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ELECTRON-SPIN POLARIZATION IN
LOW ENERGY ELECTRON DIFFRACTION
FROM TUNGSTEN (001)

by

Maarten Kalisvaart

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Thesis Director's Signature:

A handwritten signature in cursive script, appearing to read "J. K. Walter", is written over a horizontal line.

Houston, Texas

May, 1978

To Cathy

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INTRODUCTION

Low-energy electron diffraction (LEED) is presently the major technique used for the study of the atomic structure of crystal surfaces. Although the first LEED experiments were reported by Davisson and Germer in 1927, it was not until the development of the necessary ultra-high vacuum equipment and of the display-type screen (Scheibner et al., 1960) that extensive use has been made of LEED.

Thus far, only two kinds of LEED experiments have been conducted on the elastically diffracted electrons: investigations of the periodicities of the beams and measurements of their variations in intensity with electron energy and angle of incidence. The directions of the diffracted beams give information on the periodicity of the crystal surface, while intensity measurements should determine the locations of atoms within the surface unit cell.

Theoretical understanding of both the regularity and the intensity variations of the beams is well-advanced. The theory is modeled on methods developed for X-ray diffraction analyses, with one important difference: that property of electrons which makes them so sensitive to the surface--their strong interactions with the atoms of the crystal--also leads to strong multiple scattering. Early LEED calculations, termed "kinematic," ignored

multiple scattering and, consequently, agreed rather poorly with experiment. More recent calculations, however, explicitly include all multiple scattering and give reasonably good agreement with experiment (Pendry, 1974).

LEED experiments have, heretofore, ignored an important property of the electron--its spin. Although electron spin effects have been extensively studied in atomic scattering (Kessler, 1969; 1976; Walker, 1971), only recently have theoretical calculations been made for spin effects in LEED (Feder, 1971; 1972; 1973a, b; 1974; 1975; 1976; 1977; Feder, Jennings, and Jones, 1976; Feder, private communication; Jennings, 1970; 1971b, c; Jennings and Sim, 1972; Jennings, 1974). These calculations suggest that measurements of the spin polarization of the elastically diffracted electrons may not only complement intensity data but also provide additional information not obtainable from intensity studies alone. In particular, the calculations indicate that the degree of electron-spin polarization is a sensitive probe both of the top interlayer spacing and of the shape of the surface potential barrier.

The first experimental investigations of electron-spin polarization in LEED were reported by Davisson and Germer in 1929. Although they reported no observation of spin polarization, their data analysis technique has been the subject of recent discussions (Kuyatt, 1975; Feder, private communication, 1976). The Rice LEED

experiment is consequently the first to obtain unambiguous measurements of the polarization of the diffracted beams.

A conventional LEED-optics assembly was modified to allow any one of several LEED beams to be extracted for spin polarization analysis by Mott scattering. A clean tungsten (001) surface was used in the initial experiments. This surface was chosen for several reasons. First, tungsten has been extensively studied in LEED experiments by intensity measurements. Secondly, the major spin effect is a spin-orbit interaction. Tungsten, with its large atomic number ($Z = 74$), is therefore expected to produce large polarizations. Such polarizations are, in fact, predicted by theoretical calculations for atomic scattering (Gregory and Fink, 1974; Fink, private communication, 1975). Finally, both Feder and Jennings have applied their theoretical developments of spin polarization in LEED to the (001) surface of tungsten.

This experiment is the first systematic study of electron-spin polarization in LEED. Polarization and intensity are determined in the energy range 20-150 eV for the 00 beam at angles of incidence from 10° through 18° in 1° steps and for both the 10 and 11 beams at normal incidence. All measured intensities are in good agreement with those reported by other workers. Large electron-spin polarization features are noted with polarization values strongly dependent on both the energy and the angle of incidence of the primary electron beam. Polarizations

in the range +60% to -80% are observed. A preliminary study has also been made to investigate the relative sensitivities of intensity and polarization to adsorbates on the tungsten surface.

Comparisons of the present intensity and polarization data with the results of recent theoretical calculations show reasonable agreement with respect to gross features. This agreement between experiment and theory is encouraging, especially considering that the theoretical calculations were made with virtually no experimental polarization measurements to guide the choice of surface parameters.

Simultaneous measurement of intensity and polarization in LEED experiments should provide the basis for improved self-consistency in determination of these surface parameters.

I. THEORETICAL CONSIDERATIONS

A. Electron Scattering at a Crystal Surface

1. Energy Spectrum of the Scattered Electrons

Information about the scattering experienced by electrons at a crystal surface can be obtained by measuring the energy spectrum of the back-scattered electrons (Chang, 1971; Bouwman, 1973). Figure I-1 shows a typical spectrum produced when electrons with energy E_0 are incident on a crystal. Several features of this spectrum will be discussed in turn.

