INVESTIGATION OF THE SCATTERING OF LOW ENERGY ELECTRONS
FROM THE SURFACE OF SINGLE CRYSTAL ALUMINUM

by

James Michael Burkstrand

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INVESTIGATION OF THE SCATTERING OF LOW ENERGY ELECTRONS
FROM THE SURFACE OF SINGLE CRYSTAL ALUMINUM

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Elastic and inelastic low energy electron diffraction (ELEED, ILEED) observations have been made on a clean surface of Al(100). Measurements on the (10) and (11) elastic diffraction beams were made using normally incident electrons in the energy range $30 \leq E \leq 170$ eV. Peaks in the energy loss distribution are seen near 5, 10, 15, 26 and 31 eV, the dominant peaks near 10 and 15 eV corresponding to surface and bulk plasmon excitations respectively. Two types of structure are observed in the inelastic angular profiles: one closely correlated with the structure in the elastic angular profile, and the second being substructure corresponding to different ILEED conditions. Energy intensity profiles (as a function of incident energy) for the (10) and (11) elastic and inelastic diffraction beams have been measured. These profiles also show primary and secondary structure. Within the substructure of the angular and energy intensity profiles are the first experimental observations of sideband diffraction. A comparison of the experimental results and the theoretical predictions of Duke and Laramore and of Duke and Bagchi is made.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Problem</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Definition of the Measurement</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Historical Background</td>
<td>7</td>
</tr>
<tr>
<td>1.4 Theoretical Discussion</td>
<td>12</td>
</tr>
<tr>
<td>2. APPARATUS AND EXPERIMENTAL PROCEDURE</td>
<td>30</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>30</td>
</tr>
<tr>
<td>2.2 Electron Gun</td>
<td>32</td>
</tr>
<tr>
<td>2.3 Target and Target Assembly</td>
<td>32</td>
</tr>
<tr>
<td>2.4 Detector</td>
<td>35</td>
</tr>
<tr>
<td>2.5 Sputtering Ion Gun</td>
<td>37</td>
</tr>
<tr>
<td>2.6 Vacuum System</td>
<td>38</td>
</tr>
<tr>
<td>2.7 Electronic Circuitry</td>
<td>40</td>
</tr>
<tr>
<td>2.8 Target Preparation</td>
<td>43</td>
</tr>
<tr>
<td>2.9 Criteria for Surface Cleanliness</td>
<td>45</td>
</tr>
<tr>
<td>2.10 Instrument Checkout</td>
<td>49</td>
</tr>
<tr>
<td>3. DATA PRESENTATION AND DISCUSSION</td>
<td>52</td>
</tr>
<tr>
<td>3.1 Measurement of the Absolute Intensity</td>
<td>54</td>
</tr>
</tbody>
</table>
3.2 Energy Intensity Profiles........................................... 57
3.3 Energy Loss Profiles.................................................. 58
3.4 Angular Profiles....................................................... 76
3.5 Comparison of Experimental and Theoretical Profiles........ 97

4. SUMMARY OF RESULTS AND CONCLUSIONS............................111

REFERENCES........................................................................113

VITA....................................................................................117
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Crystal lattice, incident and scattered electron wavevectors</td>
</tr>
<tr>
<td>2.</td>
<td>Schematics for two electron scattering measurement systems, (a) display instrument, (b) scanning Faraday collector</td>
</tr>
<tr>
<td>3.</td>
<td>Energy distribution of electrons scattered from a clean surface of Al (100)</td>
</tr>
<tr>
<td>4.</td>
<td>Ewald sphere diagram for an elastic collision. The radius of the sphere is $</td>
</tr>
<tr>
<td>5.</td>
<td>(a) Schematic display LEED picture, (b) schematic angular profile in the (10) direction</td>
</tr>
<tr>
<td>6.</td>
<td>Inelastic collision diagram for a two-step collision involving a bulk excitation</td>
</tr>
<tr>
<td>7.</td>
<td>Inelastic collision diagram for a two-step collision involving a surface excitation</td>
</tr>
<tr>
<td>8.</td>
<td>Inelastic collision diagram for an EI Bragg collision and sideband diffraction</td>
</tr>
<tr>
<td>9.</td>
<td>Theoretical energy intensity profiles demonstrating sideband diffraction</td>
</tr>
<tr>
<td>10.</td>
<td>Theoretical energy loss profiles for a bulk excitation demonstrating sideband diffraction</td>
</tr>
<tr>
<td>11.</td>
<td>Theoretical angular profiles for a bulk plasmon excitation demonstrating sideband diffraction</td>
</tr>
<tr>
<td>12.</td>
<td>Theoretical angular profiles for a surface plasmon excitation</td>
</tr>
<tr>
<td>13.</td>
<td>Schematic of energy-angular distribution instrument showing the basic components</td>
</tr>
<tr>
<td>14.</td>
<td>Details of the target holder</td>
</tr>
<tr>
<td>15.</td>
<td>Details of the four grid retarding field energy analyzer</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>16. Schematic of vacuum system</td>
<td>39</td>
</tr>
<tr>
<td>17. Schematic of electronic circuitry for energy and angular measurements</td>
<td>41</td>
</tr>
<tr>
<td>18. Schematic of electronic circuitry for argon ion bombardment</td>
<td>44</td>
</tr>
<tr>
<td>19. Energy loss profiles in the (10) diffraction direction for a &quot;clean&quot; and &quot;dirty&quot; surface</td>
<td>50</td>
</tr>
<tr>
<td>20. Schematic of the three forms of presentation of the experimental measurements</td>
<td>53</td>
</tr>
<tr>
<td>21. Experimental measurements necessary to calibrate the intensity of the scattered electrons</td>
<td>55</td>
</tr>
<tr>
<td>22. Elastic and inelastic energy intensity profiles for the (10) diffraction beam. The intensity unit is labeled for each scale factor used</td>
<td>58</td>
</tr>
<tr>
<td>23. Elastic and inelastic energy intensity profiles for the (11) diffraction beam</td>
<td>59</td>
</tr>
<tr>
<td>24. Energy loss profiles for different primary energies showing the bulk and surface plasmons</td>
<td>69</td>
</tr>
<tr>
<td>25. Energy loss profiles for a primary energy of 56 eV and different collector angles. $\theta_{\text{Elastic}} = 31^\circ$</td>
<td>70</td>
</tr>
<tr>
<td>26. Angular profiles at 56 eV primary energy for electron loss energies of 0 and 8 eV</td>
<td>72</td>
</tr>
<tr>
<td>27. Series of energy loss profiles in the (11) diffraction beam for different primary energies, $E_p$, and collector angles $\theta$</td>
<td>73</td>
</tr>
<tr>
<td>28. Angular profiles for a constant primary energy (86 eV) and different loss energies</td>
<td>77</td>
</tr>
<tr>
<td>29. Inelastic angular profiles, $\omega = 10$ eV, in the (11) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy</td>
<td>79</td>
</tr>
<tr>
<td>Figure</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>30. Inelastic angular profiles $w = 12$ eV, in the (11) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>80</td>
</tr>
<tr>
<td>31. Inelastic angular profiles, $w = 16$ eV, in the (11) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>82</td>
</tr>
<tr>
<td>32. Inelastic angular profiles, $w = 18$ eV, in the (11) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>83</td>
</tr>
<tr>
<td>33. Inelastic angular profiles, $w = 14$ eV, in the (11) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>85</td>
</tr>
<tr>
<td>34. Inelastic angular profiles, $w = 14$ eV, in the (11) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>86</td>
</tr>
<tr>
<td>35. Angular profiles for a constant primary energy (92 eV) and different loss energies.</td>
<td>88</td>
</tr>
<tr>
<td>36. Angular profiles for a constant primary energy (96 eV) and different loss energies.</td>
<td>89</td>
</tr>
<tr>
<td>37. Angular profiles for a constant primary energy (100 eV) and different loss energies.</td>
<td>90</td>
</tr>
<tr>
<td>38. Inelastic angular profiles, $w = 10$ eV, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>92</td>
</tr>
<tr>
<td>39. Inelastic angular profiles, $w = 12$ eV, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>93</td>
</tr>
<tr>
<td>40. Inelastic angular profiles, $w = 14$ eV, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>94</td>
</tr>
<tr>
<td>41. Inelastic angular profiles, $w = 16$ eV, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.</td>
<td>95</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>42</td>
<td>Theoretical and experimental energy intensity profiles in the (11) diffraction direction</td>
</tr>
<tr>
<td>43</td>
<td>Theoretical and experimental energy intensity profiles in the (11) diffraction direction</td>
</tr>
<tr>
<td>44</td>
<td>Theoretical and experimental energy loss profiles in the (11) diffraction direction</td>
</tr>
<tr>
<td>45</td>
<td>Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a primary energy of 86 eV</td>
</tr>
<tr>
<td>46</td>
<td>Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a primary energy of 96 eV</td>
</tr>
<tr>
<td>47</td>
<td>Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a loss energy of 16 eV</td>
</tr>
<tr>
<td>48</td>
<td>Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a loss energy of 14 eV</td>
</tr>
<tr>
<td>49</td>
<td>Theoretical (s, p, d-wave scattering) elastic energy intensity profiles</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

1.1. Problem

The ultimate aim of surface physics and surface chemistry is to describe the nature of solid surfaces, including interfaces and adsorbates on a clean surface. Such a goal must also include the ability to predict reactions in unknown systems as well as the characterization of previously observed systems. This knowledge will lead to solutions of technological problems in areas such as catalysis, corrosion, microelectronics and thermionic energy-conversion.

The simplest system to study would be the surface of a metal with a vacuum interface. The basic study would then be of the electronic structure at the metal surface, since almost all the reactions at a metal surface are electronic in nature. The ideal probe to use in such a study would be one which interacted electronically with the surface and which did not penetrate beyond the surface. Electrons in the energy range $0 \lesssim E \lesssim 300$ eV are probes that come closest to meeting these specifications.

In this energy range, their interactions with the metallic ion cores and valence electrons are so strong that they penetrate only a few atomic layers into the bulk. Thus, the information gained is primarily surface information which, in principle, describes the differential cross sections for electron interactions, the dispersion relations for various electronic excitations in the metal, the nature of the coupling between the probe electron and the excitation, etc.
For reasons of historical interest, experimental feasibility, and theoretical ease and importance, we will pursue here the natures of the surface and bulk plasmon excitations in aluminum.

1.2. Definition of the Measurement

All of the experimental results reported here were made on a macroscopic size single crystal of aluminum. Then, because of the shallow penetration of the incident electrons resulting from their strong interactions with the crystal, we can approximate the target as the surface layers of a semi-infinite crystal. We will also talk about "scattered" electrons and "emitted" electrons, but this classification is not strictly correct. Since most of the incident electrons interact with electrons in the metal, the quantum mechanical principle of indistinguishability of identical particles does not allow us to make the above distinction between electrons. However, for convenience and historical reasons, we will use the notation here. We will also refer to this group of electrons as "secondary" electrons, although, we will clarify this term later.

The basic experimental variables and parameters are shown in Figure 1. We will define a coordinate system in which an x-y plane is parallel to the crystal surface and the z axis is normal to the surface. We will choose the \( \mathbf{x} \) and \( \mathbf{y} \) unit vectors to lie along the directions of the surface unit cell. Knowing the separation of the atoms in the crystal unit cell, we can then determine the crystal reciprocal lattice vectors, \( \mathbf{G} \). We will find it convenient later to know the components of \( \mathbf{G} \) perpendicular to the surface, \( \mathbf{G}_\perp \), and parallel to the surface, \( \mathbf{G}_\parallel \equiv \mathbf{g} \).
Figure 1. Crystal lattice, incident and scattered electron wavevectors.
The incident or primary electron momentum $\mathbf{K}_p$ and the secondary electron momentum $\mathbf{K}_s$ define the rest of the experimental parameters. If we measure polar angles $\theta$ from the crystal normal and azimuthal angles $\phi$ from a chosen direction on the surface, then $\mathbf{K}_p$ determines the incident angles $\theta_p$ and $\phi_p$ and $\mathbf{K}_s$ determines the secondary angles $\theta_s$ and $\phi_s$. The magnitude of $\mathbf{K}$ is related to the energy of the electron through the relation

$$\frac{2}{2m_e} K^2 = E.$$  

Since we measure angles and energies, the experimental variables are the incident beam energy $E_p$, the incident angles $\theta_p$ and $\phi_p$, the secondary beam energy $E_s$, and the secondary angles $\theta_s$ and $\phi_s$. Then, the fundamental measurement, the differential cross section is

$$\frac{d^2\sigma(\mathbf{K}_p, \mathbf{K}_s)}{d\Omega_s dE_s} = \frac{d^2\sigma(E_p, \theta_p, \phi_p, E_s, \theta_s, \phi_s)}{d\theta_p d\phi_p dE_s sin \theta_s}.$$  

In many cases it is more convenient to talk about the difference in energy between the incident and secondary electrons, $E_p - E_s = \omega$, called the loss energy.

