by Austin and Starke during a study of the reflection of electrons from metals. Primarily, the investigators of this effect studied the secondary yield i.e. the total number of electrons emitted per incident primary electron. Later, measurements of the energy distribution of the secondary electrons from single crystal surfaces were made. Back-emitted electrons began to be used increasingly for the investigation of the electronic structure of materials. A review of this topic is given by Hachenberg and Brauer (1959).

3.2 Secondary electron energy distribution

The general energy distribution of emitted electrons excited by an electron beam incident on a metal surface is given in Fig. (3.1). The spectrum, for convenience, can be divided into three regions labelled I, II, and III in the diagram.

![Image of energy distribution diagram]

Figure 3.1 The general shape of the energy distribution of secondary electrons
I. Elastically scattered electrons which include those which have suffered phonon losses.

II. Primary electrons which have lost energy in exciting plasmons or single particle excitations (this will be covered in detail in Chapter 6).

III. The true secondary region is made up of primary electrons that have been involved in multiple inelastic scattering events together with valence electrons of the solid which have been excited by the primary beam and subsequently involved in many inelastic collisions before escaping from the solid. The shape of this part of the spectrum is not very dependent on the direction and the energy of the primary beam over a large range of directions and energies. Superimposed on this smoothly varying region there is a fine structure, the origin of which is the subject of Chapter 4.

The process of secondary electron emission (SEE) is usually considered to involve three steps as follows:

i. Production of the secondaries: due to electron hole pair production, plasmon decay, Auger processes etc.

ii. Transport of the secondaries to the surface, which is either treated by the solution of the Boltzmann equation in the solid, or using some simple, mean free path considerations.

iii. Escape from the solid taking into account refraction and reflection at the surface barrier.

A complete theory of secondary electron emission would include all of these factors.
In this chapter a brief summary of the production of internal secondaries is given and the shape of a general secondary electron distribution is discussed with a view to describing the experimentally observed energy distribution curve of the secondary peak and its angular distribution. The effect of the analyser collection angle on the collected internal angular distribution of secondary electrons is also discussed.

3.3 Production of secondary electrons in solids

A quantum mechanical treatment of the initial collision between the incident electron and bound electron has been discussed by several authors (e.g. Frohlich 1932, Wooldridge 1939). The most general of these is due to Dekker and Van der Ziel (1952). Their theory is as follows. Consider a primary electron with energy \( E_p = \frac{\hbar^2 K^2 p}{2m} \) moving in a crystal of unit volume and interacting with a bound electron with wave vector \( \mathbf{K}_b \). The rate of transitions in which the primary electron is scattered into a solid angle \( d\Omega' \) around the wave vector \( \mathbf{K}_f \) and the bound electron is excited into the state \( \psi_{K_C} (\mathbf{r}) \), using first order time dependent perturbation theory is found to be

\[
P(\mathbf{p} \to \mathbf{p}', \mathbf{K}_b \to \mathbf{K}_f, \mathbf{K}_C) d\Omega = \frac{4m^2 q^2 \mathbf{K}_f}{\hbar^2} |I|^2 d\Omega'
\]  

(3.1)

where

\[
I = \int \psi_{\mathbf{K}_b} (\mathbf{r}) \psi_{\mathbf{K}_f}^* (\mathbf{r}) \psi_{\mathbf{K}_C} (\mathbf{r}) d\mathbf{r}
\]

(3.2)

is the matrix element connecting the initial and final states of the bound electron.
Various theoretical studies of SEE differ only in their choice of the matrix element $I$ given by eq. (3.2).

3.4 Cascade theory

The slow secondary electrons, after generation, will diffuse through the solid losing energy through multiple inelastic scattering, until they are either ejected as true secondary electrons or return to the sea of conduction electrons. A complete description of the cascade process must include the angular as well as the energy intensity distribution of the secondary electrons. Initially most of the theories (Baroody 1950, Dekker and Van der Ziel 1952, etc.) described the cascade process by an exponential absorption term and a mean depth of creation for the secondary electrons. Later Bruining (1954) and some others used a two or three step process in which the production, transport and escape of the secondaries are handled individually and then combined to give the externally observed energy distribution function. Here the work of Wolff (1954) is presented and used to provide an expression for the secondaries incident internally on the surface. At the surface this function is then modified by a refraction effect to give the external distribution of the secondary electrons.

Wolff used the Boltzmann diffusion equation to describe the cascade of electrons. This allows one to see in a single formalism the relationship between the secondary electron emission current and the primary beam energy, the inelastic cross sections, multiple sources and the escape probability. The Boltzmann equation for secondary transport can be written as
\[ \frac{\partial N}{\partial t}(\vec{r}, \vec{n}, E, t) + \nabla \cdot \vec{V} \cdot \nabla N(\vec{r}, \vec{n}, E, t) = \frac{\partial N(\vec{r}, \vec{n}, E, t)}{\partial t} + S(\vec{r}, \vec{n}, E, t) + \int \frac{d\vec{r}' \cdot \nabla' N(\vec{r}', \vec{n}', E', t)}{l(E')} \cdot F(\vec{n}, E, \vec{n}', E') \] .. (3.3)

where \( N(\vec{r}, \vec{n}, E, t) \) is the number of electrons, between \( \vec{r} \) and \( \vec{r} + \vec{a} \), \( \vec{n} \) and \( \vec{n} + \vec{a}, E \) and \( E + dE \) (energy is measured with respect to the bottom of the conduction band) at time \( t \), \( \vec{V} \) is the electron velocity, \( \vec{n} \) is a unit vector in the direction of \( \vec{V} \). The first term on the left hand side of eq. (3.3) represents the rate of change with time of \( N(\vec{r}, \vec{n}, E, t) \), while the second term represents the rate of change due to the gradient of \( N(\vec{r}, \vec{n}, E, t) \). The first term on the right hand side of equation (3.3) represents the number of electrons removed by inelastic and elastic scattering, \( l(E) \) is the effective mean free path given by

\[ \frac{1}{l(E)} = \frac{1}{l_E(E)} + \frac{1}{l_{\perp}(E)} \]

where \( l_E(E) \) and \( l_{\perp}(E) \) are the elastic and inelastic mean free paths respectively. \( S(\vec{r}, \vec{n}, E, t) \) represents the number of electrons produced by the primary beam. The final term represents the tertiary electrons (of energy \( E \) in direction \( \vec{n} \)) produced by inelastic scattering of secondaries with energy \( E' \) in direction \( \vec{n}' \) or excitation of valence electrons by these secondaries.

\[ F(\vec{n}, E, \vec{n}', E') \] is the probability that, an electron at \( \vec{n}'E' \) will be scattered to \( E \) and \( \vec{n} \). Here \( F(\vec{n}, E, \vec{n}', E') \) is normalised to two instead of unity because for every electron which scatters, there are two electrons in the cascade after the collision so
Wolff simplified eq. (3.3) by considering a steady state \( \frac{\partial N}{\partial t} = 0 \) with \( \nabla \cdot N = 0 \) and normally incident electrons. \( N, S \) and \( F \) are expanded into spherical harmonics as

\[
N(z, \cos \theta, E) = \frac{1}{4\pi} \sum L (2L + 1) N_L(z, E) P_L(\cos \theta),
\]
\[
S(z, \cos \theta, E) = \frac{1}{4\pi} \sum L (2L + 1) S_L(z, E) P_L(\cos \theta),
\]
\[
F(\bar{n}, E, \bar{n}', E') = F(\cos \theta, E E') = \frac{1}{4\pi} \sum L (2L + 1) F_L(E, E') P_L(\cos \theta)
\]

where \( z \) is the distance normal to the surface and \( \theta \) is the angle between \( \vec{V} \) and the normal, \( \Theta \) is the angle between \( \vec{n}' \) and \( \vec{n} \). Defining \( \psi_L \) by the relation

\[
\psi_L = \frac{\psi N_L}{L(E)}
\]

and assuming \( \psi_L \) is independent of \( z \), the solution of eq. (3.3) is given by

\[
\psi_L = \int_{E'}^{E} dE' F_L(E, E') \psi_L(E') + S_L(E) \quad \text{.. (3.4)}
\]

To solve eq. (3.4), Wolff assumed that the secondaries lose energy only by scattering with the valence electrons and neglected phonon losses \( (h\omega_{ph} \approx meV) \). He also assumed azimuthal symmetry by not considering the periodicity of the crystal. The electron-electron interaction is described by a screened Coulomb potential, in which case up to about 100 eV the scattering is spherically symmetric to a good approximation in the center of the mass system, after which it
is described by Rutherford scattering. That is to say, below 100 eV we must take the \( l = 0 \) term in eq. (3.4). With these assumptions and an approximate allowance for the effect of the exclusion principle on \( F_o \), the secondary emission current internal to the crystal is given by the following expression

\[
N(E_s) = A \left( \frac{E_p}{E_s + V_o} \right)^x
\]

where \( A \), approximates to a constant value, \( E_s \) is the kinetic energy of the secondaries and \( V_o \) is the inner potential of the metal. \( x \) is essentially constant and taken to be 2.

Streitwolf (1959) also gives a similar predicted spectrum of the form

\[
N(E_s) = \frac{1}{(E_s + V_o)^2}
\]

This time, however, the \( V_o \) used was the work function of the material.

The externally observed secondary electron spectrum is obtained by multiplying these functions by the surface escape probability.

Wolff gives the secondary emission current external to the crystal by

\[
N(E_s) = AQ(E) \left( \frac{E_p}{E_s + V_o} \right)^x
\]

eq. (3.7) applies to angle-integrated secondary electron emission when the collection angle is \( 2\pi \) radians. \( Q(E) \) is the fraction of electrons transmitted through the surface barrier, taking into account
refraction and neglecting reflection so \( T(E_s', \theta_s') = 1 \) where \( T(E_s', \theta_s') \) is the quantum mechanical transmission coefficient for electrons incident on the surface from the inside at an angle \( \theta_s' \) with energy \( E_s' + V_0 \). Only those electrons with \( \theta < \theta_c \) can escape from the solid, where \( \theta_c \) is the critical angle - see fig (3.2).

![Figure 3.2 Definition of angles](image)

Seah (1969) rewrites eq. (3.7) replacing \( Q(E) \) by an escape probability function appropriate to energy analysers accepting a small solid angle of emission. From the conservation of energy and momentum parallel to the surface, we can write

\[
k_o \sin \theta_o = k_i \sin \theta_i \quad \ldots (3.8)
\]

A beam of electrons occupying a small element of solid angle \( d\Omega_i \) inside the metal will occupy \( d\Omega_o \) outside.

\[
\frac{d\Omega_i}{d\Omega_o} = \frac{2\pi \sin \theta_o d\theta_o d\phi_o}{2\pi \sin \theta_i d\theta_i d\phi_i} \quad \ldots (3.9)
\]
where

\[ d\phi_i = d\phi_o \]

An expression for \( \theta_i \) in terms of the external parameters can be written as - see fig (3.3).

![Diagram showing refraction effects at the surface](image)

**Figure 3.3** Refraction effects at the surface

\[ \cos^2 \theta_i = \frac{E \cos^2 \theta_o + V_o}{E + V_o} \]  \hspace{1cm} (3.10)

Differentiating eq. (3.10) we obtain

\[ \frac{d\theta_i}{d\theta_o} = \left( \frac{E}{E + V_o} \right) \frac{\sin \theta_o \cos \theta_o}{\sin \theta_i \cos \theta_i} \]  \hspace{1cm} (3.11)

From eq. (3.8) we can show that

\[ \frac{\sin \theta_o}{\sin \theta_i} = \left( \frac{E + V_o}{E} \right)^{\frac{1}{2}} \]  \hspace{1cm} (3.12)
Using eq. (3.10) and (3.12) we write eq. (3.11) as

$$\frac{d\theta_i}{d\theta_o} = \frac{E^{1/2} \cos \theta}{(E \cos \theta_o + V_o)^{1/2}} \quad \ldots (3.13)$$

Hence the expression (3.9) relating the internal and external angle becomes

$$\frac{d\theta_i}{d\theta_o} = \left( \frac{E}{E + V_o} \right)^{1/2} \frac{E^{1/2} \cos \theta_o}{(E \cos \theta_o + V_o)^{1/2}} \quad \ldots (3.14)$$

Thus the external secondary electron energy spectrum is the product of eq. (3.14) with the appropriate internal energy distribution of eq. (3.5) or (3.6). Using eq. (3.5), the normally emitted ($\theta_o = 0$) secondary emission current is given by the following expression

$$N(E_s) = \frac{1}{(E_s + V_o)^x} \frac{E_s}{E_s + V_o} \quad \ldots (3.15)$$

From eq. (3.15) we can find the position of the secondary peak maximum at $E_s = \frac{V_o}{x}$ or if $x = 2$ at $\frac{1}{2}V_o$. So, according to the above, Seah showed that for copper and silver this should peak at around 7 eV; but the measured distribution peaked at 0.7 eV. Seah thus postulated that the surface refraction must be more severe than is given by the above treatment.

To find the power law controlling the emission, Seah plotted $\log N(E_s)$ versus $\log (E_s + V_o)$. $V_o$ was chosen each time to obtain a straight line. The departure from a straight line at low energies
was considered to be due to surface effects. Using this method he obtained \( x = 2.0 \) for silver and \( x = 1.6 \) for copper, both with a value of \( V_0 \) about 4.5 eV. He thus concluded that either the treatment of Streitwolf (eq. 3.6) was correct or that Wolff's equation (eq. 3.5) was correct provided that the energy is referenced to the Fermi level and not to the bottom of the conduction band.

Deducing the surface threshold function \( \frac{d\alpha}{d\theta_0} \) for normal emission (the departure of the graph from a straight line at low energies), Seah showed that an adequate description, within 2% of the experimental results, was given by the expression

\[
N(E_s) = \frac{1}{(E_s + 4.5)^x} \frac{E_s}{(E_s + 0.35)}
\]  

(3.16)

This equation will be applied in Chapter 5.

Seah also takes \( T(E_s, \theta') \), the quantum mechanical transmission coefficient as unity and therefore energy independent. We must ask ourselves whether this is appropriate at these low energies. The transmission coefficient for a step barrier is given by

\[
T = \frac{4K_{L'} \cdot K_{L''}}{(K_{L'} + K_{L''})^2}
\]  

(3.17)

so that for normal emission

\[
T = \frac{4 \sqrt{E_s} \cdot \sqrt{E_s + V_0}}{(\sqrt{E_s + V_0} + \sqrt{E_s})^2}
\]
this function is plotted for Ni in fig. (3.4). As we can see at very low energies the transmission coefficient will affect the shape of the spectrum.