The narrow peak (A) at E_0 consists of elastically scattered electrons (approximately 1-10% of the incident current) which, as will be shown in the next section, leave the crystal in discrete beams. Also included in this peak are electrons which have undergone phonon scattering but have lost energies ($<.1$ eV) too small to be resolved from true elastics. Only the electrons in this peak are investigated in LEED experiments.

Several smaller peaks (B) are spaced about 15 eV below the elastic peak and from each other. These features correspond to electrons that have experienced energy losses through excitation of bulk or surface plasmons. Bulk plasmons, which are collective longitudinal excitations of the electron gas have energies given by

Figure I-1: A schematic diagram of the energy spectrum
of electrons leaving a crystal surface.
The energy of the primary peak is E_0 .
(Bouwman, 1973)

$$E_{pl} = \hbar \sqrt{\frac{4\pi n e^2}{m}}$$

where n is the valence electron density and e and m are the electron charge and mass, respectively (Feynman, 1964). The peaks at (B) correspond to electrons which have created one or more plasmons. Peaks corresponding to energy losses of $\frac{1}{\sqrt{2}} E_{pl}$ are due to the creation of surface plasmons.

A large, broad peak (C) at low energies is created by primary electrons which have made several collisions inside the solid, creating energetic secondaries. These secondary electrons, in turn, create more secondaries, and a cascade of electrons with ever-decreasing energies is formed. The secondary electron current decreases to zero at $E = 0$ because electrons leaving the surface must overcome the work function.

The third region (D) is the long, relatively featureless section between the two peaks. In this region are found small distinct peaks (E) due to excitation losses and Auger processes. Excitation loss features are produced by a single interaction between a primary electron and bound electron which is excited from a filled band to an empty level above the Fermi energy. Auger features are the result of non-radiative de-excitation of core-ionized atoms.

2. The Diffraction Pattern

As a result of the wave-particle duality, all particles have a wavelength given by the de Broglie relation

$\lambda = h/p$. For nonrelativistic electrons, this relation can be expressed in the convenient form

$$\lambda (\text{\AA}) = \left(\frac{150}{E(\text{eV})} \right)^{\frac{1}{2}} .$$

For typical LEED energies from 20 - 500 eV, the electron wavelengths range from $3\text{\AA}$ - $.5\text{\AA}$ which are of the order of crystal interatomic spacings.

When an electron is incident on the surface of a crystal, the waves elastically scattered from different atoms interfere and give rise to the diffraction pattern. A simple treatment (Estrup and McRae, 1971) illustrates the formation by interference of discrete diffracted beams. Figure I-2 shows a one-dimensional array of identical scattering centers with spacing a . A wave with wavevector $\vec{k}_0$, where $|\vec{k}_0| = 2\pi/\lambda$, is incident at an angle ψ_0 with respect to a normal to the array. Let the elastically scattered wave have wavevector $\vec{k}'_0$ and make an angle ψ with the normal. By conservation of energy, $|\vec{k}_0| = |\vec{k}'_0|$. Assuming a very long array of scattering centers, the scattered wave can leave the array only along directions for which constructive interference of waves from adjacent scattering centers occurs. This condition can be expressed by

$$a(\sin\psi - \sin\psi_0) = n\lambda$$

where n is an integer. Multiplying by $2\pi/a\lambda$:

Figure I-2: A one dimensional array of identical scattering centers with spacing $\underline{a}$. A wave with wavevector $\vec{k}_0$ is incident on the array while the elastically scattered wave has wavevector $\vec{k}'_0$. Constructive interference occurs if the two rays shown have path lengths differing by an integral number of wavelengths:

$$a(\sin\psi - \sin\psi_0) = n\lambda$$

(Estrup and McRae, 1971).

$$|\vec{k}'_0| \sin \psi - |\vec{k}_0| \sin \psi_0 = \frac{2\pi}{a} n \quad (1)$$

However, $2\pi/a$ is just the unit reciprocal lattice distance for this linear array, and any integral multiple $n \cdot 2\pi/a$ is also a reciprocal lattice distance. Let $\underline{g}$ represent an arbitrary reciprocal lattice distance. Also, letting $k_{011} = |\vec{k}_0| \sin \psi_0$ and $k'_{011} = |\vec{k}'_0| \sin \psi$ be the components of $\vec{k}_0$ and $\vec{k}'_0$ parallel to the array, equation (1) can be written

$$k'_{011} - k_{011} = g \quad (2)$$

However, the surface of any crystal can be considered to consist of two sets of linear arrays of identical scattering centers making an angle with each other. An equation of the form (2) must apply along each array, and writing both equations together in vector form, the condition diffracted beams must satisfy becomes

$$\vec{k}'_{011} - \vec{k}_{011} = \vec{g} \quad (3)$$

where $\vec{k}_{011}$ and $\vec{k}'_{011}$ are the components of $\vec{k}_0$ and $\vec{k}'_0$ parallel to the surface, and $\vec{g}$ is a surface reciprocal lattice vector. Condition (3) shows that elastically scattered electrons leave the surface only along discrete beams whose components of momentum parallel to the surface differ from that of the incident momentum by a surface reciprocal lattice vector. The same result can be obtained more rigorously by an analysis due to Pendry (1974).