There are two basic types of systems presently used to measure the differential cross sections. These are schematically shown in Figure 2. The first type is a commercially available display apparatus with $\theta_p$ usually equal to zero. The grids can be set at an electric potential such that only those electrons which have scattered elastically from the target, $\omega = 0$, can be displayed on the screen. By using a spot photometer, one can obtain a
Figure 2. Schematics for two electron scattering measurement systems, (a) display instrument, (b) scanning Faraday collector.
measurement of

\[ \int_{\Delta \Omega_s} d\Omega_s \int_{\Delta E_s} dE_s \frac{d^2 \sigma(E_p, w = \theta_s, \phi_s)}{d\Omega_s dE_s} \]

an integration over the experimental widths in \( \Omega_s \) and \( E_s \). The other measurement which can be done is to measure

\[ \int_{w - \Delta E_s}^{w + \Delta E_s} d\Omega_s \int_{w - \Delta E_s}^{w + \Delta E_s} dE_s \frac{d^2 \sigma(E_s, w, \theta_s, \phi_s)}{d\Omega_s dE_s} \]

an angular integrated energy loss profile.

The second type of system is an energy-angle apparatus, as shown in Figure 2b. The most common type is one in which the electron gun and energy analyzer are fixed with \( \theta_s = \theta_p \) and \( \phi_s = -180^\circ \) in order to observe the specular beam.

There have been relatively few reports of apparatus which employ energy analyzers capable of rotating in the \( \theta \) direction during experimental measurements. We use such an analyzer, which will be described in Chapter 2. For the measurements to be reported, we set \( \theta_p = 0 \), which makes \( \phi_p \) undefined. If we make the target rotatable about an axis along the line of the incident beam direction, then rotating the target is equivalent to rotating the energy analyzer in the \( \phi \) direction. Thus we are able to measure

\[ \frac{d^2 \sigma(E_p, w, \theta_s, \phi_s)}{d\Omega_s dE_s} \]

The energy-angle collector has associated with it experimental widths of acceptance, \( \Delta E_s \) and \( \Delta \Omega_s \) which are present in all measurements. Thus the
intensity we really measure is the cross section integrated over these widths. But if these widths are small compared to the size of the variables, then we can approximate our measured intensity as the true differential cross section. Since \( \theta_s \) and \( \phi_s \) are the only two angles measured, we will drop the subscript "s" in the descriptions which follow. Since we change only one experimental variable at a time, we will write the intensity as a function of only that variable, i.e. \( I(\psi) \). Thus, there are four logical types of measurements to make.

First, we can fix \( E_p, w, \) and \( \varphi \) and measure \( I(\psi) \). These measurements we will call angular profiles. For reasons to be explained in a later section, we will not report \( I(\phi) \), which also could be called an angular profile. Second, we can fix \( E_p, \theta, \) and \( \varphi \) and measure \( I(w) \), which we will call energy loss profiles. If we measure \( I(E_p) \) we will call these energy distributions. Third, we can fix \( w, \theta, \) and \( \varphi \) and measure \( I(E_p) \), which we will call elastic \((w = 0)\) and inelastic \((w \neq 0)\) energy intensity profiles. However, for reasons of symmetry, we will vary \( \theta \) in such a way that the measured value of \( \theta \) will always be located at a constant difference from the collector angle at which the elastic angular profile, \( (I(\theta), w = 0) \), is a maximum. The collector angle at which \((I(\theta), w = 0)\) is a maximum will be called \( \theta_{\text{Elastic}} \). The reasons for this type of measurement will be explained in the theoretical section.

1.3. Historical Background

In 1927, Davisson and Germer\(^6\) discovered that electrons can coherently diffract from a single crystal lattice. The phrase low energy electron diffraction (LEED) has been applied to this phenomenon involving electrons with
energies in the range $15 \lesssim E \lesssim 300$ eV. Historically, LEED has implied the study of those electrons that elastically scattered from the lattice. In this work, we will denote the difference between the electrons which undergo elastic and inelastic low energy electron diffraction by ELEED and ILEED respectively. We will include in ELEED those electrons that have lost an amount of energy that is nonresolvable with our instrument, such as by phonon stimulation. There are currently several good reviews [7-10] that trace the historical development and uses of ELEED, and for this reason, we will not pursue such an outline here.

At this time we will clarify what is meant by the term inelastically scattered electrons. Figure 3 shows a typical energy distribution for a monoenergetic beam of electrons scattered from a metal. There are three distinct regions of electrons in the measured distribution. First, those electrons that are found in Region I are called elastics. These are electrons that, within the experimental energy resolution of the analyzer, have scattered from the crystal with no apparent energy loss. It is the properties of these electrons that are measured by ELEED.

The electrons found in Region II are called inelastics. These are electrons which have scattered from the crystal and in the process have lost a characteristic amount of energy. Any structure which is classified as inelastic is found with a nearly constant energy difference $\omega$ from the elastic electrons at $E_p$, regardless of the value of $E_p$. We use the phrase "nearly constant" because any given loss mechanism may produce structure within a small region of $\omega$, the exact value of $\omega$ depending on different dynamical scattering factors.
Figure 3. Energy distribution of electrons scattered from a clean surface of Al(100).
Third, the electrons found in Region III are called true secondaries. They are usually found with an energy $E_s \sim 30\text{ eV}$ and any structure in this region is found at constant secondary energies, regardless of $E_p$. These electrons are thought to be emitted as the result of a cascade process in the solid. Superimposed on the true secondaries are other peaks at fixed secondary energies which are known as Auger peaks. As the true secondary electrons are not studied as a part of this work, the interested reader is referred to the literature for current work $3,10$ and review articles $11-13$.

In working with a model for ILEED, it is necessary to know the loss mechanism that produced a certain structure in the inelastic energy region. There have been a number of articles $14-16$ which summarize the characteristic energy losses that have been measured for different materials. While it is generally accepted that the inelastic losses in the region $1 < \omega < 30\text{ eV}$ are the result of excitations of bulk plasmons, surface plasmons, or interband transitions, the specific origin of most losses in many materials is still uncertain $16$.

However, aluminum is one material in which the loss mechanisms creating the primary structure in the inelastic loss profile are generally accepted to be excitations of bulk and surface plasmons. According to the free electron calculations by Ritchie $17$, the bulk plasmon of infinite wave length in aluminum should have an energy of $\hbar \omega_p = 15.2\text{ eV}$ and the surface plasmon of infinite wave-length an energy of $\hbar \omega_s = (1/\sqrt{2})\hbar \omega_p = 10.7\text{ eV}$. These numbers are expected to be accurate because the electron energy bands in aluminum are quite close to free electron bands $18$.

From 1948 to 1959, different high energy electron transmission experiments $15$ through Al thin films showed two low energy losses occurring
around 15 eV and 7 eV which were identified as a bulk and surface plasmon excitation respectively. In 1959, Powell and Swan performed a series of high energy back-scattering experiments in which they measured losses in Al at 15.3 and 10.3 eV and identified these as the bulk and surface plasmons. By adding a thin oxide film to the surface, they were able to change the surface loss from 10.3 eV to 7 eV, while leaving the 15 eV loss unchanged. This behavior is predicted for surface plasmons by Stern and Ferrell. Thus, the presence of an oxide coating on the surface would account for the other experimental observations near 7 eV. Powell and Swan also found that the intensity of the 15 eV loss was directly proportional to the thickness of the Al film, while the 10 eV loss was independent of any thickness variation.

Swan et al. have observed the predicted coupled surface plasmons, \( \omega_S \), in Al and measured their dependence on the Al film thickness. The inelastic losses near 10 eV behaved as surface plasmon excitations would be expected. A final aid in identification comes from Williams et al. who experimentally determined the surface plasmon loss function \( \text{Im}[1/\epsilon] \) from optical data. Their results indicate the presence of a surface plasmon peak near 10.5 eV. By comparing these experimental results and theoretical predictions, it can be safely concluded that in Al, the infinite wavelength bulk plasmon occurs near 15 eV and the surface plasmon near 10 eV.

Since the discovery of LEED, a number of experimental studies have demonstrated the connection between ELEED and ILEED involving low energy losses (1 < \( \omega \) < 30 eV). These studies have led to the identification of a two-step process of inelastic diffraction as the primary mechanism in which
inelastically scattered electrons escape the crystal. In this process, the detected electron can undergo elastic scattering from the crystal lattice (diffraction) and inelastic scattering (creation of a plasmon, etc.) in either sequence. There have been several formal analyses of ILEED using a quantum field theory. However, Duke and Laramore, having expanded upon the elastic theory of Duke and Tucker and Duke, Anderson and Tucker have developed the only detailed theoretical calculations of ILEED intensities using a quantum field theory approach. A consequence of this theory is the formulation of a set of "surface" conservation laws of energy and momentum parallel to the surface and the prediction of a new phenomenon called sideband diffraction. Their calculations have been extended to include detailed predictions of inelastic scattering from clean Al surfaces.

1.4. Theoretical Discussion

In the previous section we made a distinction between ELEED and ILEED, and yet stated that a two step process of ILEED includes an elastic diffraction as one of the steps. The logical way to proceed is then to discuss the kinematic principles of ELEED.

1.4.1. ELEED

Because electrons in the energy range used for ELEED do not penetrate more than a few lattice layers into the crystal, we will consider first elastic electron scattering from the surface lattice only. We will assume the surface layer has a square primitive unit cell and that the surface is infinite in extent. The problem then is one of two dimensional coherent scattering or diffraction. A convenient procedure to discuss this is to use the Ewald
sphere construction in reciprocal space. In reciprocal space, the three
dimensional lattice is a three dimensional lattice of points separated by
reciprocal lattice vectors \( \vec{G} \), while the real two dimensional surface lattice
is a series of reciprocal lattice rods separated by surface reciprocal lattice
vectors \( \vec{g} \) and which pass through the reciprocal lattice points and are "perpen-
dicular" to the surface. The primary beam is represented by the propagation
vector \( \vec{K}_p \) and energy \( E_p = (\hbar^2/2m_e) |\vec{K}_p|^2 \), the secondary beam by \( \vec{K}_s \) and \( E_s \). A
typical Ewald sphere diagram is shown in Figure 4, where we assume the incident
beam is normal to the surface, as it is in this work. We show only a two
dimensional slice which passes along a direction \( (hk) \) in reciprocal space. The
conservation of energy
\[
E_p = E_s
\]
and the conservation of momentum parallel to the surface
\[
|\vec{K}_s| = |\vec{K}_p| + \vec{g}_{hk}
\]
determine the spatial locations of the diffracted beams. The wavevectors of the
elastically scattered electrons are found at the intersections of the Ewald
sphere with the lattice rods. The scattered angles are found from Equation
1.6 to be
\[
|\vec{K}_s| \sin \theta_{hk} = |\vec{g}_{hk}|
\]
where \( \vec{g}_{hk} \) is a surface reciprocal lattice vector in the \( (hk) \) direction.

If these backscattered electrons are collected on a display screen,
a picture similar to the schematic in Figure 5a would result. The picture consists
of a series of spots called diffraction spots or diffraction beams. Each beam
Figure 4. Ewald sphere diagram for an elastic collision.

The radius of the sphere is $|\vec{k}_p|$. 
Figure 5. (a) Schematic display LEED picture, (b) schematic angular profile in the (10) direction.
can be labeled with the indices corresponding to the appropriate reciprocal vector \( \mathbf{g}_{hk} \) in Equation 1.7. We will call the direction defined by \( \mathbf{g}_{hk} \) the \((hk)\) diffraction direction. An angular profile in a diffraction direction, such as in Figure 5b, should produce a series of peaks at angles which are solutions to Equation 1.7. We will call these peaks elastic diffraction peaks and the angles at which they maximize we will call \( \theta_{\text{Elastic}}(hk) \). For convenience, we will call the location defined by \((\mathbf{g}_{hk}, \theta_{\text{Elastic}}(hk))\) as the elastic diffraction direction.