![Graph of Transmission Coefficient vs Energy for Ni](image)

Figure 3.4 Transmission coefficient vs energy for Ni

3.5 The angular intensity distribution of secondary electrons

Jonker (1951), who recorded the angle-resolved energy distribution of the secondary current $N(E_a, \theta)$ for secondary energies ranging from 1.5 to 100 eV, showed that at each $E_a$ the secondary current varied as the cosine of the angle between the surface normal and the direction of emergence, indicative of an isotropic internal distribution function. This was, of course, an assumption of the Wolff theory.

Others however, and notably Burns (1970), detected an angular dependence that differed markedly from the previously observed cosine behaviour, giving structure in the $N(E_a, \theta)$ distribution which was superimposed on a background having an approximate cosine distribution. He attributed these features to band-structure effects, but concluded that more detailed work needed to be done on the subject.
3.5 **Analysers collection angle dependence of the internal angular distribution of electrons**

To cross the surface barrier an electron must have a normal component of momentum sufficient to overcome the internal potential of the solid. Hence, when the constraint is applied of collecting the external electrons over an angle $\theta_o$ around the crystal normal, this restricts the sampling of the internal electron distribution. From eq. (3.10) we can obtain an expression for $\theta_\perp$ in terms of the external parameter $\theta_o$ and $E_s$:

$$\theta_\perp = \cos^{-1} \left( \frac{E_s \cos^2 \theta_o + V_o}{E_s + V_o} \right)^{1/2}$$

Then we can plot a graph of the angle ($\theta_\perp$) that an electron inside the material must be incident within (upon the surface) to be collected by an external analyser of angle about the crystal normal.

This is plotted in fig. (3.5) for Al and Ni for various analyser collection angles, $\theta_o$, around the crystal normal. Here $V_o$ is taken to be 15 and 11 eV for Al and Ni respectively. As can be seen with energy analysers only accepting a small solid angle of emission, only the electrons within a very narrow cone along the surface normal inside the crystal is collected; therefore a small part of the Brillouin zone is sampled. (see chapter 5 for normal emission). The $52^\circ$ half-angle analyser (to which reference is made in this thesis when angle-integrated spectra have to be considered) samples a wider internal angle of electrons and thus collects over a large part of the Brillouin zone so that details of $E(K)$ space are smeared out. At very low energies, the wide angle analyser
Figure 3.5 Internal angle, $\theta_i$ versus internal electron energy for various analyser collection angle, $\theta_0$. 
samples a much narrower cone along the surface normal and hence shows features that correspond increasingly to those occurring in the 10° collector.

3.7 Conclusions

The various theoretical treatments of the electron cascade in the materials and the effects of the analyser collection angle on the experimentally sampled internal distribution of electrons have been considered in this chapter. In the following chapter we will discuss the origin of fine structure which is superimposed on the smoothly varying secondary cascade curve.
REFERENCES


CHAPTER 4

STRUCTURE IN THE ENERGY DISTRIBUTION OF SECONDARY ELECTRONS

4.1 INTRODUCTION

Investigations made with high resolution analysers, have revealed fine structure superimposed on the smooth secondary cascade background described in chapter 3. The origin of this fine structure in the energy distribution of secondary electrons becomes clear when we consider the processes leading to their emission listed in table (4.1)

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<tbody>
<tr>
<td>a. Direct excitation via the electron-electron interaction by sufficiently energetic electrons,</td>
</tr>
<tr>
<td>b. Due to plasmon decay via single particle excitation,</td>
</tr>
<tr>
<td>c. By direct excitation of Auger transitions</td>
</tr>
</tbody>
</table>

\[
\text{TRANSPORT}
\]

Inelastic scattering and diffraction

\[
\text{EMERGENCE}
\]

Table 4.1 Processes leading to secondary electron emission

The main purpose of this chapter is to show how the fine structure which is observed experimentally can be explained in
terms of

i different excitation mechanisms for the secondary electrons
and

ii their transport to and escape from the surface.

The effect of choice of electron analyser on the results
obtained is also discussed.

4.2 EXCITATION

The generation of secondary electrons by the primary beam (via
the electron-electron interaction), by the decay of plasmons
(generated by the primary beam) and as the results of Auger
transitions can all be treated using the single theory described
below.

The probability per second for a primary electron in state $E_p, K_p$
to be scattered down to a conduction state $E_f, K_f$ loosing
energy $\hbar \omega$ due to either the excitation of an electron from a
valence state $E_v, K_v$ to a conduction state $E_c, K_c$ or by the
excitation of plasmons (which may subsequently decay via single
particle excitation - see fig (4.1)) - is given by first order
time dependent perturbation theory as

$$P(K_p, K_v, K_f, K_c) = \frac{2\pi}{\hbar} \left| \left\langle \varphi_f(r_2) \varphi_c(r_1) | H | \varphi_p(r_2) \varphi_v(r_1) \right\rangle \right|^2 \times \delta(E_p + E_v - E_f - E_c) \quad .. (4.1)$$

The Dirac $\delta$ function in eq. (4.1) ensures the conservation of
energy and momentum conservation is given by

$$K_p + K_v = K_f + K_c + \vec{g}$$
where \( \vec{q} \) is a reciprocal lattice vector and 

\[ H \] is the perturbation Hamiltonian given by

\[
H = \frac{e^2}{\epsilon(\vec{q}, \omega) |\vec{r}_1 - \vec{r}_2|}
\]

where

\[ \epsilon(\vec{q}, \omega) = \epsilon_1(\vec{q}, \omega) + i \epsilon_2(\vec{q}, \omega) \]

is the frequency and momentum dependent complex dielectric function. Writing \( \frac{1}{|\vec{r}_1 - \vec{r}_2|} \) in momentum space

\[
\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \frac{1}{\Delta} \sum \frac{q^2}{q^2} e^{i\vec{q} \cdot (\vec{r}_1 - \vec{r}_2)} \equiv (4.2)
\]

where \( \Delta \) is the volume of the solid and

\[ \vec{q} = \vec{K}_p - \vec{K}_f \]

---

**Fig. (4.1) Schematic of the scattering process**
Eq. (4.1) can be written as

\[
P(K \rightarrow K', K'' \rightarrow K'') = \frac{2\pi}{\hbar} \sum_q \left( \frac{4\pi e^2}{q^2 \Delta} \right)^2 \frac{1}{\varepsilon(q, \omega)} | \psi_p(\mathbf{r}_1) \psi_q(\mathbf{r}_2) |^2 \delta(E_p + E_q - E_f - E_c)
\]

Eq. (4.3) can be separated in terms of \( \mathbf{r}_1 \) and \( \mathbf{r}_2 \) to give

\[
P(K_1, K_2 \rightarrow K', K'' \rightarrow K'') = \frac{2\pi}{\hbar} \sum_q \left( \frac{4\pi e^2}{q^2 \Delta} \right)^2 \frac{1}{\varepsilon(q, \omega)} | \psi_p(\mathbf{r}_1) e^{i(q \cdot \mathbf{r}_1)} | \psi_p(\mathbf{r}_1) |^2
\]

\[
\times | \psi_q(\mathbf{r}_2) | e^{-i(q \cdot \mathbf{r}_2)} | \psi_p(\mathbf{r}_2) |^2 \delta(E_p + E_q - E_f - E_c)
\]

Eq. (4.4) can be written in terms of the wave vectors as

\[
P(K_1, K_2 \rightarrow K', K'' \rightarrow K'') = \frac{2\pi}{\hbar} \sum_q \left( \frac{4\pi e^2}{q^2 \Delta} \right)^2 \frac{1}{\varepsilon(q, \omega)} | \psi_p(\mathbf{r}_1) e^{i(q \cdot \mathbf{r}_1)} | \psi_p(\mathbf{r}_1) |^2
\]

\[
\times | \mathbf{r}_1 | e^{i(q \cdot \mathbf{r}_2)} | \psi_p(\mathbf{r}_2) |^2 \delta(E_p + E_q - E_f - E_c)
\]

As pointed out by Chung and Everhart (1977) eq. (4.5) already embodies the mechanism of plasmon decay excitation of secondary electrons (the factor \( \frac{1}{q^4} \) implies that transitions involving small momentum transfers are more probable). To separate the contributions from electron-electron scattering and plasmon decay different approximations are made in the representation of the dielectric function. In eq. (4.5) \( \psi_p \) and \( \psi_q \) are also treated differently according to the material being considered.
4.2.1 Excitation by (screened) electron-electron scattering

The importance of this mechanism will depend on the electronic structure of the material considered. In Al (NFE) this mechanism is not very important because of the parabolic energy bands and there is not much structure in the density of states just above the vacuum level. However for materials like Si, graphite, W and Ni with structure in the conduction band this is a very important contribution. Hence this section is divided into two sub sections in terms of materials considered.

4.2.1.1 Materials in which the plasmon effect is dominant

Chung and Everhart (1977) presented a quantitative theory of secondary electron emission applicable to NFE metals along with numerical calculations for Al. To explain the contribution to SEE from the electron-electron interaction, they used the static form of the Linhard dielectric function (random phase approximation, RPA, dielectric function for a free electron gas) given by

$$\lim_{q \to 0} \epsilon_L(q, 0) = 1 + \frac{q_{ft}^2}{q_f^2}$$

where $q_{ft}$ is the Thomas-Fermi screening wave vector. Although this is not rigorously correct for energies much above the Fermi level, for excitation of very low energy secondary electrons the authors feel it is a good approximation. They made the assumption that the primary electron before $(\vec{K}_p)$ and after $(\vec{K}_f')$ the scattering event is in a plane wave state so in eq. (4.5)

$$\langle \vec{K}_p | e^{iq \cdot \vec{P}} | \vec{K}_f' \rangle = \delta_{\vec{K}_p, \vec{K}_f' - q}$$

Hence the transition probability (from eq. 4.5) is given by
They approximate the matrix element in eq. (4.6) by an overlap integral by writing for small $\overline{q}$,

$$e^{-i\overline{q} \cdot \overline{r}} \approx 1 - i\overline{q} \cdot \overline{r} = 1$$

$$| \langle \psi_o | e^{-i\overline{q} \cdot \overline{r}} | \psi_v \rangle | = \frac{1}{\Delta_o} \times \int_{0}^{\Delta_o} \frac{U_{K_o}^*(\overline{r})U_{K_v}(\overline{r})d\overline{r}}{U_{K_o}(\overline{r})U_{K_v}(\overline{r})} = \langle \psi_o | \psi_v \rangle \quad \ldots (4.7)$$

where $\Delta_o$ is the volume of the unit cell and $U_{K_v}$ is the periodic part of the Bloch function and the integration is over a unit-cell volume.

As they describe the crystal electrons by plane waves eq. (4.7) becomes unity. Using the above approximations Chung and Everhart arrived at the following equation

$$P(K_o \rightarrow K_v + K_{\overline{r}} \rightarrow K_{\overline{f} \overline{r}}) = \frac{2\pi}{\hbar} \sum_{\overline{q}} \left( \frac{4\pi e^2}{\Delta} \right)^2 \frac{1}{q} \frac{1}{(q^2 + q_{\overline{r}}^2)^2} | \langle \psi_o | e^{i\overline{q} \cdot \overline{r}} | \psi_v \rangle |^2$$

$$\times \delta_{K_o \rightarrow K_v} \delta_{K_{\overline{r}} \rightarrow K_{\overline{f} \overline{r}}}^q (E_o + E_v + E_{\overline{r}} - E_{\overline{f}} - E_{\overline{d}}) \quad \ldots (4.6)$$

Rösler and Brauer (1981) also developed a model for the secondary emission for NFE metals. In this model the contribution to SEE from screened electron-electron interaction was calculated using different screening approximations for the dielectric function. They showed that at high energies ($E \geq 100$ eV) screening is unimportant by reason of the large frequency argument in the dielectric function. Hence in this energy range
the unscreened excitation rate is a sufficiently good approximation. However, at lower energies the excitation rate is overestimated by this approximation. In this range \((E \leq 50 \text{ eV})\) dynamical screening becomes very important. Using the Thomas-Fermi screening the excitation rate is underestimated in the whole interesting energy range.

For Al (NPE) this excitation mechanism is not very significant - see sec. 4.2.2.2

4.2.1.2 Materials in which the electron-electron scattering is dominant

Kane (1967) using the same formalism as outlined above calculated the total scattering rate for a hot electron to decay and produce an electron-hole pair in silicon as

\[
\mathcal{W}_{SE}(E_p, E) = \frac{2\pi}{\hbar} \left( \frac{\Delta}{2\pi} \right)^2 \sum_{\alpha \beta} \left| \langle \mathbf{k}_p, \mathbf{k}_\alpha | H | \mathbf{k}_p, \mathbf{k}_\beta \rangle \right|^2 \times \frac{\sum_n \int d\mathbf{k}_p d\mathbf{k}_\alpha d\mathbf{k}_\beta \delta(E_p - E)}{\sum_n \int d\mathbf{k}_p \delta(E_p - E)} \delta(E_p + E_\alpha - E_p - E_\beta). \quad (4.9)
\]

where \(n\) are the band indices.

In contrast to the above authors he described the crystal electrons by Bloch functions and used the dielectric function \(\epsilon(q, \omega)\) obtained from an RPA calculation using pseudo potential energy bands and wave functions for Si. After evaluating the integral in eq. (4.9) by the Monte Carlo method, Kane found that the results
he obtained were in agreement with those derived from a "random-k" approximation in which momentum conservation was ignored. This follows if $\vec{K}_v$ in eq. (4.2) is regarded as a random variable, whose probability $P(\vec{K}_v)$ of falling in the energy interval $dE_v$ in band $n_v$ is proportional to the density of states $\rho_v(E_v)$ of band $n_v$

$$P(E_v) = \rho_v(E_v) dE_v / \int \rho_v(E_v) dE_v$$  .. (4.10)

with

$$\int \rho_v(E_v) dE_v = 2N$$ where $N$ is the number of unit cells and the 2 is for spin. He also assumed a constant average value of

$$| \langle \vec{K}_p \mid H \mid \vec{K}_v \rangle \rangle |^2 = |M|^2$$ independent of the $\vec{K}$ vectors of the electrons involved giving the probability $P_s(E_p, E)$ for an electron with initial energy $E_p$ to be scattered to energy $E$ (per eV per second) as

$$P_s(E_p, E) = \rho_p(E) \frac{2\pi}{h^2} |M|^2 \int_{-E_p + E}^0 dE_p \rho_v(E_v) \rho_p(E_v + E_p - E)$$  .. (4.11)

Then the scattering rate (total transition probability per primary electron energy of $E_p$) is

$$\tilde{W}_{SE}(E_p) = \int_0^{E_p} P_s(E_p, E) dE$$

Hence the final state energy distribution function of secondary electrons of energy $E$ produced by a primary electron of energy $E_p$ inside the material is given by
In eq. (4.12) the factor 2 takes into account the fact that two secondary electrons are produced in the pair production. The structure in the integrals of eq. (4.12) due to the conduction band density of states will be smeared out by the convolution so that, together with the surface escape function, they produce the smooth cascade of the secondaries (see chapter 3) peaking a few eV above the vacuum level. This leaves the factor \( \rho_{f}(E) \) so that structure in the density of conduction band states should be reproduced in the secondary electron energy spectrum.