But ELEED also shows dynamical effects of scattering from the three dimensional lattice. In an elementary sense, this can be seen by locating the reciprocal lattice points along the reciprocal lattice rods, as in Figure 4. Analogous to x-rays \(^{37}\), we expect intensity maximum to occur in the diffracted beam when

\[
K_p + \mathbf{G} = K_s
\]

Thus, as a particular diffracted beam \((hk)\) moves along the lattice rod with changing \(E_p\), we expect to see fluctuations in the beam intensity as Equation 1.8 is satisfied. This measurement is what we called in a previous section an elastic energy intensity profile. Thus, it now appears reasonable to follow the diffracted beam by varying \(g_{hk} = \theta_{\text{Elastic}}(hk)\) when measuring this energy profile. The peaks in the energy profile for which the wavevectors satisfy Equation 1.8 are generally called Bragg peaks and are found at \(E_p = E_{\text{Bragg}}\).

In an Ewald diagram, the \((hk)\) Bragg condition occurs when, if the tip of the incident wavevector ends on a lattice point, the energy sphere passes through a reciprocal lattice point on the \((hk)\) reciprocal lattice rod. The vector between the two reciprocal lattice points is a reciprocal lattice vector \(G\).
and Equation 1.8 is satisfied. In addition to the Bragg peaks, there is often a large amount of other structure in the elastic energy profile. The majority of the prominent peaks are referred to as secondary peaks due to multiple scattering and are often indexed as Bragg peaks of fractional order. There is also structure which is identified as grazing-emergence features or surface-state resonances which occurs when the propagation vector of an internal secondary beam which is not the final diffracted beam lies along the surface. There have been a large number of theories proposed to explain the details of elastic low energy electron diffraction. It is not the purpose of this work to explain these, and the interested reader is referred to reference which lists references to forty-four works, and to reference 9 which outlines the basic premises and conclusions of many of these theories.

1.4.2. ILEED

In a previous section, we briefly discussed the experimental demonstration of a two step process of ILEED as well as the development of a set of detailed theoretical calculations of ILEED which led to the prediction of side-band diffraction. We will outline here some of the basic results and conclusions of this theory.

We will call a process in which the electron undergoes an elastic diffraction from the lattice followed by an inelastic collision, such as in plasmon creation, an EI (elastic-inelastic) process. The reverse process of an inelastic collision followed by an elastic diffraction will be called an IE process. In either process, the surface conservation laws of energy and momentum parallel to the surface are obeyed for each interaction (E or I), and
thus between the incident and final electron states. Thus, if an incident
electron having a wavevector and energy \((\vec{k}_p, E_p)\) has excited a plasmon
 described by \((\vec{p}, w)\) and is found in the final state \((\vec{k}_s, E_s)\), the conservation
laws can be written

\[
\vec{k}_p || + \vec{g} = \vec{k}_s || + \vec{p} ||
\]

\[
E_p = E_s + w.
\]

These equations are analogous to Equations 1.5 and 1.6 which describe elastic
diffraction. Similarly, we expect a peak in the energy intensity profile for
loss energy \(w\) whenever the energy of the beam undergoing elastic diffraction
equals \(E_{\text{Bragg}}\), guaranteeing the conservation of total momentum at the elastic
vertex, analogous to Equation 1.8. This condition will be met once for the EI
process at

\[
E_p \approx E_{\text{Bragg}}
\]

And once for the IE process at

\[
E_p \approx E_{\text{Bragg}} + w.
\]

These equations hold if the excitation momentum and energy are small compared
to the incident electron momentum and energy, as is the case with the surface
and bulk plasmons we will consider. Besides these maxima, Duke and Laramore\(^{30-32}\)
predicted a maximum in the scattered intensity to occur whenever the total
crystal momentum is conserved; that is, for

\[
\vec{k}_p + \vec{g} = \vec{k}_s + \vec{p}
\]

Such maxima are called sideband diffraction peaks and their presence is expected
to be observed in the angular and energy profiles and probably in the energy loss profiles of electrons which have excited bulk plasmons (or any bulk loss with wavevector $\vec{p}$ ($w) \neq 0$). The detection of the phenomena is dependent on the electronic properties such as the loss dispersion relation and electron damping and on the experimental energy and the angular resolutions.

Using Equations 1.9 and 1.10 and the dispersion relation for a particular excitation, we can construct inelastic collision diagrams similar to the Ewald sphere diagram in Figure 4. We will restrict our discussion to

1. the situation where $\vec{K}_p|| = 0$, as is the case for the results reported here

2. for scattering confined to a plane, and

3. for dispersion relations $^{49-51}$ for which $w(\vec{p}) = f(|\vec{p}|)$.

For a bulk plasmon with these restrictions, the tips of all the $\vec{p}$ vectors corresponding to a single excitation energy sweep-out a circle in momentum space.

For a similarly restricted surface plasmon, $\vec{p}$ can lie in either of two directions along the surface. Using restriction (1), Equation 1.9 can be rewritten as

$$\vec{K}_s|| = \vec{g} - \vec{p}|| \tag{1.14}$$

Figure 6 shows a collision diagram for a bulk excitation of $(\vec{p},w)$ and a primary beam $(\vec{K}_p,E_p)$. Equation 1.10 then determines the secondary energy sphere. All possible values of $\vec{K}_s||$ are determined by adding to $\vec{g}$ all possible $-\vec{p}||$. Then, for a given $\vec{p}$

$$|\vec{g}| - |\vec{p}| \leq |\vec{K}_s|| \leq |\vec{g}| + |\vec{p}|. \tag{1.15}$$

Thus, all possible values of $\vec{K}_s$, for a given $w$, must lie within the shaded region
Figure 6. Inelastic collision diagram for a two-step collision involving a bulk excitation.
on the diagram and end on the secondary energy sphere, satisfying Equations 1.10 and 1.15. We can see from the diagram that for a satisfactory $\mathbf{K}$, there are two values of $-\mathbf{p}$ which can be excited and still obey the conservation laws. It is also evident from the diagram that the angular distribution of the inelastically diffracted electrons will be peaked at an angle which is about the same as that for the elastically diffracted electrons, provided that $w < < E_s < E_p$ and $|\mathbf{p}| < |\mathbf{K_s}| < |\mathbf{p'}|$. 

Figure 7 shows a similar diagram for a surface excitation. Because all the momentum of the excitation is parallel to the surface, there are only two values of $\mathbf{p} = -\mathbf{p'}$ (in this chosen plane) and hence only two possible values of $|\mathbf{K_s}|$ which satisfy both Equations 1.10 and 1.14. The angular distribution of this surface excitation for $\mathbf{p'} > 0$ is then a doublet structure corresponding to the two values of $\mathbf{K_s}$. The experimental measurement of this doublet structure will depend upon the relative probabilities of the two excitations, upon the dispersion relation, electron damping, and the energy and angular resolutions.

Figure 8 shows EI scattering by bulk excitation when the primary momentum satisfies the Bragg condition, Equation 1.8, hence Equation 1.11, where the intermediate wavevector $\mathbf{K}_I$ replaces $\mathbf{K}$ in Equation 1.8. With the Bragg condition satisfied for the incident beam, the inelastically scattered intensity is enhanced for all energy losses associated with excitations taking part in the EI process. However, additional enhancement occurs when Equation 1.13 is satisfied, that is, when total crystal momentum is conserved. The particular wavevectors $\mathbf{K}_s$ satisfying sideband diffraction are labeled. An angular profile for this loss energy $w(\mathbf{p'})$, would then be expected to show a doublet structure with a peak.
Figure 7. Inelastic collision diagram for a two-step collision involving a surface excitation.
Figure 8. Inelastic collision diagram for an EI Bragg collision and sideband diffraction.
in each of the directions of $\vec{K}_s$ for sideband diffraction. It should be noted that this splitting does not depend on the fact that total momentum is conserved. For typical plasmon losses such that $w < < E_p$ and $|\vec{p}| < < |\vec{K}_s|$, the theory shows that sideband diffraction is associated with both $E_1$ and $E_2$ Bragg diffraction and occurs for values of $E_p$ near $E_{Bragg}$ and $E_{Bragg} + w$. The effect of sideband diffraction is also expected to be seen in the energy intensity profiles and in the energy loss profiles. As the details of these effects are strongly dependent on the exact dispersion relation of the loss in question, the Ewald collision diagram is inadequate as a demonstration in these profiles. Thus we will illustrate the type of structure changes expected with some theoretical curves calculated by Laramore and Duke.

Figure 9 shows a demonstration of sideband diffraction in a series of energy profiles of specular diffraction at $0^\circ$ from W(100). A bulk loss is assumed with a very steep dispersion relation beginning at 5 eV. The elastic scattering, Figure 9a, is shown only for the case of single scattering and has two Bragg peaks in the energy range considered. For an energy loss of 5 eV, Figure 9b, the energy profile shows two peaks in the region where the elastic profile had one. These peaks correspond to the simple $E_1$ and $E_2$ Bragg scattering. As the energy loss increases, Figures 9c and 9d, the two peaks split into four as the component of momentum perpendicular to the surface becomes large enough to see sideband diffraction. Addition of multiple scattering and changes in plasmon damping can, however, lead to an absence of a four peaked structure in the energy intensity profiles. However sideband diffraction will still be observable in the energy loss profiles. Figure 10 shows a series of loss profiles for a
Figure 9. Theoretical energy intensity profiles demonstrating sideband diffraction.
Figure 10. Theoretical energy loss profiles for a bulk excitation demonstrating sideband diffraction.
bulk loss with a dispersion relation beginning at 9 eV. The motion in the peak in the loss profile as the primary energy increases in value across the Bragg energy at 68 eV is a result of different values of \((p, \omega)\) satisfying the side-band diffraction condition at different primary energies.

Figures 11 and 12 show a series of angular profiles calculated for specular reflection at 15° from Al(100). These illustrate the expected differences in the behavior of surface and bulk plasmons. The bulk plasmon angular profiles show a doublet splitting for specific values of the primary energy where side-band diffraction is undergone. The surface plasmon, on the other hand, always shows a doublet splitting (for reasonable values of \(p > 0\) and electron damping) for all values of \(E_p\). This is the same conclusion as qualitatively derived from the Ewald diagram in Figure 7.
Angular Profiles - Bulk Plasmons

Figure 11. Theoretical angular profiles for a bulk plasmon excitation demonstrating sideband diffraction.
Angular Profiles - Surface Plasmons

Figure 12. Theoretical angular profiles for a surface plasmon excitation.
2. APPARATUS AND EXPERIMENTAL PROCEDURE

2.1 Introduction

A medium resolution (~0.5eV, 3.5°) scanning LEED apparatus has been designed and developed in this laboratory by Professor F. M. Propst and Dr. T. L. Cooper. This instrument met the general criteria described in the previous chapter in that it could measure the angular and energy distributions of backscattered electrons. The design considerations and construction details along with a description of general measurements on a W(100) surface are described in the reference cited above. We emphasize here the modifications made to the instrument, both to improve the operation and to include a different target material, and we will briefly discuss the general operation of the modified instrument together with the new experimental procedures.

The basic instrument, shown schematically in Figure 13, consists of a four grid retarding field energy analyzer with a collimated Faraday collector, electron gun, target assembly and electrostatic shielding. The target is rotatable through ~345° about an axis normal to its surface. The collector is rotatable through an angle θ, 12° < θ < 90°, about an axis which is perpendicular to the axis of rotation of the target and which intersects the target surface, the incident beam direction and the axis of target rotation. The angle θ is the angular distance between the electrons detected by the collector and the incident beam (which is normal to the target surface). The combination of the two modes of rotation allow measurements to be made in any backscattered direction, and the retarding grid analyzer can measure an
Figure 13. Schematic of energy-angular distribution instrument showing the basic components.
energy loss profile (or energy distribution) in any chosen direction.

2.2 Electron gun

The electron gun provides the incident or primary electron beam with a well defined energy $E_p$. The gun is a simple triode design with cylindrical deflection units. The main lens is formed by the first two anodes and focuses the crossover formed by the lens action of the control grid and first anode. A voltage ratio of about 4:1 between the first two anodes is used to produce an image of about 1 mm diameter at the target. Operating the lens in the decelerating mode, beam currents of several microamperes at 100 eV could be produced using a .0127 mm by 1.27 mm thoriated tungsten ribbon filament.

2.3 Target and Target Assembly

A new target holder was designed and built in order to use an aluminum target. It is shown schematically in figure 14. The crystal is held in place by clamping it against a slot in an Al block. This slot prevents the crystal from rotating in the holder about an axis perpendicular to the face of the holder. The block, clamp, and screw are made of ultra-high-purity aluminum to prevent impurities from migrating to the target during annealing. This assembled block is bolted to a copper block. A Mo spacer is inserted between the Cu and the Al to prevent the possibility of the Al-Cu junction reaching a liquid phase at 548°C (a possible annealing temperature). This system is then bolted against two support rods which attach to the original target assembly. Directly behind the target is a shielded tungsten filament for electron bombardment heating.
Figure 14. Details of the target holder.
The filament and target assembly are attached to a rotary feedthrough which is aligned so that the axis of rotation is perpendicular to the target surface, and which is capable of rotating the completed assembly through 345° with a reproducibility of 1°.