Willis et al., in a series of papers, analysed angle integrated spectra from graphite (Willis et al 1971, Willis et al 1974) and angle resolved spectra for normal and off normal emission for W(100), (111), (110) low index faces (Willis 1974, Willis and Christensen 1978 and Christensen and Willis 1979), using the scattering theory of Kane (1967) in conjunction with the assumption of energy conservation for the electrons crossing into the vacuum. They emphasized that features due to the one electron densities of final states should be seen in the low energy secondary spectra.

For example calculations by Christensen and Feuerbacher (1974) and
Feuerbacher and Christensen (1974) show that $W$ has a band gap approximately 9 eV above the Fermi energy which extends throughout the Brillouin zone. This gap manifests itself as a pronounced minimum in the measured SEE. However, certain peaks could not be explained in these terms and were shown to be due to surface effects as explained in section (4.3).

4.2.2 Excitation by decay of plasmons

Plasmons excited by the incident beam can decay by exciting an electron from the valence band, see fig (4.2).

Fig. (4.2) Excitation by decay of plasmons
Qualitatively, this results in structure in the initial density of states being reproduced in the SEE spectrum, but broadened due to the plasmon linewidth. The most obvious structure is at the Fermi energy above which there are no occupied states and this will be reproduced in the SEE spectrum at an energy

$$E_s = \hbar \omega - \phi_A.$$  

4.2.2.1 Excitation by decay of volume plasmons

Quantitatively the contribution to the excitation of secondary electrons from the decay of long wavelength plasmons generated by the primary electrons can be calculated by separating out the plasmon pole contribution to \( \frac{1}{|\varepsilon(q,\omega)|^2} \) in eq. (4.5). Chung and Everhart proceed by evaluating \( \varepsilon(q,\omega) \) near \( \omega = \omega_p \) to evaluate \( P(\overline{K}_p, K_v + \overline{K}_p, \overline{K}_p) \) due to plasmon decay. For the NFE metals, and in the limit of very small \( \overline{q} \), \( \varepsilon_1 \) is very small at the plasma frequency \( \omega_p \). Therefore \( \frac{1}{|\varepsilon|} = \frac{1}{|\varepsilon_1 + i \varepsilon_2|} \) has a large resonance at \( \omega = \omega_p \) for small \( \varepsilon_2 \).

Writing

$$\varepsilon(q,\omega)\big|_{\omega = \omega_p} = \left( \varepsilon_1(q,\omega_p) + \frac{3 \varepsilon_1}{3 \omega} |_{\omega = \omega_p} (\omega - \omega_p) + i \varepsilon_2(q,\omega_p) \right)$$  

.. (4.13)

and approximating \( \varepsilon_1(q,\omega) \) in the vicinity of \( \omega_p \) as

$$\lim_{q \to 0} \varepsilon_1(q,\omega) = 1 - \left( \frac{\omega}{\omega_p} \right)^2$$  

and substituting in eq. (4.13)

we get

$$\varepsilon(q,\omega = \omega_p) = \left( \frac{3}{\omega_p} \right) (\omega - \omega_p) + i \varepsilon_2(q,\omega_p)$$  

.. (4.14)

and
Defining the damping constant \( \Gamma = \lim_{q \to 0} \frac{\hbar \omega}{\bar{\omega}} \epsilon_2(q, \omega_p) \)
we obtain

\[
\frac{1}{|\epsilon(q, \omega = \omega_p)|^2} = \frac{(\omega_p/2)^2}{[(\omega - \omega_p)^2 + (\omega_p/2)^2] \epsilon_2(q, \omega_p)^2} 
\tag{4.15}
\]

if \( \Gamma \) is very small eq. (4.16) gives a sharp Lorentzian centered at \( \omega_p \), representing the sharp plasmon loss lines. Substituting eq. (4.16) in eq. (4.5) we have

\[
P(K + K' \rightarrow K_f, K_f') = \frac{2\pi [4\pi e^2]^2}{\hbar q^2 \Lambda}
\]

\[
\left[ \frac{\omega}{\hbar} \right] \left| \langle \bar{K}_o | \bar{K}_v \rangle \right|^2 \delta_{\bar{K}_f, \bar{K}_p} \delta_{\bar{q}, \bar{q}} \delta(E_p + E_v - E_f - E_o) \times \frac{1}{[(\omega - \omega_p)^2 + (\Gamma/2\hbar)^2] \epsilon_2(q, \omega_p)}
\]

Here we restrict ourselves to small \( q \) and \( \omega = \omega_p \). Writing \( \epsilon_2(q, \omega)_{RPA} \) in the Bloch scheme where for the NFE metals with nearly parabolic energy bands, the intraband transition energy \( \delta \) functions vanish in the limit of \( q \to 0 \) and \( \omega = \omega_p \) and only vertical interband transition terms exist we have

\[
\lim_{q \to 0} P(K_v \rightarrow K_o) = \left\{ \frac{4\pi e^2 \omega_p}{\hbar q^2 \Delta} \right\} \frac{\Gamma/2}{(\bar{\omega} - \bar{\omega}_p)^2 + (\Gamma/2)^2} P(E, \hbar \omega) \tag{4.18}
\]

where
\[ \frac{4\pi e^2 \hbar \omega_p (\Gamma/2)}{\hbar \omega^2 \Delta (\hbar \omega - \hbar \omega_p)^2 + (\Gamma/2)^2} \] is the transition rate, for generating long wavelength plasmons and \( F(E, \hbar \omega) \) is identified as the electron energy distribution resulting from plasmon decay via vertical interband transitions. \( \langle F(E, \hbar \omega) \rangle \) is also the normalised optical energy distribution of the joint density of states. Therefore eq. (4.18) describes a second order process in which the incident electron firstly creates plasmons with \( \overline{q} = 0 \) which subsequently decay via vertical interband transitions, thereby producing energetic secondary electrons.

4.2.2.2 Excitation by decay of surface plasmons

Chung and Everhart (1977) also calculated the possible surface plasmon decay contribution to secondary electrons for small \( \overline{q} \) following Endriz and Spicer's (1971) analysis. In this the surface plasmon field is described by a scalar electric potential, \( \phi_s(\overline{r}, t) \), as

\[ \phi_s(\overline{r}, t) = \sum_{\overline{q}} \phi_{0}(\overline{q}) e^{i(\overline{q} \cdot \overline{s} - \omega_s t)} e^{-Q|z|} \]

where \( \overline{s} = \hat{x} \overline{a} + \hat{y} \overline{y} \) is the position coordinate parallel to the surface and \( z \) is the coordinate normal to it. \( \overline{Q} = Q_x \hat{x} + Q_y \hat{y} \) is the two dimensional wave vector of the surface plasmon field.

Since the surface plasmon field decays exponentially into the solid, one can have excitation of the bulk-crystal electrons via coupling to the electric potential \( \phi_s(\overline{r}, t) \). If each \( \overline{Q} \)th component of the surface plasmon potential has a field energy distribution into the solid given by \( e^{-2Qz} \) \((z > 0)\) i.e. in the
solid) and if it is assumed that single electron excitation is the plasmon decay mechanism, the probability per unit distance of exciting secondary electrons is given by $2Q_e^2Q_S$. If $F(E, \hbar \omega)$ is the normalized energy distribution of surface plasmon decay via single electron excitation, the differential probability per unit distance per unit energy of secondary electron excitation is given by

$$\frac{P(\vec{k}_s + \vec{k}_p)}{dE} = 2Q_e^2Q_S F(E, \hbar \omega)$$  \hspace{1cm} (4.20)

Following the analysis described above, Chung and Everhart calculated the secondary electron distribution numerically for Al, and compared the theoretical results (fig. 4.3a) with the experimental data of Everhart et al (1976)—fig. (4.3b). The results showed that the surface and volume plasmon decay make the largest contribution to the SEE of Al. In materials like W and Si which have large plasmon linewidths this contribution is not expected to be important.

![Fig. 4.3 Theoretical and experimental secondary electron energy distribution curves (a) theoretical (b) experimental](image)
Henrich (1973) suggested another mechanism related to plasmon excitation which can lead to fine structure in SEE. Inside the solid "hot" secondary electrons with energies greater than \( E_F + \hbar \omega_p \) have a high probability of exciting plasmons of energy \( \hbar \omega_p \), thus decreasing their own energy and the density of electrons above \( E_F + \hbar \omega_p \), where \( E_F \) is the Fermi energy. Energetic electrons with energies less than \( E_F + \hbar \omega_p \) are unable to lose energy in this way; hence a change in the number of excited electrons should exist at this energy in the solid. This corresponds to discontinuities in the slope of the cascade background curve at \( E_s = \hbar \omega_p - \phi_A \) and \( E_s = \hbar \omega_p - \phi_A \) rather than discrete peaks, see fig (4.4).

![Graph](image)

**Fig. 4.4** Effect of plasmon losses on the SEE distribution \( N(E_s) \)

### 4.2.3 Excitation by Auger processes

In addition to Auger electrons from the usual core hole origin it is possible for Auger electrons to be produced from hole states in the valence band. Consider the process illustrated in fig (4.5) as a scattering process, whereby a hole (fig 4.5a) reduces its energy by an Auger process (electron emission) to a
state as in fig (4.5b).

(a)  
(b)  

\[ E_k F \]

\[ \text{top of the d band} \]

Fig 4.5a & b Schematic of the Auger process in a metal

This can be treated using eq. (4.12) by considering it as hole-hole scattering (Berglund and Spicer 1964). A hole \((E_h, \overline{K}_h)\) which is created in the valence band in the absorption process scatters to an energy \((E'_h, \overline{K}'_h)\) through recombination and excites an electron hole pair \((E'_e, \overline{K}'_e)\) and \((E'_v, \overline{K}'_v)\). Following the derivation given for electron-electron scattering it can be shown that the distribution function \(N_h(E_h, E)\) for secondary electrons of energy \(E\) produced by a primary hole of energy \(E_h\) is

\[
N_h(E_h, E) = \frac{\int_{E+H}^{E+E_h} dE_e \rho_e(E_e) \rho_e(E+E_h-E_v) \rho_v(E+E_h-E_v)}{\int_{E+H}^{E+E_h} dE_e \rho_e(E_e) \rho_v(E+E_h-E_v)} \quad \cdots (4.21)
\]

the integrals in eq. (4.21) result in structure at various energies depending on the element of width determined by the width of levels
involved. Again this structure is modified by the conduction band density of states $\rho_f(E)$. To date no one has attempted the separation of $\rho_f(E)$ in the region of an Auger peak.

4.3 Transport and emergence

Secondary electrons having been excited by one of the different excitation mechanisms described above, travel to and escape from the surface. We now consider how the fine structure in the energy distribution of secondaries is affected during the transport and escape process.

In chapter 3, the transport of the secondaries to the surface is considered in terms of Boltzmann equations for a uniform distribution of secondary electrons, so diffraction effects which can cause the emission to peak in intensity in certain directions are not considered.

To calculate the wavefield outside the surface from that inside the solid the boundary conditions at the surface have to be taken into account. This results in the following effects as discussed by Willis and Christensen (1978)

i. Surface state resonances: In a 3-dimensional solid no electron states exist within the band gaps. However when the solid is terminated by a surface, it is possible for states which are localised near the surface to occur within the band gaps. These surface states can contribute to the emission and
thus appear as structure at the energy of the band gap.

ii Surface Emission (plane wave vacuum states can always tail a short way into the solid). These conditions exist for all $k_n$ in the surface Brillouin zone and contribute to the background cascade continuum intensity.

iii Vacuum bulk resonance matching: When the group velocity of a Bloch wave within the crystal is equal to the group velocity of the corresponding vacuum plane wave then enhanced transmission is obtained which can show itself in an SEE spectrum.

iv Lower band edge resonance matching: The wave functions at the lower edge of a band gap have a maximum at the atomic positions giving rise to a maximum in the wavefield close to the surface (in contrast to the wave functions at the top edge of the band gap which have minima at the atomic positions). Therefore there can be enhanced surface emission at the energy corresponding to the lower band edge.

Feder and Pendry (1978) presented a similar theory to that of Willis et al for secondary electron emission which takes into account the diffraction of the generated secondary electrons inside the solid and the boundary conditions at the surface by treating it as a LEED intensity problem. In their theory, using a thermodynamic argument they arrived at the expression for the distribution $N(E_s)$ of secondary electrons of kinetic energy $E_s$ and momentum $k_n$ parallel to the surface ($k_n$ is conserved in going from the inside of the crystal into the vacuum)
\[ N(E_g) = \left(1 - \sum_{\vec{k}_n} R_{0g}^E(E, \vec{k}_n)C_0(E) \right)/(1 + \alpha(E)) \quad \ldots \quad (4.22) \]

where \( R_{0g}^E \) is the intensity of the \( g \)th beam in low energy electron diffraction for a primary beam of energy \( E \) and parallel momentum \( \vec{k} \). The \( g \) summation extends over all beams, which actually emerge from the crystal. \( C_0(E) \) is the black body emissivity, \( \alpha(E) \) is an unknown function which is slowly varying with energy. For the purpose of numerical calculations they let \( \frac{C_0(E)}{1 + \alpha(E)} \) be unity. This term represents the cascade on which the fine structure due to \( \mu \rightarrow \mu \) is superimposed. So the calculations of fine structure is thus effectively a calculation of LEED intensities.

4.4 Angle integrated and angle resolved spectra

The collection angle of the experimental analyser used can affect the observed energy distribution of the secondary electrons. Analysing the back scattered secondary electrons using a large collection angle analyser (the angle-integrated results presented in this thesis employed an analyser with a collection angle of typically \( \pm 52^\circ \) around the crystal normal) gives a \( p_j(E) \) which is averaged over the entire Brillouin zone. Using a narrow angle of collection around the crystal normal simplifies the refraction effects at the surface so that \( p_j(E) \) of eq. (4.12) becomes the density of unfilled states along the symmetry line normal to the crystal surface. These angle-resolved measurements therefore can be used to study the unfilled density of states structure and compared with the calculated band structure for the appropriate symmetry line.
4.5 Conclusions

In this chapter we dealt with the possible mechanisms which could contribute to structure in the SEE. It is emphasised that depending on the electronic structure of the material studied one of the above mentioned excitation mechanisms may be largely responsible for the observed fine structure in the SEE. Also the choice of electron analyser affects the results considered. In the next chapter we will examine in detail this fine structure from Ni, W and Al crystals with a view to obtaining information about the electronic band structure of the above mentioned materials.
REFERENCES


5.1 Introduction

In this chapter, the secondary electron spectra of various metals obtained using angle-integrated and angle-resolved techniques are presented. Theories of different contributions to the secondary electron emission (Chapter 4) are applied to the experimental results, in order to identify the origin of the spectral fine structure superimposed on the cascade of the true secondary electrons (Chapter 3). In the case of Ni(100) and W(110) in normal emission angle-resolved spectra, this structure is shown to be related to the one dimensional density of states above the vacuum, whereas in Al(110), (111) and (100) structure due to plasmon decay is observed but no structure is seen due to the one dimensional density of states. The effect of oxygen on the SEE spectrum of Ni(100) was also investigated. A decrease of the original structure was observed.

5.2 Nickel

5.2.1 Experimental

The crystal preparation and cleaning techniques (which also apply to the Al crystals studied in this work) are described in Chapter 2. The experimental set-ups to obtain angle-resolved and angle-integrated secondary electron spectra are shown in figure (2.8) and (2.10) respectively. To measure the angle-
resolved SEE spectrum in the normal emission direction the crystal was first rotated from the normal incidence direction by 10°, the image of the (00) beam was then focused onto the photometer aperture and the crystal was rotated by a further 10° in the same direction.

Since the angle-resolved normal emission experimental data had a poor signal-to-noise ratio an attempt was made at smoothing it using a filtering technique. An existing computer program (Green 1976) was used to smooth the data, equivalent to filtering the experimental data through a low pass filter. Fig. (5.1) illustrates the smoothed and raw data for the clean Ni(100) surface.

![Figure 5.1 Illustration of the smoothed (a) and raw (b) SEE data for a clean Ni(100) surface](image-url)
This filtering approach was however, not found to be particularly useful as all the information is, in fact, contained in the unsmoothed data. Furthermore, termination effects were found to introduce false artefact peaks in the data. For this reason, it was abandoned.

5.2.2 Energy reference

In this work, the kinetic energies of the secondary electrons, $E_s$, are always measured relative to the vacuum level of the analyser. To obtain the energy relative to the Fermi level of the sample, we simply add the work function of the analyser, $\phi_A = 5$ eV (the grid wires are made of stainless steel). This can be seen from fig. (5.2).

![Energy reference diagram for SEE](image-url)
When the sample and retarding grids are not in electrical contact we have the situation shown in fig. (5.2a); when electrical contact is established charge flows until the Fermi levels equalise and we have the situation shown in fig. (5.2b). When \( V_{R} = -V \) volts as shown in fig. (5.2c) any electron just passing the grids will have an energy relative to the sample Fermi level, \( E_{s}^{F} = V + \phi_{A} \).

The primary beam energy is set by applying a negative voltage \( V = -E_{p} \) with respect to earth to the filament of the electron gun. This results in the separation of the Fermi levels of the sample (which is at earth) and the filament by \( E_{p} \) — see fig. (5.3).

![Energy reference diagram for primary electrons](image)

**Figure 5.3** Energy reference diagram for primary electrons

Thus, the vacuum level kinetic energy of the electrons incident on the sample is given by

\[
E_{p_{vac}} = E_{p} + \phi_{o} - \phi_{s}
\]

where \( \phi_{c} \) is the work function of the electron gun filament.
In this work the values are expressed as $E_p$ and have to be corrected by $\phi_c - \phi_A$, which for Al is $0.5$ and for Ni is $1.5$ eV. This correction is only important in calculating Bragg energies or beam emergence conditions.

5.2.3 Results and discussions

Fig. (5.4a) and (5.4b) show the angle-integrated and angle-resolved spectra (in the direction of normal emission) respectively from a Ni(100) crystal at $E_p = 95$ eV.

5.2.3.1. Angle-resolved spectrum of Ni(100)

As can be seen from fig. (5.4b) there is fine structure superimposed on the secondary electron cascade at $E_s = 4.3, 9, 14$ and $\sim 20$ eV (any structure appearing below $E_s = 2$ eV was disregarded as it could have been due to such artefacts as mentioned in Chapter 2) of the angle-resolved SEE spectrum of Ni(100). Since these structures are not present in the angle-integrated spectrum of fig. (5.4a) this indicates that they are due to emission only in the direction of the surface normal, i.e. they are reflecting structure in the one dimensional density of states distribution above the vacuum level as discussed in Chapter 4. Fig. (5.5) compares the spectrum of fig. (5.4b) with the calculated band structure of Szmulowicz and Pease (1978) along the T-X direction of Ni. It can be seen that quite good correspondence is obtained between the positions of the experimental fine structure and the main maxima of the density of unoccupied states - see table (5.1).
Figure 5.4 Comparison of angle-integrated (a) and angle-resolved normal emission (b) SEE spectra of \( \text{Ni}(100) \) at \( E_p = 95 \text{ eV} \).
Figure 5.5 Comparison of normal-emission SEE spectrum of Ni(100) with the calculated band structure.
<table>
<thead>
<tr>
<th>PEAK</th>
<th>SEE</th>
<th>CALCULATED &quot;DOS&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.3</td>
<td>( X_1 ) 9.28</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>( X'_5 ) 14.71</td>
</tr>
<tr>
<td>3</td>
<td>19</td>
<td>( X_3 ) 19.89</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>( X'_1 ) 23.15, ( \Gamma'_2 ) 23.85</td>
</tr>
</tbody>
</table>

Table (5.1) Comparison of secondary electron peak energies with DOS peaks (in eV above \( E_F \))

Work was also performed by Kato et al (1980) using a single-pass cylindrical mirror analyser, but in their experiments the \( \vec{K} \) direction was not as narrowly defined as in our experiment so detailed comparisons are not possible.

Our results together with the calculations of Szmulowicz and Pease show that the additional information obtained with angular resolution in secondary electron energy loss experiments makes SEE spectroscopy an effective technique for the investigation of final densities of states. Further, the use of the angle-integrated mode in conjunction with the angle-resolved mode of operation, enables features due to other loss processes, principally the Auger lines to be separated out.

5.2.3.2 Angle-integrated spectrum of Ni(100)

Typical angle-integrated SEE spectra taken at primary beam energies of 90 and 130 eV from clean Ni(100) are shown in fig. (5.6) and (5.7) respectively. As can be seen from the
Figure 5.6  Angle-integrated SEE spectrum of the Ni(100) surface at $E_p = 90$ eV.

Figure 5.7  Angle-integrated SEE spectrum of the Ni(100) surface at $E_p = 130$ eV.
figures; the SEE spectrum of the Ni surface exhibited a secondary electron cascade peak at about $E_s = 2.5$ eV with 5 shoulders at approximately $E_s = 10.5, 17, 26, 37$ and 54.5 eV. The absence of any energy shift of the above mentioned emissions with different primary energies suggest that these losses are true secondary electrons and not the energy losses of the primary incident electrons. The features at $E_s = 10.5, 17$ and 26 eV cannot be explained in terms of plasmon decay into single electron excitations. Ni(100) has a surface plasmon loss peak at $\Delta E = 7$ and bulk plasmons at $\Delta E = 10$ and 20 eV (as assigned by us and other workers). If these plasmons decay and energy is transferred to the 3d electrons near $E_F$, it will result in secondaries at $E_s = h\omega - \phi_A$ values of 2, 5 and 15 eV ($7-5, 10-5$ and 20-5 respectively) above the vacuum level, showing no correspondence with the observed experimental values stated above. The origin of these peaks is uncertain. Peaks at the energies of the order of 10 eV have been reported by Holloway and Hudson (1975) from Ni. Seah (1969) has observed them from Ag and Cu and interpreted them as being due to surface related excited states. Benndorf et al (1978) have reported peaks at $E_s = 13, 18$ and 25 eV from Cu and concluded that the interpretation of these results was not possible using the available data. It seems likely that the group of peaks observed from Cu at $E_s = 13, 18$ and 25 eV will have the same origin as the group of peaks in Ni at $E_s = 10.5, 17$ and 26 eV as they are adjacent elements in the periodic table and have broadly similar band structure.

The feature at 54.5 eV is assigned to the $M_{23} M_{45} M_{45}$ Auger transition. Using the formula of Chung and Jenkins (1970) where
\[ E_{xy} = E_v - E_x' - E_y' \] .. (5.1)

and where \( E_v \) is the binding energy of the electron ejected from the \( v \) shell of the atom by the incident beam,

\[ E_x' = \frac{[E_x(z) + E_x(z+1)]}{2}, \quad E_y' = \frac{[E_y(z) + E_y(z+1)]}{2} \] .. (5.2)

\( E_x(z) \) and \( E_x(z+1) \) are the atomic binding energies for the \( x \)-shell electron in atoms having atomic numbers \( z \) and \( z+1 \) respectively. \( E_y(z) \) and \( E_y(z+1) \) are the same for the \( y \)-shell electron. Using eq. (5.1) Coghlan and Clausing (1973) arrived at a value of \( E_\theta = 57 \) eV for the \( M_{23} M_{45} M_{45} \) Auger transition with respect to the vacuum. The simple estimate deviates by 2.5 eV from our experimental value. Baro et al's (1975) experimental result deviates by 3.5 eV from the Coghlan and Clausing value. They suggest that the Auger spectrum of Ni and other metals with narrow d bands is "atomic-like" related to the presence of a double hole at the valence band level in the final state along with the existence of a hole on the same atom in the initial state and this explains the deviation. Using Coghlan and Clausing's tables we also assign the broad loss at \( E_\theta = 37 \) eV to an \( M_1 M_{23} M_{45} \) Auger transition.

5.2.3.3 Application of LEED reflectivity data to SEE from Ni(100)

The fine structure superimposed on the cascade of true secondary electrons of Ni(100) was analysed in terms of Feder and Pendy's (1978) theory of Angle-Resolved Secondary Electron Spectroscopy "ARSES" (Chapter 4). The measured ARSES were compared with
Feder and Pendry's formula \( N(E) = C(E) \cdot (1 - R(E)) \) (where \( C(E) \) is a function describing the slow electron cascade) using the reflection coefficient, \( R(E) \), as measured by Andersson and Kasemo (1970). Several different cascade \( C(E) \) functions were tried, of which Seah's (1969) cascade function (Chapter 3)

\[
C(E) = \frac{1}{(E_0 + 4.5)^x} \frac{E_0}{(E_0 + 0.35)^x} = \frac{1}{(E_0 + \phi_s)^x} \frac{E_0}{(E_0 + \chi)}
\]

(5.2)
gives the most reasonable fit to experiment. The parameters \( x \) and \( \chi \) in Seah's formula were fitted such that the cascade curve always remained greater than \( N(E) \) (since \( T = 1 - R(E) \) \( \frac{N(E)}{C(E)} < 1 \)). The values thus found are \( x = 1.4 \) and \( \chi = 1.5 \).

In order to compare the final state structure with the reflection coefficient measurements, the experimental data \( N(E) \) has been divided by the cascade function of Seah, so that the resulting experimental fine structure can be compared to the corresponding \( (1 - R(E)) \) results of Andersson and Kasemo where \( R(E) \) is the specular elastic reflection coefficient measured at normal incidence. The results for clean Ni(100) do not exhibit clearly identifiable fine structure and any apparent structure was found to be partly due to the choice of cascade function. Comparison of our results with the results of Andersson and Kasemo thus do not provide backing for the theory of Feder and Pendry.

5.3 Oxygen Adsorption on Ni(100)

5.3.1 Experimental
Exposures were made at an oxygen partial pressure of $5 \times 10^{-8}$ mbar. The background pressure was $1 \times 10^{-10}$ mbar at the beginning of the experiment, rising to $5 \times 10^{-10}$ mbar at the end. An ordered $p(2 \times 2)$ pattern was seen for exposures up to 60 Langmuirs (i.e. 1200 sec at $5 \times 10^{-8}$ mbar) then a $c(2 \times 2)$ pattern at 80 L followed by a pattern with extra diffraction spots above 100 L which were attributed to NiO nucleation and island growth. Our coverages to obtain the $p(2 \times 2)$ overlayer were higher than noted by other studies. This may have resulted from errors in our pressure measurement inlet system. Realistic sample exposures are, however, particularly difficult to obtain, especially in the case of systems pumped dynamically during exposure as in our experiments. The identification of each overlayer structure was performed by LEED.

5.3.2 Results and Discussions

5.3.2.1. Angle-integrated spectra

Typical angle-integrated spectra taken at a primary beam energy of 147 eV from a clean and oxygen covered Ni(100) with successive oxygen exposures of 40, 50 and 80 Langmuirs are shown in fig. (5.8). Exposure of the sample to oxygen resulted in changes in the SEE spectra but no prominent new features could be seen. The secondary cascade peak decreased slightly. In no case was a significant shift in the positions of the low energy secondary peaks at $E_g = 10.5, 17$ and 26 eV observed. Moreover, the amplitudes of these secondary peaks decreased quite uniformly with increasing exposure. It seems unlikely that
Figure 5.8 SEE spectra obtained with a primary beam energy of 147 eV for clean Ni at increasing exposures to oxygen.
these features could be explained in terms of volume effects since these would not be sensitive to the oxygen coverages used here. Since surface states are very sensitive to gas adsorption or contamination these peaks may be related to surface states. This is a necessary but not sufficient condition for classification of a peak as due to a surface state. So oxygen adsorption measurements did not help us in the identification of the clean surface fine structure. On exposure to oxygen the \( M_{23} M_{45} M_{45} \) Auger transition diminished in intensity and became less apparent due to the rising secondary background see fig. (5.8). The behaviour of the \( M_1 M_{23} M_{45} \) transition during oxidation is not understood, again due to its very low intensity and high-secondary background.

5.3.2.2 Angle-resolved spectra

To see the effect of the adsorption of oxygen on the clean Ni(100) surface, in fig. (5.9) the clean angle-resolved spectrum of fig. (5.4b) is compared with that obtained by the adsorption of a half a monolayer of oxygen. On exposure to oxygen most of the original structure is removed. So the effect of final density of states on the spectra is apparently being smoothed out by the adsorbate layer.