The target is an ultra-high-purity (99.999%) Al single crystal which was obtained from Professor M. Metzger. It is 3.8 cm × .9 cm × .24 cm in size with a 2-56 clear hole drilled near the top to permit attachment to the Al holder. This hole was EDM spark-cut so that little or no mechanical damage was introduced into the experimental region. The surface preparation of the target will be described in section 2.8.

Surrounding the target and attached to the target flange is the shield assembly. This serves the major purpose of shielding the scattering and measurement regions from external electric fields which would perturb the incident and scattered electron trajectories. To complete the field free region, there is a Helmholtz coil external to the system. Careful allignment and current control has reduced the residual magnetic field in the target region to less than 15 milligauss.

With the suppressor raised to a positive voltage with respect to the shield, the majority of the electrons hitting the suppressor are trapped, thus reducing the possibility of any electrons which have scattered from the walls being detected by the analyzer.

The snout of the detector and the drift tube of the gun protrude through a slot in the shield, and all these are kept at the same potential as the target to insure a field free scattering region.
2.4 Detector

The original detector was a two grid retarding potential analyzer. We have modified this to a four grid analyzer, shown schematically in figure 15. The two new grids were wound with the existing precision instrument. The grids consist of 12.7 μm tungsten wire with a spacing of 63.5 μm brazed to a tungsten plate. The retarding potential curve obtained with this type of analyzer is differentiated by superimposing a small oscillating voltage on the retarding voltage. The AC part of the signal to the collector is then proportional to the current of electrons having energy E and energy spread dE. The energy E is equal to the retarding voltage and the energy spread is basically the size of the oscillating voltage. Only the general principles of the detector will be given here, as the details of the design considerations and construction have been given before.

Electrons enter the detector through the apertured snout, which geometrically limits the direction the detected electrons to that originating from the target. The apertures both reduce the number of electrons detected which have scattered from the snout and define the angular resolution of the instrument. In this experiment, the operating angular resolution is about 3.5°.

These columnated electrons pass through the entrance grid and arrive in a retarding field region. The voltage responsible for this is called the retarding voltage, $V_R$, and is placed between the retarding and entrance grids. Two grids are used to do the retarding because the resultant field is more uniform across the grid region. This improves the energy resolution and
Figure 15. Details of the four grid retarding field energy analyzer.
decreases the negative derivative effect - a change in the grid transparency as a function of the electron energy. The operating energy resolution is about .5 eV at 100 eV.

The electrons which energetically pass through the retarding grids are accelerated to the shielding grid and pass through and strike the collector where they are measured as a current. The loss of current from electrons backscattering from the collector is minimized by (1) platinum-black plating the collector plate to reduce secondary electron emission, and (2) applying a "suppressor" voltage between the shielding grid and the collector.

The method of detecting the desired signal will be explained in section 2.7.

2.5 Sputtering Ion Gun

Until recently, there had been no work done on clean single crystals of aluminum. In 1967, Jona perfected a technique for producing clean surfaces of Al crystals. The method, explained in detail in section 2.9, involves sputtering the crystal surface with argon ions. To use this method, we designed and built a simple sputtering ion gun which would fit in the existing system.

It consists of a cylinder rolled from 16-mesh stainless steel screen and closed on the end not facing the target. The axis of the tube makes an angle of about 25° with the target normal and intersects the target at the point where the incident electron beam does. The tube is 2.54 cm in diameter, 1.75 cm in diameter, 1.75 cm long and the front of the tube is 1.43 cm from the face of the target. Two tungsten filaments are supported outside the tube as
the source of the ionizing electrons. By applying a voltage between the hot filaments and the tube, we are able to generate $\text{Ar}^+$ ions in and around the tube. These ions can then be attracted to the target by applying the proper voltage between the target and the tube.

The ion spot produced on the target is about 0.8 cm in diameter, or about the width of the target and about eight times the size of the incident electron beam. This final design was determined and the spot size measured by sputtering an Al film from a Cu substrate with the experimental conditions as used in the actual cleaning. Nonuniformity in the ion beam can be effectively eliminated by rotating the target during sputtering.

2.6 Vacuum System

Once a clean experimental surface is established, it is necessary to keep it uniformly clean during the period that measurements are taken. To assure this, the experimental apparatus described in the previous subsections is housed in the ultra-high vacuum system shown schematically in figure 16.

The vacuum chamber is pumped with two mercury diffusion pumps in series which are backed with a standard mechanical pump. The main diffusion pump is kept free of any contaminants from the mechanical pump by the fore diffusion pump. Backstreaming of gasses, including mercury, into the vacuum chamber is greatly reduced by the thermoelectric baffle and two liquid nitrogen cold traps in series with the main diffusion pump. The vacuum chamber is further pumped with a titanium sublimation pump which is directly attached to it. High purity research (reagent) grade gasses are admitted to the system through a
Figure 16. Schematic of vacuum system.
gas manifold constructed from glass tubing and Granville-Phillips leak and 1/2-inch type C valves.

The system is bakeable to 450°C except for the baffle, diffusion pumps, and gas bottles. To achieve pressures in the low $10^{-10}$ Torr range, the chamber and top trap (lower trap filled with liquid N$_2$) are baked at 250°C for eight hours, followed by an eight hour baking of the chamber by itself. After the chamber cools the valve is closed and the two traps are baked at 250°C for eight hours, concluding with a bake of the top trap only for another four hours. After the traps are filled, the valve is opened and the sublimation pump flashed, a base pressure of about $1 \times 10^{-10}$ Torr is reached after about six hours. The background gas was measured previously and was found to be almost all hydrogen.

2.7 Electronic Circuitry

Figure 17 shows a schematic of the electronic circuitry as it is set up when measurements of either angular profiles or energy loss profiles are being made. Capacitors used to eliminate 60 cycle and high frequency noise are not shown.

The electron gun is connected to a simple voltage divider which keeps the focusing voltage ratio constant as the primary beam energy is changed. All electron gun elements are referenced to the drift tube, which is at ground potential. The gun is shown operating in the decelerating mode. It can be operated in the accelerating mode by simply interchanging the drift tube and anode connections. The monoenergetic electron beam produced by the gun enters the scattering area enclosed by the shield assembly. No detectable changes
Figure 17. Schematic of electronic circuitry for energy and angular measurements.
could be found by attracting scattered electrons to the suppressor, so the whole shield assembly was kept at ground potential. The electrons then scatter from the target, and some of these arrive at the snout of the collector. Both the target and snout are at ground potential to insure a field free region for scattering.

Passing through the entrance grid, the electrons arrive near the retarding grid, which is kept at a variable voltage $V_R$ above ground. The differential cross section is proportional to the derivative of the collector current with respect to $V_R$. To measure the derivative, we superimpose on the retarding voltage a small oscillating voltage, $\Delta V \sin \omega t$. The AC component of the collector current with frequency $\omega$ is proportional, to first order in $\Delta V$, to the cross section of the detected electrons with energy $eV_R$. For the measurements reported here, $\Delta V = .5 \text{ v}$, and $\omega = 2\text{kHz}$.

The collector current passes through a five megohm wire-wound resistor. The voltage across this resistor is amplified by a PAR model CR4-A low noise amplifier. This signal is then fed to a phase-sensitive PAR model JB-5 lock-in amplifier, the output of which drives the y-axis of an EAI model 1130 x-y recorder.

The x-axis of the recorder is driven by either of two potentiometers, depending on the profile being measured. When angular profiles are measured, the appropriate potentiometer used is directly coupled to the rotary feed-through of the collector with a set of gears. When energy loss profiles are measured, the potentiometer used is directly coupled to the potentiometer which changes the retarding voltage. Both the collector and retarding voltage potentiometer can be driven with a motor to assure smooth sweeps of each profile.
Figure 18 shows a schematic of the basic circuitry used when the target is sputtered with argon ions.

2.8 Target Preparation

The ultra-high-purity aluminum crystal was spark cut to within 2 degrees of the (100) face. It was mechanically polished flat to less than ten microns with silicon carbide grit. The surface was etched in a dilute solution of HF between different grits to remove any work hardened material. The crystal was then chemically polished in a solution made up of eighty parts (by volume) of phosphoric acid, fifteen parts of sulfuric acid, and five parts of nitric acid. The crystal was polished for five minutes in this solution, which was kept at 80 to 90°C. Following this, the crystal was electropolished flat in a few minutes in a solution made up of ninety-three parts (by volume) ethanol and seven parts perchloric acid. Polishing was carried out with the bath temperature at about -15°C and at a current density of 0.1 to 0.15 amp/cm² and with constant, but mild, agitation. The perchloric acid polishing solution was chosen over others primarily because it leaves a relatively thin (~30 Å) oxide layer on the surface. But because of the explosive nature of this solution, we caution the reader to refer to Tegart before handling perchloric acid.

The polished target was then inserted in the target holder and placed in the assembled vacuum system. To clean the target surface before taking any measurements, we used the basic method perfected by Jona and subsequently verified by others. The target first was submitted to a bombardment of argon ions at 450 eV and about 3-5 μA/cm². This was followed by a vacuum
Figure 18. Schematic of electronic circuitry for argon ion bombardment.
anneal at 500°C for one hour. Five or six treatments consisting of bombardment followed by annealing produced a clean surface. The crystal was rotated at 6°/min during ion bombardment to assure uniform cleaning. Every third cycle, we extended the annealing time to two hours to assure that the damage introduced by the ion bombardment was annealed away.

The target temperature had been calibrated by using two pieces of 1100 Al (99.5% pure) which were machined to the same size as the experimental crystal, polished, and separately placed in an identical target holder. A chromel-alumel thermocouple was attached to the targets to measure their temperatures. It was found that the temperatures could be reproduced within ±10°C at 500°C for the same target and between the two targets.

2.9 Criteria for Surface Cleanliness

There are many different criteria reported in the literature for determining when a surface is clean or not. Some people use the clarity and lack of secondary structure of ELEED pictures taken from a display instrument as an indication of a clean surface. Others use the reproducibility of the elastic energy intensity profile, while still others observe the Auger electron spectra and note the presence or absence of peaks corresponding to different elements. The major question which can be raised is to ask about the sensitivity of each test.

The information gained from LEED will be related to the scattering from a periodic array. Any adsorbate not in a periodic structure will only contribute to the background of both the pictures and energy profiles. It
is generally accepted that extra ELEED spots or beams are probably detected with periodic coverages of .1 to .25 of a monolayer. As far as this author can determine, there have been no quantitative experiments relating diffuse background changes to amounts of adsorbates.

One of the advantages of Auger analysis is that it can tell you the kinds of absorbates (except for hydrogen and helium) on the surface. But there have been relatively few calibration experiments which relate adsorbate coverage to the strength of the corresponding Auger peak. One of the better ones was done by Weber and Johnson, in which they could deposit as little as .01 monolayer of alkali metals on Ge and Si surfaces. They found they could detect as little as .02 monolayer of Cs on Si using a standard three grid retarding field analyzer. Their limiting factor was the size of the background on which the Cs Auger peak was superposed. However, using the same type of system, Weber and Peria reported they could only detect about .1 monolayer of Cs on Si. Thus the sensitivity is probably instrument and technique dependent. Of the calibration experiments referenced, only two deal with the study of a gas on a surface. Musket and Ferrante report a sensitivity of .02 monolayer of O₂ adsorbed on W (110), assuming a saturation coverage of O₂ equivalent to one monolayer. Changing this assumption changes the measured sensitivity. Similarly, Chang assumes an O₂ saturation of .5 monolayer on Si (111) and arrives at a sensitivity of ~ .005 monolayer.

Turning our attention to the work done on aluminum, we find that Jona, Farrell and Somorjai, and Bedair et. al. assumed a clean surface
on the basis of reproducible ELEED patterns and elastic energy profiles. But Marsh\textsuperscript{60} combined ELEED patterns and Auger analysis and basically confirmed the conclusions of Jona about surface cleanliness. However, after adding O\textsubscript{2} to the surface and then regenerating a reproducible ELEED pattern by heating the crystal, Marsh found he could still measure a trace of O\textsubscript{2} in the Auger spectra, assuming a sensitivity of $\sim$ .25 monolayer. This O\textsubscript{2} could be removed with argon bombardment. The results of Jona and Marsh yield a sticking coefficient of O\textsubscript{2} on Al (100) of about $5 \times 10^{-3}$ for low coverages. We will assume the sticking coefficient of H\textsubscript{2} to be about 3-4 times that of O\textsubscript{2}, as is the case with O\textsubscript{2} and H\textsubscript{2} adsorption on W. These assumptions are made for purposes of qualitative discussion.

We have used four basic tests of the cleanliness of our target surface. The least sensitive, but one which gives the order of magnitude of cleanliness and is most attainable, was the reproducibility of the ELEED pattern and the elastic energy profile. However, we found that the elastic diffuse background changed a little faster than these as a function of time, hence as a function of background gas adsorption. Noticeable changes occurred about 12 hours after cleaning, or, on the basis of the assumed sticking probabilities and the measured pressure, after about .05 monolayer of background gas was adsorbed.

We also observed the Auger spectra of the surface after multiple cleanings and found no evidence of contaminants. Robertson\textsuperscript{68} has recently reported that the low energy Auger line of Al covered with approximately one monolayer of oxygen is at 53-54 eV, while the Auger line of clean Al is at
66-67 eV. The line at 54 eV is of the same value as that commonly reported\textsuperscript{63} for "clean" Al. Moreover, Jona\textsuperscript{69} and this author, independently and at the same time, had also measured the Auger line at 66 eV for clean Al. However, the present apparatus was not designed to do high sensitivity Auger work (better than \textasciitilde{} .1 monolayer sensitivity).

It is possible to monitor our surface cleanliness to coverages better than the \textasciitilde{} .1 monolayer of O\textsubscript{2} coverage provided by the Auger measurements by using the technique of electron loss spectroscopy and the reproducibility of the surface plasmon loss profiles. It has been found by Edwards\textsuperscript{70} and this author that when O\textsubscript{2} is added to a clean surface of W, a new peak in the energy loss profiles may be measured at 7 eV. This author determined that it is most easily found near energy and angular conditions of Bragg resonances, and its presence is detectable with about .05 monolayers of O\textsubscript{2} on the surface, using accepted values of the sticking probabilities. This loss peak was also measured on the Al surface in the presence of O\textsubscript{2}. If we assume the same sensitivity as on W, we can say our surface is free of O\textsubscript{2} to less than .05 monolayers.

The most sensitive test to change appears to be the reproducibility of the surface plasmon angular and loss profiles. Changes in the peak positions and intensities could be measured 6-8 hours after argon bombardment and annealing, or with about .02 to .03 monolayer coverage of background (mostly H\textsubscript{2}) gas, or \textasciitilde{} .01 monolayer of O\textsubscript{2}. Again, we use the assumed values of the sticking probabilities on Al. We could return the surface plasmon structures to the original values after sputtering and annealing the surface.
Figure 19 shows a striking example of the types of changes measured between a clean surface and one which had adsorbed some background gas amounting to about .35 to .5 monolayers (using the assumed sticking probabilities and pressure measurements). The loss peak at 11 eV has decreased in intensity and shifted to 10 eV with the addition of gas on the surface. This is in general agreement with the predictions of the theory\textsuperscript{21} and experiments\textsuperscript{19,20} done on Al films. The loss profile of the clean Al surface could be reproduced by argon bombardment and annealing of the "dirty" surface. One of the problems of using this type of criteria for a measure of surface cleanliness is that the surface plasmon losses from different primary beam energies and in different directions reacted with different degrees of sensitivity to the same contamination. We intend to do some work in the future to investigate the behavior of the surface plasmon dispersion relation as a function of gas coverage.

All our measurements reported here as being taken on a clean surface of Al were taken within 5-6 hours after each sputter-anneal cycle and in a background pressure of \( \sim 1 - 2 \times 10^{-10} \) Torr. Thus, we expect no more than .01 to .05 monolayer of adsorbate on the surface during our clean measurements.

2.10 Instrument Checkout

Before the instrument was assembled with the Al crystal, the new four grid energy analyzer was checked for its operating characteristics with a new W (100) target. With the original two grid analyzer, Cooper\textsuperscript{4} reported seeing large splittings in some of the inelastic angular profiles of electrons scattered from W (100). The shapes of some of these splittings led him to conclude that some of these were real, while others probably were experimental in nature.
Figure 19. Energy loss profiles in the (10) diffraction direction for a "clean" and "dirty" surface.
The addition of the third and fourth grids substantiated this hypothesis. We were able to reproduce the angular splitting in some cases, but were not able to in other cases. The majority of these cases agreed with the conclusions of Cooper. Computer calculations of the electron trajectories showed that the probable cause of the two grid splitting was an effect known as the negative derivative effect. That is, the effective transparency of the grids increases over the optical transparency as the electrons which approach the retarding grid approach zero energy. As they approach the grid, slow moving electrons which would have collided with a grid wire had they maintained a straight line path, are deflected away from the wire by the component of the electric field which is parallel to the grid plane and which exists (with any strength) near the grid wires. To eliminate this effect, the new grids were wound with a wire spacing of one-half the original wire spacing, and placed together so the wires of one were perpendicular to the wires of the other in the retarding plane. Besides eliminating the negative derivative effect, the new grids improved the energy resolution of the instrument. This improvement was noted in the halfwidth of the elastic energy peak and in the halfwidth of the peaks in the elastic angular profiles.
3. DATA PRESENTATION AND DISCUSSION

This chapter is organized into two parts: (1) a presentation of the experimental measurements together with a general discussion of the results, (2) a detailed comparison of theoretical profiles and experimental measurements.

The experimental measurements will be displayed in the three forms as discussed in chapter 1. Figure 20 schematically reminds us that the three forms are energy intensity profiles, energy loss profiles, and angular profiles. The energy intensity profiles measure the scattered intensity as a function of the incident or primary energy. The energy loss profiles measure the scattered intensity as a function of the energy loss, and the angular profiles measure the intensity as a function of the scattered polar angle or collector angle. In each case, the other parameters are held constant.

The profiles will be presented in a set of normalized units, so that the diffracted beam intensities can be compared with each other and with the intensity of the incident beam. The method for making these comparisons, the first of their kind for inelastically diffracted electrons, together with an intensity analysis is given in the next subsection.

The theoretical profiles used in the last subsection were calculated by Duke and Bagchi\textsuperscript{36,71} of the Department of Physics, University of Illinois.
Figure 20. Schematic of the three forms of presentation of the experimental measurements.
3.1 Measurement of the Absolute Intensity

The object of this section is to determine the percentage of electrons scattered into a particular region of the energy-angle space, and then use this as a calibration for the rest of the measurements. To accomplish this, we must perform three tasks. First, we must measure the total electron current incident on the target. Second, we must measure the electron current scattered into a particular beam in the desired energy-angle space. Finally, we must compare the experimental measurement (detector output) of this beam profile with the scattered percentage of incident current to get a conversion factor for the electronic output.

Figure 21 shows the measurements made in the calibration experiment to determine the desired conversion factor. In this calibration run, the incident electron current to the target, $I_0$, was measured at $5.0 \times 10^{-6}$ amperes, which is the sum of the target current and the current to the electronic shielding. Since the electron gun is the only source of electrons, and since the current is conserved, this measurement gives the correct incident current. We next took an angular profile of the elastically scattered electrons, as shown in Figure 21 (a). To measure the currents, we located our collector at $34^\circ$, to correspond to the peak in the elastic angular profile. We then measured the retarding energy curve and the energy loss profile, as shown in the other two panels. It is easy to show that with a collector of energy acceptance width approximately equal to the incident electron beam width (about 1 eV in our case) that the total scattered elastic current is approximately the current at a loss energy of 1.5 times the energy width. In these measurements we found $I_{\text{Elastic}} \approx 1 \times 10^{-8}$ A.
$I_0 = 5 \times 10^{-6} \text{ Amp} \quad E_p = 115 \text{ eV}$

g = (1 0)

(a) Collector Current vs Retarding Potential for Collector Angle, $\theta$ of 34°

(b) Angular Profile of Elastic Electrons ($\omega = 0$)

(c) Energy Loss Profile for $\theta = 34°$

Profile Results from Differentiation of Retarding Potential Curve, (b)

Figure 21. Experimental measurements necessary to calibrate the intensity of the scattered electrons.
The measured height of the elastic beam is .76 units; these units are applicable when the values of all variables such as amplifier gain, etc., set in the calibration experiment are used. Then an experimental height of .76 units corresponds to a percentage reflection equal to \( 0.1 \times 10^{-8} / 5 \times 10^{-6} \) or \( 0.02\% I_0 \). Thus, one unit equals approximately \( 0.026\% I_0 \). This factor has been applied to all the measurements, with proper account being taken for amplifier gain, etc. To make the measurements easier, we will convert the scale to what we will call "normalized units", in which one normalized unit equals \( 0.01\% I_0 \). If a curve has been amplified for clarity, this will be denoted on the profile as a gain in parenthesis after the fixed variable, such as \( E_p = 100\text{eV}(\times 10) \), indicating that the particular profile is for a primary energy of 100 eV and is shown amplified by a factor of 10. For convenience, we have also included the amplification factor on the intensity scale shown on the experimental profiles. Thus the absolute intensity of each curve can be read directly.
3.2 Energy Intensity Profiles

This section will be devoted to the discussion of the experimental measurements of the elastic and inelastic energy intensity profiles. The profiles to be discussed are those of the (10) and (11) diffraction beams resulting from the diffraction of electrons incident normally on a clean surface of Al(100). In obtaining the energy intensity profiles, a series of angular profiles was taken over the range of incident electron energies for each desired loss energy. The intensity was then measured at the desired collector angle by subtracting the extrapolated incoherent background and normalizing to unit incident beam current. The inelastic intensity for each incident energy was measured at the collector angle at which the elastic angular profile at that incident energy was a maximum. This collector angle is what we called $\theta_{\text{Elastic}}$ in the first chapter. Figures 22 and 23 show the measured elastic ($\omega=0$) and inelastic ($\omega=8-18 \text{ eV}$) energy intensity profiles for the (10) and (11) diffraction beams respectively.

The extrapolation was done by smoothly joining the profiles on each side of the diffraction peak. The incoherent background possibly consisted of electrons which had excited single particle-hole excitations and phonons and of electrons which excited plasmons, but which scattered incoherently from regions of imperfection of the crystal surface. While no detailed study was made of the effect, it was noted that this background generally increased as gas became adsorbed on the surface.
Figure 22. Elastic and inelastic energy intensity profiles for the (10) diffraction beam. The intensity unit is labeled for each scale factor used.
Elastic and Inelastic Intensity Profiles

Al(100) g = (1,1)
θ = θ_{Elastic}

1 u (×1) = 0.01%
1 u (×20) = 0.005%
1 u (×50) = 0.0002%

Figure 23. Elastic and inelastic energy intensity profiles for the (11) diffraction beam.
3.2.1 Elastic Energy Intensity Profiles

The (10) elastic energy intensity profile has two major peaks at 54 and 107 eV. The (11) profile has three major peaks at 43, 86 and 152 eV. Each profile has some minor peaks we will discuss later. The first thing to notice is that the major peaks in each profile are distinct, well separated in energy, and of a narrow halfwidth (10-12 eV). These peaks correspond to classical Bragg peaks resulting from a single scattering if an inner potential correction of about 14 eV is used. This is most easily seen by comparing our experimental peak locations with those predicted theoretically by Laramore and Duke \textsuperscript{72} and found in Table 1. The inner potential of 14 eV locates all of our experimental peaks within 1 eV except for one which is within 2 eV.

We can also compare our elastic measurements with those of Jona \textsuperscript{48} and Farrell and Somorjai \textsuperscript{62}. Their experimentally determined peak locations are also found in Table 1. For the most part, the agreement with the work of Jona is very good, while that with Farrell and Somorjai is adequate. It should be noted that both Jona and Farrell and Somorjai used spot photometers and display type LEED screens for their experimental measurements. Farrell and Somorjai did not normalize their curves to eliminate variations in incident electron current, and both they and Jona did not eliminate the diffuse and incoherent elastic background and could not make absolute intensity measurements. With this in mind, we can at best only approximately compare our peak shapes with those of Jona. Doing this, it is found that the relative heights of the (11) and (10) peaks compare quite well, although Jona's (10) peak at 84 eV is much more
Table 1. Comparison between experimentally observed and theoretically predicted positions of the principal peaks (in eV) in the elastic energy intensity profiles of the (11) and (10) diffraction beams from Al(100). $V_I$ is the inner potential correction.