5.3.2.3 Correlation with LEED reflectivity data

Experimental fine structure spectra were found to be relatively insensitive to the cascade function used. Fig. (5.10) shows the SEE distribution curve for \( E_p = 95 \) eV of fig. (5.9) from \( c(2 \times 2)0 \) on
Figure 5.9 Comparison of the angle-resolved normal emission spectrum of clean Ni(100) with that of c(2 x 2)O on Ni(100) at $E_p = 95$ eV.
Figure 5.10 Normal-emission SEE spectrum at $E_s = 95$ eV for $c(2 \times 2)0$ on Ni and background cascade curve due to the theory of Seah.
Ni with the Seah's cascade fit. In fig. (5.11) the experimental fine structure spectrum and \((1 - R(E))\) function of Andersson and Kasemo (1973) (see ref. Andersson et al. 1973), are plotted. The agreement is seen to be good with respect to the energy positions of the peaks. The shape of the hollow at very low energies in the \((1 - R(E))\) data is exhibited fairly well in the fine structure data and the peaks at \(E_g = 6.5\) and 16 eV are reproduced. The reflection coefficient \(R(E)\) exhibits a variation of 6% in going from the minimum at 6.5 eV to a maximum at around 11.5 eV. A similar variation of about 6-7% is reflected in the experimental fine spectrum but since the signal to noise ratio is poor, nothing much can be said except that there is a reasonable agreement. One problem of special significance in this work, especially when comparing data with \(R(E)\) measurements at low energies, is that work function changes in the electron gun cathode during adsorption have an effect on the LEED gun emission current and energy as discussed by Demuth and Rhodin (1974) so the \(R(E)\) data at low energies may not be very reliable.

5.4 Tungsten

Studies were also made of emission of true secondary electrons from the W(110) surface in collaboration with Dhanak (1983) (for the crystal preparation and cleaning techniques see Dhanak 1982) and correlated with the one-dimensional density of final states function along the corresponding symmetry line.

The energy distribution spectrum of secondary electrons emitted
Figure 5.11 The experimental fine structure spectrum and $1 - R(E)$ function from Ni(100) at normal incidence due to Anderson and Kasemo (1973)
normal to the W(110) surface at $E_p = 107$ eV is shown in fig. (5.12) in comparison with the calculated density of states and the energy bands of Christensen and Feuerbacher (1974) and Feuerbacher and Christensen (1974) for the W(110) symmetry direction. It can be seen that the separation and position of the peaks agree very well with the calculations. The dip between the pair of low energy peaks at $E_g = 1.5$ and 6 eV above the vacuum level is quite deep indicating the existence of a band gap. So the above mentioned peaks are attributed to emission from the regions of high density of states either side of a band gap in the (110) direction as predicted by the calculations of Christensen and Feuerbacher. Fine structure at high energies also show some correspondence with the predicted density of states indicating the usefulness of the angle-resolved normal emission SEE measurements for investigating the high density of states regions above the vacuum level. In fig. (5.13) the spectrum of fig. (5.12a) is compared with the results of Willis et al (Willis 1974, Willis and Christensen 1978 and Christensen and Willis 1979) using the two band gap peaks for alignment of the two spectra. Comparing the energy position of the peaks the correspondence is very good. The peaks A and B of Willis et al's results coincide quite well with those of our results ($E_g = 1.5$ and 6 eV). The energy positions of the structure at C, E, F and G agree well with those of the structure observed in our results. The additional emission peak D observed by Willis et al does not seem to appear in the present results. Although there is a very good agreement concerning the
Figure 5.12 SEE distribution curve normal to a W(110) surface (a) with the calculated density of states along ΓN (b).
Figure 5.13 Comparison of our SEE distribution curve normal to the W(110) surface with that of Willis (1978).
energy positions of the fine structure features the shape of the cascade of the two curves is completely different and the cascade maximum in SEE in their results appears at 18 eV. It is known that the secondary cascade peak (due to electrons emitted from the solid as a result of multiple inelastic processes) has a maximum value at an energy of a few electron volts. In this work it was reasonably certain that there were no artefacts due to stray fields, and stray secondaries especially at $E > 7$ eV (LEED superstructure patterns were perfect in symmetry even at 10 eV). Thus it seems likely that Willis et al's spectrum suffers seriously from instrumental effects.

5.5 Aluminium

Angle-integrated and angle-resolved spectra of Al(100), (110) and (111) surfaces.

Figures (5.14, 15 and 16) present SEE spectra for different primary beam energies from the Al(100), (111) and (110) surfaces respectively. The two prominent peaks at $E_g = 5$ and 10 eV are common to all spectra indicating that these structures are independent of the primary beam energy and the crystal orientation. The energy at which these structures appear and their shape is in good agreement with the previous results obtained with the same type of analyser. Several interpretations have been proposed to account for the origin of these structures. Here we attribute the $E_g = 5$ and 10 ev peaks to a decay of the Al surface and volume plasmon into single electron excitations respectively. The Al volume plasmon loss is at 15.3 eV. If this decays and energy
Figure 5.14 Angle-integrated SEE spectra of Al(100) at different primary energies.
Figure 5.15 Angle-integrated SEE spectra of Al(111) at different primary energies.
Figure 5.16 Angle-integrated SEE spectra of Al(110) at different primary energies.
is transferred to the electrons at the Fermi level it will result in secondaries at \( E_s = \hbar \omega_p - \phi_A = 15.3 - 5 = 10.3 \text{ eV}. \)

Similarly surface plasmon decay will give structure in SEE at \( \hbar \omega_s - \phi_A = 10.6 - 5 = 5.5 \text{ eV}. \)

As is suggested by Henrich (1973) (Chapter 4) there could be another mechanism where excited secondary electrons lose energy in a plasmon excitation process which would exhibit discontinuities in slope at kinetic energies of \( \hbar \omega_p - \phi_A \) and \( \hbar \omega_s - \phi_A \). Looking at the spectra it is obvious that SEE spectrum exhibits humps rather than discontinuities in slope. So these results tend to disagree with Henrich's model.

These features could not be attributed to an Auger like mechanism since electrons arising from the Auger decay of Al core level states do not have energies in this low energy range. The fine structure appearing in the Al SEE spectrum cannot be attributed to final state effects (excitation of valence electrons into high lying empty states) since there is not an enhanced density of states at \( E_s = 10 \) and \( 15 \) eV above the Fermi level (Connolly 1970). At this stage the correlation between the secondary electrons and the characteristic energy loss spectrum of electrons reflected from Al checked. Fig. (5.17a, b) shows the plot of the surface plasmon loss intensity and the secondary current at \( E_s = 5 \text{ eV} \) and fig. (5.17c, d) shows the plot of the bulk plasmon loss intensity and the secondary current at \( E_s = 10 \text{ eV} \) as a function of primary beam energy for Al(100). Similarly figures (5.18) and (5.19) show
Figure 5.17(a,b) Surface plasmon loss intensity (a) and secondary current at $E_s = 5$ eV (b) (both normalized to the elastic peak height) as a function of $E_p$ from Al(100).
Figure 5.17(c,d) Bulk plasmon loss intensity (c) and secondary current at $E_s = 10$ eV (b) (both normalized to the elastic peak height) as a function of $E_p$ from Al(100).
Figure 5.18(a,b) Surface plasmon loss intensity (a) and secondary current at $E_p = 5$ eV (both normalized to the elastic peak height) as a function of $E_p$ from Al(110).
Figure 5.18(c,d) Bulk plasmon loss intensity (c) and secondary current at $E_s = 10 \text{ eV}$ (d) (both normalized to the elastic peak height) as a function of $E_p$ from Al(110).
Figure 5.19(a,b) Surface plasmon loss intensity (a) and secondary current at $E_s = 5$ eV (both normalized to the elastic peak height) as a function of $E_p$ from Al(111).
Figure 5.19 (c,d) Bulk plasmon loss intensity (c) and secondary current at $E_s = 10$ eV (b) (both normalized to the elastic peak height) as a function of $E_p$ from Al(111).
the correlation for Al(110) and (111) surfaces respectively. As can be seen a good correlation was obtained and this is interpreted as extra evidence that these peaks are due to plasmon decay giving rise to structure in the SEE spectrum.

Fig. (5.20) shows the angle-resolved SEE spectra of Al(111) (100) and (110) in the direction of normal emission at $E_p = 75$ eV. As can be seen they are similar to the angle-integrated spectra, and do not exhibit any extra structure, indicating that there is not much structure in the density of states just above the vacuum level. This is, in a way, expected for nearly-free electron like materials such as Al. The only structure obtained in these spectra is that due to plasmon decay which is the dominant excitation mechanism.

5.6 Artefacts due to insulators in SEE

At this point we would like to stress that any insulators which are exposed to either the incident electron beam or the scattered electrons can result in distortion of the secondary electron spectrum due to charging of the insulators. Previously the SEE experiments from Al were done using a different crystal mounting where alumina washers were used to insulate the crystal. These insulators become charged affecting the trajectories of the electrons at low energies and hence the low energy secondary region of the spectrum as shown in fig. (5.21) for the three low index faces of Al. The other spectra presented in this thesis were obtained with a different set up where there were no insulators involved and are believed to be unaffected by artefacts.
Figure 5.20. Angle-resolved normal emission SEE spectra of Al(111), (100) and (110) surfaces at $E_p = 75$ eV.
Figure 5.21. Structure due to artefacts in the SEE spectra of Al(100), (110) and (111) surfaces.
5.7 Conclusions

This chapter has shown that SEE spectroscopy can be used to investigate the band structure of materials. In the case of Ni, a comparison of angle-integrated with angle-resolved SEE spectra enabled us to identify features in electron emission in the direction of the crystal normal as due to structure in the final densities of states above the vacuum level. This is in good agreement with the calculations of Szmulowicz and Pease. Thus our results provide evidence that the fine structure on SEE spectrum of Ni is due to fine structure in the one-dimensional density of states. On oxygen exposure, Ni SEE spectra did not produce any new structure due solely to Oxygen. The main effect of oxygen on Ni was to eliminate most of the fine structure of clean Ni. The theoretically expected correlation between the fine structure of SEE spectra and LEED reflectivity measurements was not found to hold for clean Ni while for oxygen adsorbed on Ni there was a good correlation with respect to the energy position of the peaks.

In W for the $(110)$ direction, the SEE spectrum is compared with the calculated density of states of Christensen and Feuerbacher. Very good agreement is obtained with the experimental results for the two band gap peaks and the fine structure at higher energies. Comparing our results with those of Willis et al again shows good agreement with the band gap peaks and their high energy features agree well with the present results despite his instrumental problems which led to an unrealistic secondary cascade peaking at 18 eV.
Altogether, our results on Ni and W provide good evidence that the SEE peaks of many transition metals are band-like in origin and give valuable information on the density of final states. Thus the angle-resolved technique highlights the features due to final densities of states above the vacuum level and can help to check the accuracy of band structure calculations.

In conclusion, the combination of angle-integrated and angle-resolved-normal emission techniques can usefully be applied in SEE on other materials and the assignment of the low energy secondary electron emission features can be made. Once the structure due to final densities of states have been identified the remaining features due to Auger features or the other losses can be examined.

Finally, we showed that, in the case of the free electron-like metal, Al, the plasmon decay mechanism dominates the structure in SEE of Al.
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CHAPTER 6

ELECTRON ENERGY LOSS SPECTROSCOPY

6.1 Introduction

In chapter 3 we presented a typical energy spectrum for low energy electrons scattered from a solid (see fig 3.1). In this and the next chapter we will consider the processes giving rise to peaks in region II, \( \Delta E = \hbar \omega = 1\text{–}30 \text{ eV} \). Peaks in this region are due to single particle and collective oscillations.

Single particle excitations: The incident beam excites electrons from occupied to unoccupied states in the same band (intraband excitations) or in a different band (interband excitations).

Collective oscillations: Bohm and Pines (1953) considered the long range Coulomb interaction of the conduction electrons in metals and showed that collective oscillations analogous to the plasma oscillations observed in gas discharges could occur. They named these oscillations "plasmons". They calculated the frequency for long wavelength \( q = 0 \), plasmons in a free electron gas to be

\[
\omega_p = \sqrt{\frac{ne^2}{mc_0}}
\]

where \( n \), \( e \), \( m \) are the electron density, electronic charge and electron mass respectively, \( c_0 \) is the permittivity of free space.

The plasmon has a dispersion \( \omega(\vec{q}) \) given by Ferrell (1957) as

\[
\omega^2(\vec{q}) = \omega^2_p + q^2 < \gamma^2 > + \frac{q^2 (\Delta \gamma^2)^2}{\omega_p^2} + \frac{\hbar^2 q^4}{4m^2} + ...
\]

\( \text{.. (6.2)} \)
where $V_F$ is the velocity of an electron at the Fermi level.

There is a cut-off wave vector, $q_c$, above which the concept of collective oscillations of electrons breaks down. This is given by

$$q_c = \frac{\omega_p}{V_F} \quad \ldots (6.4)$$

and above this value the plasma oscillations are heavily damped.

The only theory available to describe quantitatively the inelastic scattering of low energy ($\sim 100$ eV) electrons by these excitations in real solids is the dielectric theory of energy losses, which has also been used so successfully in describing the inelastic scattering of high energy ($\sim 10$ keV) electrons.

In this chapter we discuss the dielectric theory of inelastic scattering and introduce the concept of loss functions to describe energy loss spectra. We will also see in this chapter that for these electronic excitations the probability of scattering of the incident electrons is strongly peaked in the forward direction i.e. $q$, the momentum transfer in the process is small, $\ll |q|$. This means that elastic scattering by the lattice and the inelastic scattering by the phonons has to be taken into account before information on the energy loss processes can be found as is discussed in the next chapter. As a result of the limited penetration of the electron wavefield into the solid we have to consider both bulk and surface excitations.
6.2 Dielectric theory of energy losses

Hubbard (1955) and Frohlich and Pelzer (1955) showed that the dielectric theory could be used to describe the elastic scattering of high energy (10 keV) electrons by solids. The complex optical dielectric constant \( \varepsilon(\omega) \) can be determined from light reflection measurements by means of Kramers-Kronig Analysis (K.K.A.). \( \varepsilon(\omega) \) represents the response of a solid to a transverse electro-magnetic field and can be shown to be identical with the longitudinal dielectric constant, \( \varepsilon_{\text{long}}(\sigma, \omega) \) which represents the response of a system to a longitudinal electric field (the Coulomb field of the incident electron). In the dielectric theory the differential cross section for the inelastic scattering of an electron with an energy change \( \Delta E = h\omega \) and a momentum transfer \( \hbar q \) is given by Frohlich and Pelzer as

\[
\frac{\Delta^2 \sigma}{\Delta \omega \Delta \Omega} = \frac{1}{2\pi^2 n a_o} \frac{1}{E_p} \frac{1}{\theta^2 + \frac{E^2}{E_p}} \text{Im}(-\frac{1}{\varepsilon(\omega)}) \quad \ldots (6.5)
\]

where

\( n \) is the number of electrons per unit volume and \( a_o \) is the Bohr radius.

\[
q^2 = q_\perp^2 + q_\parallel^2 = \frac{K^2}{E_p} (\theta^2 + \frac{E^2}{E_p})
\]

with

\[
|q_\perp| = |K_p| \theta
\]

and

\[
|q_\parallel| = \frac{\hbar \omega}{2E_p} \quad \text{See Fig (6.1)}
\]

\[
\theta_E = \frac{\hbar \omega}{2E_p}
\]
Figure 6.1 Scattering geometry of inelastically scattered electrons

$K_p$: incident wave vector
$K_s$: scattered wave vector
$q$: excited plasmon wave vector

In Fig (6.2) $\frac{\partial^2 \sigma}{\partial \Omega \partial \Omega}$ is plotted as a function of $\theta$ for

Arbitrary units

$\theta_E = \frac{10}{2 \times 100}$

$\theta_E = \frac{10}{2 \times 10,000}$

Figure 6.2 Plot of $\frac{\partial^2 \sigma}{\partial \Omega \partial \Omega}$ as a function of $\theta$ for different $\theta_E$.
$E_p = 100 \text{ eV and } 10 \text{ keV and } \bar{\hbar} \omega = 10 \text{ eV}$ to show angular variation of the inelastic scattering. From this figure we see that the probability of inelastic scattering is concentrated in a small angular range $\approx \theta_{\text{E}}$ around the forward direction.