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jona$^{48}$</td>
<td>Laramore and Duke$^{72}$</td>
</tr>
<tr>
<td>Farrell and Somorjai$^{62}$</td>
<td>$V_I=14$</td>
</tr>
</tbody>
</table>

**(11) beam:**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>This work</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>43</td>
<td>43</td>
</tr>
<tr>
<td>90</td>
<td>88</td>
<td>86</td>
</tr>
<tr>
<td>151</td>
<td>143</td>
<td>152</td>
</tr>
</tbody>
</table>

**(10) beam:**

<table>
<thead>
<tr>
<th>Experiment</th>
<th>This work</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>55</td>
<td>54</td>
</tr>
<tr>
<td>84</td>
<td>74</td>
<td>(75)</td>
</tr>
<tr>
<td>105</td>
<td>98</td>
<td>107</td>
</tr>
</tbody>
</table>
pronounced than ours. However, the full width at half maximum of Jona's peaks are about 20 eV, a factor of two larger than ours. This might be an effect of our having a cleaner surface or to our subtracting the incoherent background.

The peak in the (10) profile at 75 eV can be seen more clearly on a semi-log plot. At this point, though, all that is important to notice is that this peak is almost negligible compared to the two prominent peaks. This will be discussed in more detail in the next subsection on the inelastic profiles.

We should also note the presence of some secondary structure in the profiles. There are two low energy peaks in the (10) beam profile at 33 and 40 eV. The (11) profile shows two peaks at 54 and 63.5 eV and some less prominent peaks at 112, 121 and 130 eV. Jona's profiles show these secondary peaks near 34 and 42 eV in the (10) profile and at 68 and 120 eV in the (11) profile. These are probably multiple scattering resonances. We discuss the nature of the 63.5 eV peak in more detail in the next subsection, as we get a clue to its nature from the inelastic profiles. We compare the elastic intensity profiles with the theoretical profiles in more detail in Section 3.5.
3.2.2. Inelastic Energy Intensity Profiles

At this point, it is appropriate to recall the discussion given in the first chapter concerning inelastic low energy electron diffraction (ILEED). The two step model of ILEED says that the electron may undergo elastic diffraction from the lattice and inelastic scattering, such as by plasmon excitation, in either sequence. This is what we called EI and IE scattering. In the inelastic energy profiles, we expect one peak to occur at about the Bragg energy when electrons undergo EI scattering, and one peak at the Bragg energy plus the loss energy when IE scattering occurs. In addition, Duke and Laramore predicted that these two peaks split into four peaks when the sum of the incident electron momentum, final electron momentum and the excitation momentum (of a bulk loss mode) equals a reciprocal lattice vector of the solid (assuming that the peaks are resolvable). This effect is demonstrated in Figure 9.

An examination of the inelastic intensity profiles for both diffraction beams, Figures 22 and 23, shows that the structure for each loss energy is closely correlated with the structure in the corresponding elastic profile. That is, the gross structure in the inelastic profile occurs at about the same energies as the structure in the elastic profile. The dotted region of the profiles was that region in which the inelastic diffraction peaks were not defined well enough to permit an accurate measurement of their intensity. The dotted line represents the estimated intensity in this region.

Confining our attention to the energy region around the major peaks in the elastic profile, we first note that a peak occurs in the inelastic profiles
at about the energy that the elastic profile has a Bragg peak (within ~ 1 eV). This inelastic peak at $E_{\text{Bragg}}$ is principally associated with those electrons whose scattering amplitude for elastic diffraction followed by an inelastic scattering (EI) is large. Around each of these peaks at the Bragg energies, there occur other peaks in the inelastic profile, their number, energy position and intensity depending on the particular loss energy and primary energy.

We expect to see a peak in the inelastic profile for loss energy $w$ at $E_{\text{Bragg}} + w$ which is principally associated with those electrons whose scattering amplitude for an inelastic scattering followed by elastic diffraction is large (IE scattering). Indeed, peaks are experimentally observed at $E_{\text{Bragg}} + w$ within ± 1 and 2 eV for a majority of the inelastic energy profiles in both the (10) and (11) diffraction beams. The clearest example of this is seen around the (11) Bragg peak at 86 eV. For electron losses between 10 and 16 eV, we find a prominent peak at 86 eV, corresponding to EI scattering, and a second peak located above this which moves away in energy as the loss energy increases, corresponding to IE scattering.

However, for a loss energy of 18 eV, the inelastic profile around $E = 86$ eV has become a four peaked structure. As the electrons which have lost 18 eV are those which have primarily excited bulk plasmons, the presence of four peaks is an indication of sideband diffraction. This will be more fully substantiated in the section on angular profiles. Again, if we refer to Figure 9, we expect this four peaked structure in the inelastic energy profile to be an effect of sideband diffraction. There are also other regions of both beam profiles which show multiple peaked structures for the inelastics, for instance, around the (11) Bragg peak at 152 eV and around the (10) Bragg peak at 107 eV. While some of the structure of the 18 eV profile near 152 eV
might be due to sideband diffraction, the presence of a third peak in the profiles of the 8 and 10 eV losses suggests that multiple scattering effects might be the primary cause. This is plausible, as these higher energy electrons will penetrate more deeply into the crystal, and hence will "see" more ion cores with which they may interact. However, there are no multiple-scattering peaks in the elastic profile near this primary energy, which tends to cast some doubt on this explanation. The profile of the 18 eV loss in the neighborhood of the (10) 107 eV Bragg peak has four peaks at $E_p \approx 106$, 113, 124, and 128 eV. The 106 and 124 eV peak would correspond to $E_{\text{Bragg}} + w$. The 113 eV structure is present in some of the other profiles and is probably a multiple scattering resonance, while the peak at 128 eV is not seen in the other profiles and might be due to sideband diffraction.

There are a number of interesting phenomena present in the inelastic profiles. First, the rather prominent peak in the elastic (11) profile at 63.5 eV is present in the inelastic profiles of $w = 14$, 16, and 18 eV. Since the peak is present for surface plasmon losses, and not for the bulk plasmons, we are first led to the speculation that the 63 eV peak is a surface phenomenon in which the electron beam does not penetrate into the crystal deep enough to make excitation of a bulk plasmon probable.

We consider such a surface phenomenon to occur when, in a multiple-scattered electron beam, one of the intermediate electron beams propagates along the surface, and the wavelength of this intermediate beam is some integral multiple of the distance between the scattering ion-cores. On the surface, the distance between the ions in the (10) direction is 2.86 Å. An electron with an
energy of 74 eV has a wavelength of about 1.43 Å, exactly one-half that of the ion core separation. Thus, assuming a reasonable value for the inner potential of about 11 eV, it is possible that the 63 eV peak may be due to a multiple-scattering resonance along the (10) direction in which the intermediate beam propagates along the surface. This conclusion is further strengthened by an examination of the (10) elastic and inelastic profiles. First, the (10) elastic profile has a definite shoulder near 63 eV. Second, the inelastic profiles for losses between 10 and 16 eV have peaks at 63 eV. These peaks are probably not due to IE diffraction associated with the Bragg peak at 54 eV, as these other peaks do not move as the loss energy is varied. If we examine the angular profiles and the loss profiles at primary energies around 63 eV, we find that the loss mechanisms are almost entirely surface plasmons, explaining the presence of the 63 eV peak in the w = 14 and 16 eV energy profiles.

Taking all this behavior into account, it becomes reasonable to infer that the 63 eV peak in the (11) energy profile is indeed a multiple scattering resonance along the surface. We shall also see the presence of a peak in the theoretical profiles near 62 eV which is a multiple scattering peak.

With this in mind, we can now question the nature of the peaks in the (10) inelastic energy profiles near a primary energy of 74 eV. These peaks may either be IE peaks associated with the 63 eV peak, or EI peaks associated with the small elastic peak at 75 eV, or some other phenomenon. It is unlikely that these are EI scatterings, as the elastic peak is not readily seen on such a linear plot, and we would not expect the inelastic structure associated with this to be so large, as it happens for no other energy region we have examined. Because the 10, 12, and 14 eV peaks move upward in primary
energy, we can more reasonably infer that these peaks are the IE scattering of the surface resonance. It then remains a mystery as to why the $w = 16$ eV peak is located at the same energy as the $w = 10$ eV peak is.

Another interesting observation is that there is no secondary IE structure associated with the diffraction peak at 43 eV in the (11) beam. All the inelastic profiles have only one peak (an EI peak), except for a possible shoulder for $w = 18$ eV. It is possible that the other structure is mixed with that of the elastic peak $\sim 54$ eV, although it doesn't appear likely after examining the profiles.

It is more likely that most of the intensity of the plasmon losses can be found at angles away from $\theta_{\text{elastic}}$. This can be explained by remembering that the excitation wavevector for a given loss energy has remained the same, while the wavevectors of the electrons near 43 eV energy are considerably smaller than those of electrons near 86 eV or 142 eV. A vector diagram which conserves momentum parallel to the surface demonstrates that the angular spread in the resulting inelastic electrons at lower energies will be larger than the angular spread at higher energies. This is measured experimentally and can be seen in the angular profiles in section 3.4.
3.3 Energy Loss Profiles

In this section, we will briefly survey the types of results measured in the energy loss profiles.

Figure 24 shows a series of energy loss profiles. As we discussed in section 1.3, the prominent peak near \( w = 10 \) eV corresponds to the excitation of a surface plasmon, the peak near 15 eV to the excitation of a bulk plasmon. As shown in this figure, we have also measured the presence of a loss peak at 26 eV and another at \( w = 31 \) eV. The 26 eV loss possibly corresponds to the excitation of both a bulk and a surface plasmon, while that at 31 eV is possibly that of two bulk excitations. These higher energy losses became more prominent as the energy of the incident electrons was increased. Although we never painstakingly searched for it, we never observed a 20 eV loss peak, which would correspond to the excitation of two surface plasmons.

We also have observed a series of loss peaks between 4.0 and 6.0 eV, and one at \(-8.0\) eV. Figure 25 shows three energy loss profiles taken in the (10) diffraction direction at different collector angles. The peak in the angular distribution of the 56 eV elastic electrons occurred at a collector angle of 31°. Besides the surface and bulk plasmon losses, we see a loss peak at 4 eV, a shoulder at \(-5.5\) eV, and a shoulder at \(-8.0\) eV each occurring on a different profile. We believe that the 4 to 6 eV losses are due to a single loss mechanism. Small changes in the collector angle moved the position of the loss peak a great deal within this energy loss range. This is evident from the figure. The presence of these losses also was observed only in a primary energy
Figure 24. Energy loss profiles for different primary energies showing the bulk and surface plasmons.
Figure 25. Energy loss profiles for a primary energy of 56 eV and different collector angles. $\theta_{\text{Elastic}} = 31^\circ$. 

$\theta = \theta_{\text{Elastic}}$

$1u(10) = .001%$

$1u(\times 20) = .0005%$

$1u(\times 50) = .0002%$

$E_p = 165 \times 50$

$165 \times 20$

$100 \times 20$

$95 \times 20$

$90 \times 10$

$85 \times 10$

$80 \times 10$
range around the (10) Bragg energy at 54 eV. These facts lead to the speculation that these peaks are a phenomena of sideband diffraction for a highly angularly dependent bulk excitation such as an indirect interband transition. Unfortunately, the angular and energy resolution of the present instrument prohibits an accurate measurement of the losses' behavior as a function of the experimental variables and hence a determination of their nature.

The nature of the 8 eV shoulder is even more mysterious. Its presence is measured only within ± 1° of the elastic peak and within ± 2 eV of 56 eV primary energy. It was found in a detailed search only after observation of the peculiar doublet in the w = 8 eV angular profile, as seen in Figure 26. As a loss of 8 eV is below the surface plasmon threshold (~10 eV), the pronounced angular doublet is hard to justify without the presence of another loss mechanism. But its highly localized nature in energy and angle makes it impossible to determine its nature with this instrument.

In section 2.9, we briefly described the behavior of the energy loss profiles as a function of surface cleanliness. Figure 19 demonstrated that a small addition of contamination on the surface leads to a rather significant change in the loss profile - both in intensity and peak shape and position. However, it was not the purpose of this work to make a detailed and systematic study of the effects of gas adsorption on the inelastic profiles. We have found, though, that the effects are significant and warrant future study.

Finally we shall look at the effects of different diffraction conditions on the energy loss profiles. Figure 27 shows a series of energy
Figure 26. Angular profiles at 56 eV primary energy for electron loss energies of 0 and 8 eV.
Figure 27. Series of energy loss profiles in the (11) diffraction beam for different primary energies, $E_p$, and collector angles $\theta$. 
loss profiles taken at different primary energies ($E_p = 80 - 100$ eV) and at three different relative collector angles. Recalling the discussion in section 1.4.1, we have defined $\theta_{\text{Elastic}}$ as the angle at which the elastic angular profile is a maximum. In other words, this is the angle relative to the surface normal at which the wavevector of the diffracted electron intersects the reciprocal lattice rod in an Ewald construction. We have chosen the various primary energies so as to encompass the (11) Bragg energy at 86 eV. Recalling Figure 24, we see that this choice of primary energies moves from a range primarily of $\text{EI}$ diffraction to a range primarily of $\text{IE}$ diffraction.