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) \quad \ldots (6.6)$$

$$\Im(-i) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega) + \varepsilon_2(\omega)} \quad \ldots (6.7)$$

$\varepsilon(\omega)$ describes the individual properties of the metal $\Im(-\frac{i}{\varepsilon})$ is called the volume loss function; peaks in the loss function arise from single particle and collective oscillations (plasmons).

### 6.3 Value of the plasmon frequency

The dielectric constant for an electron gas of density $n$ and relaxation time $\tau$ is given by

$$\varepsilon(\omega) = \varepsilon_1 + i \varepsilon_2 = 1 - \frac{\omega_p^2}{\omega(\omega + \frac{\omega_p^2}{\tau})} \quad \ldots (6.8) \text{(Raether, 1965)}$$

with

$$\varepsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2} \frac{1}{1 + (\frac{\omega_p}{\omega \tau})^2} \quad \ldots (6.9)$$

$$\varepsilon_2(\omega) = \frac{1}{\omega \tau} \frac{\omega_p^2}{\omega^2} \frac{1}{1 + (\frac{\omega_p}{\omega \tau})^2} \quad \ldots (6.10)$$

In the dielectric theory, solution of $\varepsilon(\omega) = 0$ gives the plasma frequency $\omega$, where
\[ w = w_1 + \omega_2 \quad \text{(6.11)} \]

with

\[ \omega_1^2 = \frac{\omega_p^2 (1 - \frac{1}{2\omega_p \tau})}{(2\omega_p \tau)^2} \quad \text{(6.12)} \]

\[ \omega_2 = -\frac{1}{2\tau} \quad \text{(6.13)} \]

If damping is neglected, \( \omega_p \tau \gg 1 \), then \( \omega_2 = 0 \) so \( \omega_1 = \omega_p \)
which is the same as the classical frequency. Here \( \omega_2 \) describes
the damping of the excitations.

The loss function \( \text{Im}(-\frac{1}{\varepsilon(w)}) \) which is zero for \( w = 0 \) and \( w = \infty \)
reaches a maximum at \( w = \omega_p \) or \( \varepsilon_1(w) = 0 \) (volume plasmon)
when \( \varepsilon_2(w_p) = 0 \). Its energy half width \( \Delta E^\frac{1}{2} \) is given by \( \Delta E^\frac{1}{2} = \frac{\hbar}{\tau} \)

Fig (6.3) gives the characteristic frequency dependence of \( \varepsilon_1, \varepsilon_2 \)
and \( \text{Im}(-\frac{1}{\varepsilon}) \).

![Graph](image)

**Figure 6.3** \( \varepsilon_1 \) and \( \varepsilon_2 \) and \( \text{Im}(-\frac{1}{\varepsilon}) \) as a function of \( w \) for
a free electron gas.
5.4 Single electron excitations and real metals

The model described above is an approximation since in general the electrons are bound to the crystal and this affects the dielectric constant. Taking single particle excitations into account modifies the real and imaginary parts of the dielectric constant as follows (Following Pines 1963)

\[
\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \tau^{-2}} - \frac{e^2}{\varepsilon_0 m} \sum_{l} \frac{F_{ll'}}{\omega - \omega_{ll'}}, \quad ..\ (6.14)
\]

\[
\varepsilon_i(\omega) = \frac{\omega_p^2}{\omega \tau} \frac{1}{\omega^2 + \tau^{-2}} + \frac{e^2}{2\varepsilon_0 m} \sum_{l} \frac{F_{ll'}}{\omega_{ll'}} \delta(\omega - \omega_{ll'}), \quad ..\ (6.15)
\]

where

\[
\omega_p = \sqrt{\frac{n_e e^2}{\varepsilon_0 m^*}} \quad ..\ (6.16)
\]

is the conduction band plasma frequency

\[n_e\text{ the conduction band electron density,} \]
\[m\text{ the free electron mass,} \]
\[m^*\text{ the optical mass of the conduction electrons,} \]
\[\tau\text{ the frequency dependent relaxation time,} \]
\[F_{ll'}\text{ the oscillator strength for transitions between states } l \text{ and } l' \text{ and} \]
\[\omega_{ll'}\text{ is the oscillator frequency} \]

Equations (6.14) and (6.15) may be written in the form

\[
\varepsilon_r(\omega) = \varepsilon_r^{(p)} + \delta\varepsilon_r^{(b)} \quad ..\ (6.17)
\]
\[ \varepsilon_2(w) = \varepsilon_2^F + \delta \varepsilon_2^{(b)} \] \hspace{1cm} \text{(6.18)}

which separates the contribution to \( \varepsilon_1 \) and \( \varepsilon_2 \) due to interband transitions characterised by an effective mass, \( m^* \), and life time \( \tau \), i.e.

\[ \varepsilon_2^F(w) = 1 - \frac{w_p^2}{w(w + \frac{1}{\tau})} \] \hspace{1cm} \text{(6.19)}

from that \( \delta \varepsilon^{(b)} \), due to the interband transitions. The solution of \( \varepsilon_2(w) = 0 \) leads to a plasma frequency

\[ w_{p2} = \frac{w_p}{\sqrt{1 + \delta \varepsilon_1^{(b)}(w_p)}} \] \hspace{1cm} \text{(6.20)}

i.e. in the presence of single particle excitations the position of the plasmon peak in the loss function is shifted relative to its position in a free electron metal.

6.4.1 Plasmon frequency shifts

Examples of plasmon frequency shifting in real metals are given below.

i. SILVER: The real and imaginary parts of the dielectric constant and the loss function \( \text{Im}(\frac{1}{\varepsilon(w)}) \) for Ag is shown in fig (6.4) (Ehrenreich and Philipp 1962). At low frequencies \( \varepsilon_2 \) falls off rapidly in the intraband region, then rises due to the onset of interband transition at \( \hbar \omega_c = 3.9 \text{ eV} \). Fig(6.5) shows the division of the experimental values of \( \varepsilon_2(w) \) into free and interband contributions \( \varepsilon_2^F \) and \( \delta \varepsilon_2^{(b)} \) respectively. As can be
Figure 6.4 The real and imaginary parts of the dielectric constant and the loss function \( \text{Im} - \frac{1}{\varepsilon} \) for Ag.

Figure 6.5 Decomposition of the experimental values of \( \varepsilon_1 \) for Ag into free \( \varepsilon_1(F) \) and bound \( \varepsilon_1(b) \) contributions.
seen, in the absence of interband transitions, one would have 
\[ \varepsilon_1(\omega) = 0 \] at \( \omega_{pl} = 9.2 \text{ eV} \). The interband transitions cause 
the zero to be reduced to a value slightly below \( \omega_c = 3.9 \text{ eV} \), 
where \( \varepsilon_2 \) is also small and there is a sharp peak in the energy 
loss spectrum (see fig 6.4) at this energy. Thus conditions for 
plasma resonance are satisfied. This resonance results from the 
cooperative behaviour of both the d and the s electrons. The 
second peak in \( \text{Im}\left(-\frac{1}{\varepsilon}\right) \), at 7.5 eV, where \( \varepsilon_1 \) and \( \varepsilon_2 \) are both 
small, represents the free s electron plasma resonance lowered in energy 
from the free electron value due to strong interband transitions 
at higher energies.

ii ALUMINIUM: The real and imaginary parts of the dielectric 
constant \( \varepsilon_1 \) and \( \varepsilon_2 \) and the bulk loss function, \( \text{Im}\left(-\frac{1}{\varepsilon}\right) \) for 
Al, is plotted in fig (6.6) (Ehrenreich et al 1963). \( \varepsilon_2(\omega) \)

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure66.png}
\caption{The dielectric constant and the bulk loss function for Al.}
\end{figure}
exhibits a peak at 1.5 eV and has no further structure at high energies. At very low frequencies it is possible to separate $\varepsilon'(\omega)$ from $\delta\varepsilon^{(b)}(\omega)$ since the interband transitions which give the peak in $\varepsilon_2(\omega)$ do not set in until about 1 eV. So, in this frequency range, $\delta\varepsilon_1^{(b)}$ and $\delta\varepsilon_2^{(b)}$ are negligible. Extrapolating the data from this region gives $\hbar\omega_{p1} = 12.7$ eV in the absence of interband transitions. However, a small peak in $\varepsilon_2$ at 1.5 eV due to an interband transition influence the position of the plasma loss by the term $\delta\varepsilon_1^{(b)}$ which has a value $-0.3$, near the plasma resonance - see fig (6.7), so the resulting plasma frequency is $\hbar\omega_{p2} = 15$ eV in agreement with the maximum in the energy loss function.

![Figure 6.7](image_url)  
**Figure 6.7** The real part of $\delta\varepsilon^{(b)}$ for Al.
iii. NICKEL. Fig (6.8) shows the real and imaginary parts of the dielectric constant and the loss function for Ni from 3 to 24 eV. (Wehse and Arakawa 1969). The band calculations for Ni predict the presence of interband transitions down to very small energies due to the d band crossing the Fermi level. Therefore it is not possible to separate the free electron contributions $\varepsilon^F$ from the bound electron contributions $\delta\varepsilon^{(b)}$ of the dielectric constant as for Ag. Thus the combined effects of free and bound electron behaviour have to be taken into account when the optical data is interpreted. The energy loss function $\text{Im}(\frac{-1}{\varepsilon})$, shows two peaks at 10 and 20 eV and the behaviour of $\varepsilon_1$ and $\varepsilon_2$ in this range indicates that these peaks are associated with the plasma resonance. The 10 ev loss may also be due to parallel band transition as explained in chapter 8.

![Figure 6.8 Dielectric and loss functions of Ni](image-url)
6.5 Surface excitations

Ritchie (1957) showed that when the boundary conditions at the interface between two media are taken into account surface modes of the collective oscillations are possible and are called "surface plasmons".

When the dielectric theory is applied to the problem of surface losses a factor, \( \text{Im}\left(-\frac{1}{\varepsilon + i}\right) \), the surface loss function enters into the expression for the inelastic scattering cross section. Quantum mechanical treatment of the dielectric theory of energy losses due to surface plasmons excited outside the solid for low energy electrons is given by Mills (1975) as

\[
\frac{d^2\sigma}{d\Omega d\omega} = |\beta|^2 \frac{m_e^2}{2\pi \cos \theta_i} \frac{K_s}{K} \cdot \frac{1}{q^2} \ p(q_n, \omega)
\]

where \( K \) is the incident wave vector,
\( K_s \) the scattered wave vector,
\( \theta_i \) the incident angle,
\( q_n \) the momentum parallel to the surface and
\( |\beta|^2 \) is a factor taking into account contributions from single and two step inelastic scattering (see next chapter).

The function \( p(q_n, \omega) = \frac{2q_n}{\pi} \ \text{Im}\left(-\frac{1}{\varepsilon + i}\right) \quad (6.22) \)

\( \text{Im}\left(-\frac{1}{\varepsilon + i}\right) = \frac{\varepsilon_2}{(\varepsilon_1 + 1)^2 + \varepsilon_2^2} \quad (6.23) \)

exhibits a maximum when \( \varepsilon_2 \) is small and \( \varepsilon_1 = -1 \).
6.5.1 Value of the surface plasmon frequency

Consider a semi-infinite free electron metal with dielectric constant \( \epsilon_s \), bounded by a material of dielectric constant \( \epsilon_o \). From the continuity of the normal component of the electrical displacement, \( d \), at the boundary one arrives at the relation

\[
\epsilon_o = -\epsilon_s
\]  

.. (6.24)

For a free electron gas (\( \epsilon = 1 - \frac{\omega^2}{\omega_p^2} \)) the frequency of the surface oscillations, \( \omega_s \), using eq. (6.8) is given by

\[
\omega_s = \frac{\omega_p}{\sqrt{1 + \epsilon_o}}
\]

.. (6.25)

where \( \omega_p \) is the volume plasma frequency of the semi-infinite medium. In the case of the plasma bounded by vacuum eq. (6.25) reduces to

\[
\omega_s = \frac{\omega_p}{\sqrt{2}}
\]

.. (6.26)

it can be seen from eq. (6.25) that with a dielectric constant \( \epsilon_o > 1 \), the surface plasmon frequency is lower than \( \omega_s \).

As an example of the effect of chemisorption on the surface excitation spectrum, Ibach and Rowe (1974) measured the energy loss spectra of Si(III) crystal at \( \hbar \omega_p = 100 \) eV for different oxygen coverages which is shown in fig (6.9). Losses due to bulk and surface interband transitions are indicated by E and S respectively. During oxygen absorption the intensities of \( S_1 \) and \( S_3 \) decrease, while the intensity of \( S_2 \) seems to increase, suggesting that the \( S_2 \) loss corresponds
probably to transitions involving surface states as well as to oxygen related transitions. They explained quantitatively the splitting of the surface plasmon loss peak and their shift with increasing oxygen coverage by a model of a single oscillator discussed by Wilson (1960). They have taken the dielectric constant as the sum of two contributions namely a free electron gas and a single oscillator. Representing the dielectric constant of Si as

$$
\varepsilon_{Si} = 1 - \frac{\omega_p^2}{\omega^2}
$$

and oxygen transition by

Figure 6.9 Energy loss spectrum from Si(111)
\[ \varepsilon(\omega) = \varepsilon^* + \varepsilon^0 \]

where \( \hbar \omega_p = 15 \text{eV} \)

and \( \sigma \) is the oscillator strength of the oxygen associated transition which is assumed to be increased with increasing oxygen coverage \( \theta \). \( \omega_o \) is the oxygen transition frequency and \( \Gamma \) is the broadening parameter.

The calculated values of the real and imaginary parts of \( \varepsilon(\omega) \) and the surface loss function for \( \sigma = 0.3, \theta = 1, \Gamma = 1 \) \text{eV} and \( \hbar \omega_o = 11 \) \text{eV} is shown in fig (6.10). As can be seen an oxygen transition around 11 eV can explain the observed shift of the surface plasmon to lower energy values.

Figure 6.10 Dielectric and surface loss function of free electron gas + single oscillator
6.6 Conclusions

In this chapter we have seen how the dielectric theory which has been used so successfully in high energy loss experiments can also be used to interpret the results of low energy electron loss experiments. The content of this chapter will be used to discuss the energy losses from Ni in Chapter 8.
REFERENCES


CHAPTER 7

INELASTIC SCATTERING AND ELASTIC SCATTERING EFFECTS

7.1 Introduction

In the previous chapter we discussed the basic theory of inelastic scattering in solids, and in this chapter we consider how inelastic scattering information (on collective and single particle excitations and their dispersions) can be extracted from energy loss spectra. From chapter 6 we see that the momentum transfer $\hbar \Delta q$ in inelastic excitation is small (i.e., $\Delta q \ll q$) so the electrons observed in a back reflection experiment must also have been elastically scattered by the lattice (or inelastically scattered by phonons which with the energy resolution of typical experiments is unresolved from the elastic scattering). This scattering has two consequences:

i. Peak positions in the energy loss spectra can be influenced by diffraction and this has to be taken into account when analysing these spectra.

ii. The inelastically scattered intensity is concentrated around the direction of the diffracted beam.

7.2 Two step process of inelastic scattering

Davisson and Germer (1927) using the retarding potential method observed inelastic scattering in the directions of the diffracted beams and suggested that the observed intensity was due to a two step process "DL" consisting of diffraction of the incident electrons followed by inelastic scattering of the reflected electrons as they left the Ni(111) crystal used in their experiments. Later Turnbull and Fransworth (1938) studied the energy distribution of electrons inelastically scattered from an Ag(111) crystal. Their
experimental results showed the existence of another two step process "LD" in which the primary electrons are first inelastically scattered in the forward direction, and are then diffracted by the crystal. Tharp and Scheibner (1967) using a hemispherical collector and retarding potential, measured the energy distribution of the electrons inelastically scattered from the (110) surface of a tungsten single crystal which gave strong confirmation of the two-step process.

A third contribution to the inelastically scattered intensity could arise from the single step process of inelastic diffraction; however this contribution will be negligible in LEED because of the forward scattering nature of the loss process. All three contributions lead to the same final state and contribute to the intensity of inelastic scattering as shown in fig. (7.1).

Weber and Webb (1969) established quantitatively the two step process in the inelastic scattering of low energy electrons and extracted inelastic scattering data independent of the elastic scattering. They measured the inelastically scattered current of electrons from a Ag(111) surface which was found to be peaked in the Bragg reflection directions and showed that this arose from a two step process involving both elastic and inelastic scattering. Assuming only single energy losses and taking into account both the surface and bulk contributions to the inelastic intensity, they developed a model in which the Bragg and phonon contributions to the inelastic scattering could be separated out and an energy loss spectrum independent of the elastic scattering could be found. They compared the experimental energy loss spectra with theory using the dielectric constant formalism and known optical constants.
Figure 7.1  The three contributions to the inelastic scattering in a given direction

- o- Single step
--- Two step process DL
- --- Two step process LD
The theory predicts the positions of peaks in the energy loss spectra quite well and gives the peak magnitudes within a factor of two.

Duke et al (1970) presented a quantum field theory of inelastic electron diffraction taking into account the coherence of the diffraction before and after loss processes (see fig. 7.2).

Figure 7.2 Coherence of DL and LD processes

Dotted line represents the inelastic wavefield

This immediately explained the factor-of-two discrepancy obtained by Weber and Webb who summed the intensities rather than the amplitudes of the two processes. Briefly, Duke’s conclusions are as follows:-

In an ELS experiment the observed inelastically scattered intensity in any direction is the coherent sum of the contributions from the two step processes of diffraction before loss and diffraction after loss. That is, if $A_{LD}$ is the scattered amplitude from the LD process
and $A_{DL}$ is the scattered amplitude from the DL process, then the observed intensity $I$ is given by

$$I = |A_{LD} + A_{DL}|^2$$

to determine $I$ is difficult under general conditions as the amplitudes $A_{DL}$ and $A_{LD}$ are unknown. However by a suitable choice of the diffraction conditions either the DL or LD process can be made to dominate.

### 7.3 Separation of LD and DL processes

As the inelastic scattering is sharply peaked in the forward direction then the intensity of the LD and DL processes will be peaked in different directions for the non-specular beams. These directions are given by the following equations for in plane scattering

$$K(Ep) \sin \theta_{s}^{DL} = K(Ep) \sin \theta_{z} + g \quad (7.1)$$

$$K(Ep - \Delta E) \sin \theta_{s}^{LD} = K(Ep - \Delta E) \sin \theta_{z} + g$$

where

$$K(Ep) = \sqrt{\frac{2mEp}{h^2}}$$

$Ep$ is the primary beam energy,

$\theta_{z}$ is the angle of incidence,

$g$ is the surface reciprocal vector,

$\theta_{s}^{DL}$ and $\theta_{s}^{LD}$ are the angles between the surface normal and
the directions of the DL and LD contributions for inelastic scattering in the forward direction, see fig. (7.3), that is in the directions of elastic diffraction for electrons of energy $E_p$ and $E_p - \Delta E$ respectively incident at $\theta_{i}$ to the surface normal resulting in "inelastic beams" in these directions.

Figure 7.3 DL and LD processes
The angular separation of the inelastic beams is given by

\[
\sin \frac{\theta_{p}^{D}}{\varepsilon} - \sin \frac{\theta_{s}^{D}}{\varepsilon} = \frac{g}{K(E_p)} \frac{\Delta E}{2E_p} \quad \ldots(7.2)
\]

\[
\Delta \theta = \theta_{p}^{D} - \theta_{s}^{D} = \frac{g}{K(E_p) \cos \theta_{s}^{D}} \frac{\Delta E}{2E_p} \quad \ldots(7.3)
\]

showing that the conditions can be chosen such that \( \Delta \theta > \theta_E \)

where \( \theta_E = \frac{\Delta E}{2E_p} \) is the angular spread of the inelastic scattering. So, if energy loss spectra are taken in the directions defined by \( \theta_{p}^{D} \) and \( \theta_{s}^{D} \), the major contribution will come from the \( LD \) and \( DL \) process respectively. From equation (7.1) we see that, for \( g = 0 \), the \( DL \) and \( LD \) inelastic beams occur in the same direction. However for \( E_p = E_B \) (where \( E_B \) is the Bragg energy) the major contribution to the intensity will come from the \( DL \) process, whereas when \( E_p = E_B + \Delta E \) the major contribution to the intensity arises from the \( LD \) process. At these energies there is also an enhancement of the \( DL \) and \( LD \) process respectively in the directions of the non-specular inelastic beams.

### 7.4 Diffraction effects in energy loss spectra

As an illustration of the effect of elastic scattering on the observed energy loss spectra we calculate the expected angle-resolved energy loss spectrum in the direction of the \((00)\) beam, from Al(111), in the region of a Bragg peak. In fig (7.4) we show our experimental I-V curve for the \((00)\) beam at \( \theta = 10^\circ \) and in the \( \{110\} \) azimuth from Al(111) in the region of a Bragg peak at \( E_p = 102 \) eV.
For the purpose of calculation this can be represented by a Lorentzian

\[ I(E_p) = \frac{\gamma e^2 \Gamma}{(E_p - E_B)^2 + \gamma e^2} \]

where \( \gamma \) is the height of the peak and \( 2\Gamma e^2 \) is the FWHM (see the full lines in fig. 7.4).

Figure 7.4 Lorentzian representation of the Bragg peak at \( E_p = 102 \text{ eV} \) (solid line) and experimental I-V curve for the (0,0) beam of Al(111) at \( \theta = 10^\circ \) in (110) azimuth (crosses).

A typical energy loss spectrum for Al at \( E_p = 94 \text{ eV} \) is shown in fig (7.5a). This true energy loss function \( N(E) \) can be represented by the sum of the two Lorentzian oscillators, \( A(E) \) and \( B(E) \) at \( \hbar \omega_{sp} = 10.6 \text{ eV} \) for the surface plasmon and \( \hbar \omega_{bp} = 15 \text{ eV} \) for the bulk plasmon respectively.
\[ A(E) = \frac{\gamma_{sp}^2 \alpha}{(E - \hbar \omega_{sp})^2 + \gamma_{sp}^2} \]

\[ B(E) = \frac{\gamma_{bp}^2 \beta}{(E - \hbar \omega_{bp})^2 + \gamma_{bp}^2} \]

where \( \alpha = 100 \) and \( \beta = 30 \).

Also \( \Gamma_{sp} = 3 \) eV

\( \Gamma_{bp} = 1.5 \) eV to take into account plasmon damping and instrumental linewidth; the sum \( N(E) = A(E) + B(E) \) is illustrated in fig (7.5b). The energy loss spectra \( N(E)_{E_p} \) expected, for example at \( E_p = E_B + E = E_B + 15 \) eV is

\[ N(E)_{E_p} = (A(E) + B(E)) \frac{I(E_p)}{I(E_B)} + (A(E) + B(E)) \frac{I(E_p - E)}{I(E_B)} \]  

(7.4)

and is shown in fig (7.6) with the true \( N(E) \) of fig (7.5b) for comparison (dotted curve).

The expected curves for different values of \( E_p \) are similarly obtained and shown in fig. (7.7) with the \( N(E) \) of fig (7.5b) for comparison (dotted curve).

The first term on the RHS of equation (7.4) is the contribution from the diffraction before loss process and the second term is the contribution from the diffraction after loss process. It can be seen from fig. (7.6) and fig. (7.7) that the elastic scattering has a pronounced effect on the observed energy loss spectrum even before taking account of the coherence of the DL and LD processes.

Shifts of up to 1 eV and large changes in the relative intensities of the surface and bulk plasmon peaks occur. To obtain the true energy loss spectrum one must choose \( E_p = E_B \) to maximise the DL
Figure 7.5a  Energy loss spectrum for Al at $E_p = 94$ eV

Figure 7.5b  The true energy spectrum $N(E) = A(E) + B(E)$
Figure 7.6 The energy loss spectra $N(E)$ expected at $E_p = E_B + 15 \text{ eV}$ (---) and the true energy loss function $N(E) = A(E) + B(E)$ (-----) contribution. As can be seen in fig. (7.7) the $E_P = E_B$ spectrum is identical to the true energy spectrum $N(E)$ of fig (7.5b) but otherwise is distorted if $E_P \neq E_B$.

From the above, if this is done for a non-specular beam then the LD contribution, and thus the distortion of the spectrum, will be even smaller.

7.5 Grazing emergence beam

If energy loss spectra are obtained at an arbitrary angle of incidence then there will be an unknown mixture of surface and bulk contributions i.e.

$$N(E) = \chi(\text{Im} - \frac{i}{c} + Y(\text{Im} - \frac{i}{c + i}))$$
Figure 7.7 The true energy spectrum $N(E) = A(E) + B(E)$ dotted line, the expected $N(E)$ curves for different values of $E_P$ - other lines.
In a material with a complicated energy loss function, to obtain \( \varepsilon \), it is necessary to know \( X \) and \( Y \). Electrons at glancing angle of incidence and emergence excite mainly surface losses so \( X = 0 \) and \( Y = 1 \). Consider now what we expect to see in the direction of a diffracted beam emerging nearly parallel to the surface. The contribution to the inelastically scattered intensity in this direction are as follows:

i. Loss (outside the solid) followed by diffraction
ii. Loss (inside the solid) followed by diffraction
iii. Diffraction before loss (inside the solid)
iv. Diffraction before loss (outside the solid)

According to eq (7.1) the \( LD \) contribution will be small for \( E_p = E_{\text{Bragg}} \) and the emergent beam condition gives the maximum separation of the \( DL_p \) and \( L_p D \) components. From Froitzheim et al (1975) the probability of an emergent beam exciting surface plasmons is given by

\[
\frac{ds}{d\omega} = \frac{4|R|^2}{\pi a_B k_S^2 \cos \theta_s} \frac{1}{\hbar \omega} F(\hbar \omega, \theta, \Delta \theta, \Delta \phi) \text{Im} \left( \frac{-1}{\varepsilon(\omega) + i} \right) \ldots (7.5)
\]

where

- \( F \) is the finite aperture size correction factor
- \( a_B \) is the Bohr radius
- \( k_S \) scattering wave vector
- \( R \) is the elastic scattering amplitude

For \( E_p = E_B \) and at sufficiently large angles of emergence \( \theta_s > 80^\circ \) then contribution iv will make the major contribution to the observed inelastically scattered intensity. So energy loss spectra obtained under these conditions will show only surface losses.
7.6 Results

Angle-resolved energy loss spectra of emergent beams can be obtained with the present apparatus by tilting the crystal with respect to the electron beam as shown in fig. (7.8) and focussing the emergent beam on the photomultiplier aperture.

![Figure 7.8 Emergent beam condition](image)

A condition was selected such that electrons of energy 68.8 eV incident at 52° to the surface normal in the \( \langle 110 \rangle \) azimuth of Al(111) crystal gave rise to an emergent \( (60) \) beam which satisfied the Bragg condition inside the solid. (See fig. (7.9) which was drawn using an inner potential of 15 eV - Hughes et al 1978). The energy loss spectrum obtained under these conditions is shown in fig. (7.10). Only the Al surface plasmon loss at 10.6 eV is seen.

To illustrate how important it is to choose correctly the diffraction conditions an example will be given showing the effects of diffraction on energy loss spectra obtained at the beam emergence condition. For electrons incident in the \( \langle 110 \rangle \) azimuth of Al(111) at 50° to the surface normal at an energy of 31.5 eV the \( (40) \) beam is emergent at \( \theta_s = 84° \). Fig (7.11) shows energy loss spectra obtained for \( \theta_c = 50° \) and \( \theta_s = 84° \) for different primary beam energies. In
Figure 7.9  Ewald construction for an incident electron energy of 68.8 eV

--- outside

----- inside
contrast to the spectrum shown above - fig(7.10) - where the DL contribution dominates, these spectra are dominated by the LD contribution, therefore we have contributions from bulk losses. The Ewald construction for $E_p = 41.5$ eV is drawn in fig (7.12)
Figure 7.11  Angle-resolved energy loss spectra at different primary beam energies from Al(111)
Fig. 7.12 Ewald construction for an incident electron energy of 41.5 eV
a-inside b-outside

Al(111)
θᵢ = 50°
and it can be seen that the $LD$ contribution will dominate as the $DL$ contribution involves inelastic scattering through a large angle. The same applies for $Ep = 46.5$ eV only here the bulk plasmon loss is further enhanced by the Bragg scattering.