The first thing to be noted is the relative growth and decay of the surface and bulk plasmons as a function of primary energy and scattering angle. First, for the collector angles constant with respect to $\theta_{\text{Elastic}}$, we note that for primary energies below the Bragg energy, there is a large surface plasmon loss peak at $\omega = 10$ eV and only a shoulder of a bulk plasmon loss. As the incident energy increases through the Bragg energy, the bulk plasmon loss grows relative to the surface plasmon until at $E_p = 100$ eV, there is a large bulk plasmon loss peak at $\omega = 15$ eV and only a shoulder of a surface plasmon loss. The rate of increase and decrease is dependent on the angle relative to $\theta_{\text{Elastic}}$, as can easily be seen by comparing the three panels. This can also be seen by comparing the profiles for a constant incident energy, for example, those of $E_p = 95$ eV. For a collector angle less than $\theta_{\text{Elastic}}$, the loss profile consists of a large surface plasmon loss and a shoulder of a bulk
plasmon loss. As the angle is moved to angles greater than $\theta_{\text{Elastic}}$, the
loss profile consists of a large bulk plasmon loss and a shoulder of a surface
plasmon loss.

Careful examination of the loss profiles show that the position of
the peaks are a function of the primary energy. For instance, at $\theta_{\text{Elastic}}$, the
surface plasmon loss peak is at 10 eV for $E_p = 80$ eV and at about 11 eV for
$E_p = 95$ eV. One can reasonably ask whether this shift is a real change as a
function of different diffraction conditions, or whether it is an apparent
change caused by the addition of a large bulk plasmon peak located near the
surface plasmon. If we assume that the loss peaks are Gaussian curves with
widths equal to the experimental widths (~2 eV) and separated by 5 eV then a
numerical calculation shows that the addition of a second peak which is equal
in height to the first will shift the first peak position by about 0.3 eV. Thus,
the 1 eV experimental shift is probably a real shift which is a function of
the incident electron energy. That this shift is real is further substantiated
by comparison with the theoretical profiles as seen in Figure 44 of Section 3.5.
3.4 Angular Profiles

This section will be devoted to an analysis of the measured angular profiles. First, it is worthwhile to review some of the qualitative predictions made in section 1.4. The angular profiles of the surface plasmons are expected to consist of doublets due to the directional limitations of the excitation along the surface (recall Figures 7 and 12). The angular profiles of the bulk plasmons are expected to be single peaked, except in regions of sideband diffraction, where this peak splits into two peaks (recall Figures 8 and 11).

To distinguish which loss energies are associated with a particular excitation, it is necessary to study the energy loss profiles, such as Figure 27. In general, it appears that the losses between ~9 and ~12 eV are associated with purely surface plasmons, losses between ~16 and 19 eV with bulk plasmons, and losses between ~13 and 15 eV can be associated with both bulk and surface plasmons. We can see from Figure 27 that the relative strength of the excitations in the 13 to 15 eV loss regions is dependent on both the primary energy and the angle relative to $\theta_{\text{Elastic}}$. We will refer to this figure as we identify the structure in the various angular profiles.

Initially we concentrate our attention on electrons diffracted into the (11) plane in the region of the (11) Bragg peak at 86 eV. We will do this because this Bragg peak is the most intense, and the inelastic structure is the most pronounced in this region.

Figure 28 shows a series of angular profiles at a constant primary energy ($E_p = 86$ eV). Note that the elastic profile ($\varphi = 0$) is symmetrical and
Figure 28. Angular profiles for constant primary energy (86 eV) and different loss energies.
well localized in angle in what is commonly called a diffraction beam. If we examine the inelastic profiles \( w \neq 0 \), we see that they too are found in localized beams which are located very near the elastic beam. This is a consequence of inelastic two-step diffraction. Without a diffraction from the lattice, we would not expect to find the inelastics so well localized in angle. But there are dynamical scattering effects present, as can be seen in the internal structure of the inelastic profiles. These can be seen more clearly in the next set of figures.

Figures 29 and 30 show a series of angular profiles for losses of 10 and 12 eV respectively, taken at a number of different primary energies. The range of primary energies includes values both above and below the (11) Bragg energy of 86 eV. The black dot on each profile indicates the position of the peak in the elastic angular profile for that particular incident energy. The first thing to note is that the inelastic profiles are all peaked in approximately the direction of the elastic diffraction beam. Thus, the diffraction effect we saw in Figure 28 for one primary energy holds for a number of primary energies which span a range of different diffraction conditions. In addition to the gross structure, there is a large amount of substructure present.

The angular profiles for both the 10 and 12 eV losses show the same type of behavior. At incident energies below and near \( E_{\text{Bragg}} \), the angular profiles are single peaked to the low angle side of the elastic peak. As the incident energy approaches \( E_{\text{Bragg}} + w \), the profile splits into two peaks, with
Angular Profiles
Al(100) g = (1,1)
w = 10 eV

\[ \text{Intensity (normalized units)} \]

\[ \text{Collector Angle, } \theta \text{ (degrees)} \]

Figure 29. Inelastic angular profiles, \( w = 10 \text{ eV} \), in the (11) direction. Each black dot indicates the position of \( \text{Elastic} \) for each primary energy.
Angular Profiles
Al(100) g=(1,1)
w = 12 eV

Figure 30. Inelastic angular profiles, \( w = 12 \) eV, in the (11) direction. Each black dot indicates the position of \( \theta \) Elastic for each primary energy.
the high angle peak becoming dominant as the incident energy is increased. With further increases, the profile becomes a single peaked structure again, but with the peak located on the high angle side of the elastic peak.

This behavior is not exactly that expected of surface plasmon angular profiles if one considers a purely kinematic model of inelastic diffraction. This type of model, such as given by the Ewald collision diagram in Figure 7, predicts a sharp double peaked structure in the inelastic angular profiles for all incident energies. Even a quantum field theoretical treatment (QFT) $^{31,32}$, whose initial results are shown in Figure 12, predicts a doublet structure at all energies. But as we see in this figure, and as will be seen in the next section, the QFT treatment also predicts that large intensity differences can occur between the two peaks. Large internal damping effects, such as through decreased plasmon lifetimes, can then make these two peaks appear as a single peak. If the surface plasmons in question have a small wavevector, the finite angular resolution can make even two peaks of equal intensity appear as a singlet. But it should be noted again that the doublet structure is seen over a range of primary energies for the surface plasmon angular profiles.

Looking at the energy loss profiles, Figure 27, it appears that the angular profiles of the 16 and 18 eV losses should be representative of bulk plasmon angular profiles. Figures 31 and 32 show a series of angular profiles for these two losses which were taken over a range of primary energies which includes the 86 eV Bragg energy.
Figure 31. Inelastic angular profiles, $w = 16\text{ eV}$, in the (11) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.
Figure 32. Inelastic angular profiles, \( w = 18 \text{ eV} \) in the (11) direction. Each black dot indicates the position of \( \theta_{\text{Elastic}} \) for each primary energy.
It should be noted first that the profiles are more or less localized around the elastic beam, indicating inelastic diffraction. As in the profiles of the surface plasmons, these angular profiles also display the motion of the inelastic peak from the low angle side to the high angle side of the elastic peak. The behavior of the diffraction substructure is an experimental verification of sideband diffraction. As the incident energy sweeps in value across the Bragg energy, the profiles change exactly as predicted. The profile begins as a singlet peak, which changes to a large doublet as the incident energy $E_p$ increases. The high angle peak decreases in size relative to the low angle one until at some $E_p < (E_{\text{Bragg}} + w)$, there is only a singlet peak remaining. The singlet then splits into a doublet for larger energy, and as the incident energy is increased further, the profile returns to a small singlet. However, the presence of a doublet peak is not necessarily evidence of sideband diffraction. Certain structure can be associated with a surface plasmon loss and hence the cause of an apparent splitting. This will be discussed in more detail in the following paragraphs and in the next section where we compare experimental and theoretical profiles.

As mentioned before, we expect that the profiles of the 14 eV loss will contain structure due to excitations of both the bulk and surface plasmons. Figures 33 and 34 show a series of angular profiles of electrons which lost 14 eV to the solid. The general behavior is similar to the profiles of the other losses: that of a singlet peak on the low angle side of the elastic peak changing to multiple peaks, and ending as a singlet peak on the high angle side of the elastic peak as the incident electron energy is increased to values greater than the Bragg energy.
Figure 33. Inelastic angular profiles, \( w = 14 \text{ eV} \), in the (11) direction. Each black dot indicates the position of \( \theta_{\text{Elastic}} \) for each primary energy.
Figure 34. Inelastic angular profiles, \( w = 14 \) eV, in the (11) direction. Each black dot indicates the position of \( \theta_{\text{Elastic}} \) for each primary energy.
The presence of these multiple peaks make the $w = 14$ eV angular profiles interesting. Figure 34 shows four of these profiles a little more clearly. The angular profile resulting from a bombardment of electrons with $E_p = 90$ eV clearly shows three peaks, with $E_p = 92$ eV two peaks with a hint of a third, and with $E_p = 96$ and 98 eV only two peaks. The two peaks which are on either side of the elastic peak by about $1^\circ - 1.5^\circ$ are a result of sideband diffraction of the bulk plasmon loss. The angular splitting is smaller than that seen in the 16 and 18 eV loss angular profiles because the wavevector of the excitation is smaller. The third peak is located $7^\circ$ to the low angle side of the elastic peak. Using the law of conservation of momentum parallel to the surface, equation 1.9, a straightforward calculation leads to the result that the excitation's momentum parallel to the surface is about $0.6 \text{ Å}^{-1}$.

As we will see in the next section, this value is much too big for a bulk plasmon near this energy loss, but is about correct for a surface plasmon. We can make another analysis which, although qualitative, leads to the same conclusion. If we examine Figure 27 again, we see that for $E_p = 90$ eV and $\theta < \theta_{\text{Elastic}}$, the energy loss profile indicates that the 14 eV loss has a stronger surface plasmon component than bulk plasmon. However, for $\theta \geq \theta_{\text{Elastic}}$, the bulk plasmon component dominates at $w = 14$ eV, which is what we just concluded from the angular profiles.

We can also qualitatively judge what some of the angular structure is due to by examining plots such as shown in Figures 35, 36 and 37. Knowing that the angular profile of the 10 eV loss is due to the surface plasmon excitation, we can follow this structure as it moves in angle as we increase the loss energy.
Figure 35. Angular profiles for a constant primary energy (92 eV) and different loss energies.
Figure 36. Angular profiles for a constant primary energy (96 eV) and different loss energies.
Figure 37. Angular profiles for a constant primary energy (100 eV) and different loss energies.
For instance, if we examine Figure 35, we can observe the surface plasmon peak beginning at 10 eV move to slightly lower angles as we increase the loss energy to 13 eV. As we increase the loss energy to 17 eV the surface plasmon peak moves out more rapidly to lower angles, a consequence of the increasing plasmon wavevector. But at the same time we can see another peak just to the low angle side of the elastic peak grow for $w = 14$ and 15 eV. This peak, together with the peak on the high angle side is a bulk plasmon peak. This same effect is seen in Figure 36. In Figure 37, $E_p = 100$ eV, the strength of the surface plasmon peak decreases rapidly, and is about gone for $w = 14$ eV. Above $w = 14$ eV, the bulk plasmon peaks are much larger (and closer in angle to the elastic peak) and show a definite doublet at $w = 18$ and 19 eV due to sideband diffraction. The conclusion that this structure is due to bulk plasmon excitation also follows from examining the loss profiles in Figure 27 for $E_p = 100$ eV.

Thus, if we look at Figure 31 again, the doublet for $E_p = 90$ and 92 eV probably consists of a surface plasmon peak on the low angle side of the elastic peak and a bulk plasmon on the high angle side. However the doublet at $E_p = 98$ eV and again at $E_p = 106$ eV is undoubtedly a bulk plasmon doublet due to sideband diffraction.