7.7 Conclusions

In this chapter we have shown how to obtain energy loss spectra free from the effects of elastic scattering and thus obtain the true energy loss function at arbitrary angles of incidence. We have also shown how to obtain the surface loss function from energy loss spectra at the beam emergence condition. This has been discussed with reference to results from Al which has a known simple loss spectrum. In the next chapter we will apply these methods to find the correct loss functions for Ni which has a complicated electronic structure.
REFERENCES


CHAPTER 8
IDENTIFICATION OF THE SURFACE PLASMONS IN ELS

8.1 Introduction

In materials such as Ni with a complex loss spectra, it has always been a problem to separate the surface and the bulk contributions. Previous work on the Ni surface for example (Benndorf 1979, Sakisaka et al 1979) disagrees about the assignment of loss peaks arising from the bulk and surface-like excitations.

In this chapter we present angle-integrated spectra and results of energy analyses of diffracted beams emerging almost parallel to the crystal surface which are used to determine the surface loss function free from the effects of bulk excitations. We see from Chapter 7 that the probability for the excitation of surface losses is given by

\[ P_0 \propto \text{Im} \frac{1}{\varepsilon + i \frac{1}{\cos \theta_s}} \quad \text{(8.1)} \]

which applies to excitation outside the surface of the solid. The contribution from bulk losses is independent of angle of incidence and as \( \theta_s \rightarrow 90^\circ \) the energy loss spectrum is well presented by the surface loss function. At grazing angles, the low velocity perpendicular to the surface and hence the time the electron spends in the surface region leads to a large cross section for the excitation of surface plasmons (Lucas and Sunjic 1972). In eq. (8.1) \( \theta_s \) refers to the angle outside the crystal
surface which is larger than $\theta_s^i$ inside the surface due to refraction. The probability of surface excitation taking place inside the solid is given by

$$P_i \propto \text{Im} \left( \frac{-1}{\varepsilon + i} \frac{1}{\cos \theta_s^i} \right)$$

which for the energies used here will be much smaller than $P_o$. Hence eq. (8.1) represents the major contribution to the inelastic intensity of the grazing emergence beam. ELS of the specularly scattered electrons with grazing incidence electron beams have been obtained using a specialized spectrometer designed by Froitzheim et al (1975). The excitation of surface losses is dominant in these experiments. The theory of ELS developed by Evans and Mills (1973) describes these experiments quantitatively. Thus both theory and experiment show that beam emergence ELS is an ideal method for obtaining the surface loss function of materials which have a complex and unknown electronic structure. We use this condition to identify the surface plasmon energy for Ni(100) and show the effect of oxygen in the ordered p(2 x 2) and c(2 x 2) overlayer structures on the ELS spectra.

Previously the method of identifying volume or surface plasmons has been to compare ELS data with the appropriate loss functions $\text{Im} \left( \frac{1}{\varepsilon} \right)$ or $\text{Im} \left( \frac{1}{\varepsilon + i} \right)$. This can only be done if $\varepsilon(\omega)$ is known from optical data.

**8.2 Experimental**

For ELS the direct display LEED system was used as a retarding field analyser in one of two modes:
i) Angle-integrated, using the entire LEED screen as collector;

ii) Angle-resolved, using a telescope photometer to record energy loss spectra (Rawlings and Dobson 1975) with a resolution of $3^\circ$, the energy resolution in this mode was 0.8 eV.

Angle-resolved energy loss spectra of emergent beams were obtained by tilting the crystal with respect to the primary electron beam (see fig 7.8) and varying the primary energy until a diffracted beam emerged almost parallel to the surface and was displayed on the LEED screen. Then the emergent beam was focussed on to the photomultiplier aperture and an energy analysis performed.

In this work the measured electron signal was plotted as the function $N(E)$. Other authors, whose results will be compared later with the present work, used two different data presentation schemes. Sakisaka et al use $\frac{d^2N(E)}{dE^2}$, while Benndorf et al use $\frac{dN(E)}{dE}$. With the latter two procedures relative peak heights become distorted with respect to the true $N(E)$, and the importance of small inflections or slope changes in the $N(E)$ spectra may be magnified out of all proportion to the quantitative or physical significance of these features. The second differential approach is particularly troublesome in this respect because new peaks can be generated. As an illustration of the above effects we represent an $N(E)$ curve by the sum of two Lorentzian oscillators $L(E)$ and $K(E)$.
\[ L(E) = \frac{\Gamma_L^2 L}{E^2 + \Gamma_L^2} \]
\[ K(E) = \frac{\Gamma_K^2 K}{(E - E_0)^2 + \Gamma_K^2} \]

where \( L = 20 \), \( \Gamma_L = 1 \text{eV} \), \( K = 500 \), \( \Gamma_K = 3 \text{eV} \) and \( E_0 = 5 \text{eV} \).

The sum \( N(E) = L(E) + K(E) \); \( \frac{dN(E)}{dE} \) and \( \frac{d^2N(E)}{dE^2} \) are shown in fig (8.1a, b, c). As can be seen the first derivative can fairly be representative of the original function but in the second derivative mode, the sharp and small peak "L" of function \( N(E) \) turns out to be the prominent peak while the wide, large peak "K" of the \( N(E) \) is now not of much importance. Accordingly in our work, we have used the \( N(E) \) spectra to evaluate the relative sizes of importance of the ELS peaks.

8.3 Results and Discussions

An ELS spectrum obtained in the beam emergent mode is presented in fig (8.2). This result is representative of many beam emergent conditions, i.e. at differing \( E_p \) and \( \theta \), the only differences being in the magnitude and position of the minor features – all spectra were, however, characterised by the strong feature at \( \sim 7 \text{ eV} \) and another peak at \( \sim 14 \text{ eV} \).

Fine structure as shoulders on the main peak was a very sensitive function of the angle and energy and is certainly related to diffraction effects of the scattered electrons. The main features at 7 eV and 14 eV were not much affected. In fig (8.3) the angle-resolved grazing emergent spectrum compared with the angle-integrated spectrum at \( E_p = 147 \text{ eV} \).
Figure 8.1 Comparison of $N(E)$, $\frac{dN(E)}{dE}$ and $\frac{d^2N(E)}{dE^2}$ representation of an energy loss spectrum
Figure 8.2 Electron energy loss spectrum of a grazing-emergent beam from Ni(100)

The angle-integrated ELS exhibits two main features at around 10 and 20 eV, with some other features at higher energies. Table (8.1) represents a compilation of loss energies observed in this study in comparison with the results of other workers.

Comparing the two spectra of fig (8.3) we do however expect that some surface plasmon contributions should be present in the ELS data, but because of the superpositions of two peaks at 7 and around 10 eV, we observe only one broader peak.
Figure 8.3 ELS spectra obtained in the angle-integrated (a) and in the grazing-emergent (b) modes.
Table 8.1 Observed Loss Energies in this and Other Works

<table>
<thead>
<tr>
<th>Loss Energies of Observed Peaks (in eV)</th>
<th>Interpretation of Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benndorf et al (1979)</td>
<td>Sakisaka et al (1979)</td>
</tr>
<tr>
<td>4.1</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>7.2</td>
<td>-</td>
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<tr>
<td>-</td>
<td>9.1</td>
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<td>10</td>
<td>-</td>
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<tr>
<td>-</td>
<td>14</td>
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<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>26.9</td>
<td>27</td>
</tr>
<tr>
<td>32.4</td>
<td>33</td>
</tr>
<tr>
<td>38.3</td>
<td>38</td>
</tr>
<tr>
<td>-</td>
<td>50</td>
</tr>
<tr>
<td>66</td>
<td>67</td>
</tr>
</tbody>
</table>

All spectra were obtained in the angle-integrated mode, except as indicated:

<sup>a</sup> Grazing Emergent Condition

<sup>a</sup> Angle-resolved but not grazing emergence
Fig (8.4) shows the comparison between the angle-resolved grazing emergent electron energy loss spectrum with the surface loss function $\text{Im} = \frac{1}{\varepsilon+i}$, taken from the work of Vehse and Arakawa (1969). Similarly fig (8.5) represents the angle-integrated EELS of fig (8.3) and the volume loss function, $\text{Im} = \frac{1}{\varepsilon}$. The agreement between the grazing emergent data and the surface loss function is quite good as regards the main peak positions, as is the agreement between the angle-integrated data and the volume loss function, indicating that the grazing emergence data gives a very clear indication of the surface plasmon losses. This result provides confirmation of the interpretation of the 7 eV loss offered by Benndorf et al. Sakisaka et al did not observe this feature, probably because of their choice of primary beam energy and angles of incidence and detection, although they do identify a 14 eV loss feature with a surface plasmon. This is also consistent with our observation. The 14 eV feature can result from either a multiple surface plasmon excitation or as the surface loss function shows, another fundamental surface mode.

Bulk related losses are observed at 10 and 20 eV (fig 8.5) where the agreement with the optical data is very good. Sakisaka et al attributed peaks at 9 and 19 eV to bulk plasmon excitations which they associated with the 4S electrons and the coupled 3d and 4S electrons respectively. There is, however, another possible mechanism apart from a bulk plasmon loss which can contribute to the 10 eV loss. Examination of the Augmented plane wave (APW) calculations of Szmulowicz and Pease (1978) show the existence
Figure 8.4  The angle-resolved grazing emergent ELS (a) and the surface loss function (b) for Ni(100).

Figure 8.5  Angle-integrated ELS (a) and volume loss function (b) for Ni(100).
of several 10 eV parallel band transitions from states just below the Fermi level to unoccupied states above. Parallel band transitions are transitions between initial and final states having a constant energy difference for a wide range of initial $\overline{K}$ values and $\overline{K} = \overline{K}'$ (direct transitions). Particularly important transitions in this respect are the $Z_1^+(\chi_0^p \rightarrow L_1^p)$ and $Z_1^-(\chi_0^p \rightarrow W_1^p)$. The probability amplitude for these transitions is very high, as there are contributions from many $\overline{K}$ values. Moreover, as noted by Szmulowicz and Pease, these bands are quite flat, leading to an increased transition probability amplitude. The peak at 10 eV thus may be due to both single (parallel band) and collective (plasmon) electron excitations. This work will be published, see Özkök et al (1983).

8.4 Energy loss spectra from oxygen overlayers on Ni(100)

The electron energy loss spectra from oxygen overlayers have also been recorded to see if any change is to be observed. LEED evidence has established that two distinct structures are formed during the initial stages of oxidation of the Ni surface. These are the p(2 x 2) at up to 0.25 monolayer coverages, followed by the c(2 x 2) at coverages up to 0.5 monolayer. Typical angle-integrated ELS spectra taken at primary beam energies of 96 and 147 eV with successive oxygen exposures of 40, 60 and 80 Langmuirs (one Langmuir (1L) = $10^{-6}$ torr sec) are shown in figures (8.6) and (8.7) respectively. Exposures of the sample to oxygen produces significant changes in the main peaks at 10 and 20 eV of the ELS spectrum.
Figure 8.6 Energy loss spectra obtained with a primary beam energy of 96 eV for clean Ni and increasing exposure to oxygen.
Figure 8.7 Energy loss spectra obtained with a primary beam energy of 147 eV for clean Ni and increasing exposures to oxygen.
Before proceeding to an analysis of oxygen covered ELS it is important to note that in common with the studies of Sickafus and Steinrisser (1972), we observe large changes in the $N(E_s)$ spectra for different primary energies. We agree with their conclusion that this results from diffraction effects in the two step process, i.e. loss followed by diffraction or diffraction followed by loss. (see chapter 7). To extract the true energy loss function from experimental spectra it is necessary to choose the energy such that the diffraction before loss process dominates. This has been done in fig (8.7) for $E_p = 147$ eV. Examination of I-V curves from clean Ni(100) (Demuth and Rhodin 1974) shows that the (01) beams satisfy a strong Bragg condition at $E_B = 74$ and 146 eV, therefore obtaining an angle integrated spectra at normal incidence at $E_p = 147$ eV where $E_p$ is almost equal to $E_B$ the DL contribution constitutes the major part of the inelastically scattered intensity and thus the "true $N(E_s)$"spectrum is obtained.

To show the drastic effect which diffraction has on the observed spectra fig (8.6) shows the ELS spectrum of Ni(100) at a primary beam energy of 96 eV at normal incidence which is strongly affected around 22 eV energy loss (due to a strong Bragg condition at 74 eV) by the LD contribution, indicating that extreme care must be taken in the interpretation of such spectra.

We shall now consider changes in the spectra induced by oxygen exposure at a primary beam energy of 147 eV (fig 8.7). In the transition from clean Ni to the p(2 x 2) structure (up to 60L
oxygen exposure the peak at about 9.5-10 eV appears to shift in energy to 10.5-11 eV and decreased in intensity. In the p(2 x 2)-c(2 x 2) transition the peak at 10 eV remains shifted and reduced further in intensity. An examination of the I-V curve from p(2 x 2)0 and c(2 x 2)0 on Ni(100) shows that the (01) beams satisfy a Bragg condition at around 134 and 132 eV respectively, which may also contribute to the shift of the 10 eV peak to a higher energy whereas the reduction in the peak height can be explained in terms of reduction of the surface plasmon loss at 7 eV in the presence of an oxygen overlayer. Further the small decrease in intensity of the peak at 20 eV in both cases confirms our interpretation of the bulk plasmon loss which is not expected to be much affected by the oxygen coverages used here. Apart from the above mentioned effects, up to the oxygen exposures used, there were no new losses detected in this energy range. In angle-resolved grazing emergent ELS, a sharp reduction in the surface plasmon loss peaks occurred in the presence of an oxygen overlayer, further evidence that they are surface related features.

Our angle-resolved grazing emergence loss measurements have enabled a clear identification to be made of the surface plasmon at 7 eV energy loss, confirming the earlier interpretation by Benndorf et al and the position of this loss can now be considered well established. Our reinterpretation of the losses observed by Sakisaka et al now also fit into this overall scheme.

The position of a bulk related plasmon loss is confirmed at 20 eV and an interpretation put forward for the previously explained
10 eV loss peak.

8.5 Conclusions

Effects of oxygen adsorption on the spectra proved to be further confirmation of the interpretation of peaks at 10 and 20 eV as bulk related, and the energy analysis of an emergent beam shows a diminution in the amplitude of the surface plasmon loss. The use of a grazing emergent electron beam in ELS affords an excellent method for distinguishing the surface and bulk related losses and therefore can be used to identify the features in materials with complex electronic structure.
REFERENCES


Rawlings, K.J. and Dobson, P.J. (1975) "LEED beam spectroscopy: inelastic electron diffraction with a direct display system". J. Phys. C: Solid state phys. 8, 3993-4000.