In addition to identifying the dynamical origin of various details in the measured intensities, we also can determine the dispersion relations of the surface and bulk plasmons from plots such as shown in Figures 35, 36 and 37. We can do this by either making a straightforward kinematic calculation, using the law of conservation of momentum parallel to the surface, as done in a
Figure 38. Inelastic angular profiles, $w = 10$ eV, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.
Figure 39. Inelastic angular profiles, $w = 12 \text{ eV}$, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.
Angular Profiles
Al(100), g = (1,0)
w = 14 eV

$\lambda(\times 50) = 0.0002\%$
$\lambda(\times 100) = 0.0001\%$

Figure 40. Inelastic angular profiles, $w = 14$ eV, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.
Angular Profiles
Al(100), g=(1,0)
w = 16 eV

Figure 41. Inelastic angular profiles, w = 16 eV, in the (10) direction. Each black dot indicates the position of $\theta_{\text{Elastic}}$ for each primary energy.
preceeding paragraph, or we can use a quantum field theoretical treatment as done by Duke and Bagchi. 36 The QFT treatment should yield a more accurate dispersion relation, because it takes account of the various dynamical scattering factors present. We refer the interested reader to reference 36 for details of the calculation.

Finally, we will include the next four figures for comparative purposes only. Figures 38 to 41 show a series of angular profiles in the (10) plane for energy losses $w = 10, 12, 14$ and $16 \text{ eV}$ taken over a range of primary energies which includes the (10) Bragg peak at $107 \text{ eV}$. We should note the inelastic electrons are partially diffracted into beams and that these diffraction peaks move from the low angle side of the elastic peak to the high angle side as the incident energy increases above the Bragg energy. However, there is a definite lack of substructure present. This could be due to two things. First, the absolute intensity of the beams is lower in this diffraction direction by a factor between 2.5 and 5. This then might hide some of the structure. Second, the surface and bulk plasmon loss peaks in this diffraction direction have a smaller half-width than in other directions. Thus, at loss energies at which the excitation should have a large wavevector and hence produce an observable angular splitting, the excitation strength is greatly reduced.
3.5 Comparison of Experimental and Theoretical Profiles

In this section, we briefly will compare some of our experimental profiles with some theoretical profiles calculated by Duke and Bagchi\textsuperscript{36,37} and by Laramore and Duke.\textsuperscript{72,73}

The profiles for both elastic and inelastic intensities calculated by Duke and Bagchi are shown in Figures 42-48 together with the corresponding experimental profiles. The elastic profiles calculated by Laramore and Duke are shown in Figure 49. There are significant differences in the models used in these two sets of theoretical calculations. Laramore and Duke used a finite temperature version of the inelastic collision model\textsuperscript{33,34} with an electron-ion-core potential described by s, p, and d partial wave phase shifts to describe the elastic scattering from the solid. Bagchi and Duke, on the other hand, used a isotropic scattering version (s-wave scattering only) of the inelastic collision model which was also temperature independent in order to calculate a series of inelastic profiles. The less complete latter model was used for the calculations in order to place reasonable limits on the computation time of the profiles. However, these profiles are expected to give qualitative fits of the lineshapes and peak positions of the experimental profiles. Further calculations\textsuperscript{75} indicate that multiple-scattering phenomena can introduce additional structure into the profiles, but that the "kinematic" effects persist, i.e., they are merely augmented by the dynamical effects.

Figures 42 and 43 show a set of experimental and theoretical energy profiles for loss energies $w = 0, 10, 14$ and 16 eV. The theoretical profiles are those of Duke and Bagchi. The vertical axis of the experimental profiles is in units of percent reflectivity, while that of the theoretical profiles is in cross section units of square angstroms.
Figure 42. Theoretical and experimental energy intensity profiles in the (11) diffraction direction.
Figure 43. Theoretical and experimental energy intensity profiles in the (11) diffraction direction.
The theoretical inelastic profiles seen in these two figures were calculated using the dispersion relations of the plasmons previously determined$^{36}$ and the parameters used in the calculation of the elastic profile. Before proceeding, it should be noted that these inelastic profiles, together with those to follow and those published by Duke and Bagchi$^{36}$, are the only inelastic profiles calculated to be compared with experiment. Because of the nature of the calculations, we can only compare relative intensities of the inelastics if we normalize the experimental and theoretical elastic peak heights to unity.

Examining Figures 42 and 43, we see then that the inelastic peak shapes and positions of the experimental and theoretical profiles agree quite well. In the worst case, for \( \omega = 14 \text{ eV} \), the IE peak differs by only 3 eV between experiment and theory. The agreement between the relative intensities of the EI to IE peaks for the different losses is also found to be quite good. The absolute intensities of the theoretical inelastic (\( \omega \neq 0 \)) profiles in Figures 42 and 43 are too small by a factor of 8. This makes the theoretical profiles larger than the experimental profiles (after normalization) by a factor of less than two. Thus the empirical electron-plasmon vertex used by Duke and Bagchi does, in fact, give approximately the correct relative intensities of the elastic and inelastic cross sections.

Figure 44 shows a series of experimental and theoretical energy loss profiles, equivalent to the conditions described for Figure 27. As the primary energy increases above the Bragg energy at 86 eV, the strength of the
Figure 44. Theoretical and experimental energy loss profiles in the (11) diffraction direction.
bulk plasmon loss peak grows relative to that of the surface plasmon. This is
seen in both the experimental and theoretical curves. Differences in relative
intensities of the two losses can be explained by remembering that the
experimental profiles contain the electrons which have scattered both
cohertently and incoherently from the solid.

Finally we will compare some theoretical and experimental angular
profiles. Figures 45 and 46 show a series of angular profiles in the (11)
diffraction direction for different loss energies and with two different primary
energies \(-E_{\text{Bragg}}\) and \(E_{\text{Bragg}} + 10\) eV. The theoretical profiles in Figure 45
clearly shows the surface plasmon doublet for \(w = 10\) eV and demonstrates that
these peaks move apart for larger \(w\) (and hence larger momentum). For
\(w = 14\) eV, the profile shows a small bulk plasmon peak near \(\theta_{\text{Elastic}}\) and just
the remains of the large angle surface plasmon. For \(w = 16\) and 18 eV, the
theoretical profile only shows a surface plasmon peak on the low angle side
of \(\theta_{\text{Elastic}}\). The experimental profiles agree fairly well, with the absence
of the surface plasmon doublet being explained by our finite angular resolution.
The major discrepancy is in the additional peak on the high angle side of
\(\theta_{\text{Elastic}}\) for \(w = 16\) and 18 eV. This is apparently a bulk plasmon loss, with
a larger intensity than predicted by the theory. Figure 46 is similar to
Figure 45, except that the surface plasmon doublet is seen experimentally for
\(w = 12\) eV, and the \(w = 14\) profile shows the surface and bulk plasmon peaks seen
in the theory. The systematic error in \(\theta_{\text{Elastic}}\) between the experimental and
theoretical profiles will be discussed at the end of this section.
Figure 45. Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a primary energy of 86 eV.
Figure 46. Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a primary energy of 96 eV.
Figure 47 shows a series of $w = 16$ eV angular profiles for different primary energies on either side of the (11) Bragg energy at 86 eV. The experimental profiles are in adequate agreement with the theoretical profiles. We can follow the low angle surface plasmon peak and watch it disappear as a function of primary energy. At the same time, the theory shows a bulk plasmon peak beginning to grow for $E_p = 94$ eV, and eventually shifting to the high angle side of $\theta_{Elastic}$ for larger primary energy. This is seen in the experiment, although the bulk plasmon begins to appear near $E_p = 90$ eV with a strength greater than in the theory. We can also see the sideband diffraction splitting for $E_p = 106$ eV in both the theoretical and experimental profiles.

Finally, Figure 48 shows a set of theoretical and experimental angular profiles for $w = 14$ eV. The theoretical profiles were calculated with a set of parameters for illustrative purposes only. The theoretical profiles show the two surface plasmon peaks on the very low and very high angle sides of $\theta_{Elastic}$, together with a bulk plasmon loss. The bulk plasmon is first seen as a singlet on the low angle side of $\theta_{Elastic}$ at $E_p = 84$ eV, after which it becomes a doublet about $\theta_{Elastic}$ for $E_p = 88$ and 90 eV. For larger values of $E_p$, the peak gradually becomes a single peak located on the high angle side of $\theta_{Elastic}$. This is the behavior we see in the experimental profiles (also refer back to Figures 33 and 34). As was pointed out in Figure 34, we clearly see the low angle surface plasmon and the two bulk plasmon peaks due to sideband diffraction at $E_p = 90$ eV, together with the motion of the peak across $\theta_{Elastic}$. 
Figure 47. Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a loss energy of 16 eV.
Figure 48. Theoretical and experimental inelastic angular profiles in the (11) diffraction direction for a loss energy of 14 eV.
There is a systematic error of $3^\circ$ to $6^\circ$ between the theoretical and experimental values of $\theta_{\text{Elastic}}$ in some of the angular profiles. As outlined in detail in reference 4, there are at least 16 sources of alignment error, nine of which are angular errors. Some of these, such as the alignment of the electron beam direction and the alignment of the crystal lattice planes with the target axis of rotation affect the real positions of the diffracted electron beam in space. Other errors, such as due to the uncertainty in the zero position of the collector affect the value in scattered angle which we assign to the detected beam. Each alignment is no better than $0.5^\circ$-$1^\circ$ accurate. Thus, we displayed all the experimental angles as values of the collector angle. While the absolute value may be in doubt by a few degrees, relative positions are accurate to within one-half a degree.

Finally, we can compare the shapes and absolute intensities of the experimental and theoretical elastic energy profiles because in the case of elastic diffraction, accurate microscopic calculations of these profiles have been carried out. The theoretical profiles, as shown in Figure 49, were calculated by Laramore and Duke using the model described previously. The experimental profiles are seen in Figures 22 and 23.

The theoretical and measured line shapes of both the (10) and (11) beams agree well. The major peaks are in about the same places (refer to Table 1) and the secondary structure also is reproduced. See, e.g., the multiple scattering peak at about 62 eV in the (11) profile. The profiles differ in that the experimental peaks are about half as wide as the theoretical peaks.
Figure 49. Theoretical (s, p, d-wave scattering) elastic energy intensity profiles.
The absolute intensities of the calculated and observed peaks are found to be in quantitative agreement. The absolute intensity of the (11) Bragg peak at 86 eV was calculated to be .055% \( I_0 \). The agreement between the other (11) peaks is equally good. The absolute intensity of the (10) Bragg peak at 54 eV was calculated to be about .090% \( I_0 \) and was measured to be .044% \( I_0 \), a difference of about a factor of 2. This excellent agreement cannot be fully appreciated until one realizes that the next best calculation for Al, one by Hoffstein and Baudreaux 74 based on a band-structure matching formalism, predicts a reflected intensity of about 20% \( I_0 \) for the (11) Bragg peak at 86 eV, a difference of about a factor of 80 with experiment.

The differences between the calculations of Laramore and Duke and our experimental measurements of the intensities of the (10) Bragg peaks can probably be explained by assuming a larger misalignment in this direction than in the (11) direction. This can come about as a consequence of rotating the target to bring the (10) diffraction plane into the plane of the collector rotation (see reference 4 for details). In general, the agreement between the calculated and observed intensities is surprisingly good with regard to the absolute magnitude as well as the line shape of both the elastic and inelastic intensities. Although the models used in the calculations are simplified, they seem to describe the scattering phenomena quite adequately.
4. SUMMARY OF RESULTS AND CONCLUSIONS

The data presented in the last chapter clearly demonstrated the existence of inelastic low energy electron diffraction. At the same time, the two-step model of ILEED was verified, as we reported for the first time two clear peaks in the inelastic energy intensity profiles representing EI and IE diffraction, and measured systematic correlations between the elastic and inelastic angular profiles based upon this model.

Examining the inelastic profiles in detail, we established the dependence of inelastic diffraction on different diffraction conditions. The energy loss profiles demonstrated a new behavior in the change in the relative heights of the surface and bulk plasmon losses as the primary energy is swept across a Bragg energy. This may lend itself as a new test in distinguishing between the two types of losses in materials where the losses are not clearly known. We also observed the predicted doublet structure in the surface plasmon angular profiles which is due to the localization of the excitation momentum along the surface. We reported for the first time the experimental observation of sideband diffraction for a bulk plasmon excitation. We observed the predicted sideband diffraction in the inelastic angular profile and possibly in the inelastic energy profile.

The energy loss profiles indicate the occurrence of some low energy losses whose presence is detected only under certain energy and momentum conditions. A high resolution energy-angular instrument probably would yield information on the nature of these losses.
Finally, we briefly demonstrated that ILEED is sensitive to surface conditions. The experimental profiles, when coupled with a complete theory of inelastic diffraction, yield\textsuperscript{36} an adequate description of the plasmon dispersion relations, coupling relations, damping parameters, etc., thus increasing our knowledge of the chemical and electronic properties of solid surfaces.
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VITA

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