The complete electronic wave function must everywhere satisfy Schrödinger's equation which, in atomic units, is:

$$(-\frac{1}{2} \nabla^2 + V(\vec{r})) (\psi_i(\vec{r}) + \psi_s(\vec{r})) = E (\psi_i(\vec{r}) + \psi_s(\vec{r})) \quad (4)$$

where $\psi_i(\vec{r}) = e^{i\vec{k}_0 \cdot \vec{r}}$, with $2E = |\vec{k}_0|^2$, is the incident wave and $\psi_s(\vec{r})$ is the scattered wave. E is the electron energy, and $\vec{r}$ is a position vector with respect to an arbitrary origin. It is desired to determine the form of $\psi_s(\vec{r})$ outside the crystal and, in particular, to show that $\psi_s(\vec{r})$ consists of discrete beams.

Let $\vec{a}$ and $\vec{b}$ be the primitive surface translation vectors. The symmetry of the surface then requires that $V(\vec{r}) = V(\vec{r} + l\vec{a} + m\vec{b})$ where l and m are integers. Replacing $\vec{r}$ by $\vec{r} + l\vec{a} + m\vec{b}$ in Schrödinger's equation, and using the symmetry of $V(\vec{r})$, it is easily shown that $\{\psi_i(\vec{r} + l\vec{a} + m\vec{b}) + \psi_s(\vec{r} + l\vec{a} + m\vec{b})\}$ satisfies the same equation as does $\{\psi_i(\vec{r}) + \psi_s(\vec{r})\}$. But

$$\psi_i(\vec{r} + l\vec{a} + m\vec{b}) = e^{i\vec{k}_0 \cdot (\vec{r} + l\vec{a} + m\vec{b})} = \psi_i(\vec{r}) e^{i\vec{k}_{011} \cdot (l\vec{a} + m\vec{b})}$$

where $\vec{k}_{011}$ is the component of $\vec{k}_0$ parallel to the surface. Thus the incident wave at $\vec{r} + l\vec{a} + m\vec{b}$ differs from that incident at $\vec{r}$ only by a phase factor. Since the scattered wave is proportional to the incident wave, it must be true that

$$\psi_s(\vec{r} + l\vec{a} + m\vec{b}) = \psi_s(\vec{r}) e^{i\vec{k}_{011} \cdot (l\vec{a} + m\vec{b})} \quad (5)$$

Although the scattered wave does not necessarily have the periodicity of the surface, it can be written in the Bloch form by defining $\chi_{\vec{k}_{011}}(\vec{r})$ by

$$\psi_s(\vec{r}) = e^{i\vec{k}_{011} \cdot \vec{r}_{\parallel}} \chi_{\vec{k}_{011}}(\vec{r}) \quad (6)$$

where $\vec{r}_{\parallel}$ is the component of $\vec{r}$ parallel to the surface.

Substitution of this expression into (5) shows that

$\chi_{\vec{k}_{011}}(\vec{r}) = \chi_{\vec{k}_{011}}(\vec{r} + l\vec{a} + m\vec{b})$. Because of this periodicity, $\chi_{\vec{k}_{011}}(\vec{r})$ can be expressed as a Fourier series over the surface reciprocal lattice vectors $\vec{g}$ (Kittel, 1971)

$$\chi_{\vec{k}_{011}}(\vec{r}) = \sum_{\vec{g}} a_{\vec{g}}(z) e^{i\vec{g} \cdot \vec{r}_{\parallel}} \quad (7)$$

where the surface is chosen as the x-y plane and z is chosen positive into the surface. The surface reciprocal lattice vectors $\vec{g}$ have only x and y components and satisfy

$$\vec{g} \cdot \vec{a} = 2\pi \cdot \text{integer} \quad (8)$$

$$\vec{g} \cdot \vec{b} = 2\pi \cdot \text{integer}.$$

The solution of this pair of equations is $\vec{g} = h\vec{A} + k\vec{B}$ where

$$\vec{A} = \frac{2\pi(b_y, -b_x)}{(a_x b_y - b_x a_y)}, \quad \vec{B} = \frac{2\pi(-a_y, a_x)}{(a_x b_y - b_x a_y)}$$

and h and k are arbitrary integers.

Substituting the Fourier expansion (7) into the expression (6) for $\chi_{\vec{k}_{011}}(\vec{r})$, an expression for the scattered wave is obtained:

$$\psi_s(\vec{r}) = \sum_{\vec{g}} a_{\vec{g}}(z) e^{i(\vec{k}_{011} + \vec{g}) \cdot \vec{r}_{\parallel}} .$$

If this expression, in turn, is substituted into Schrödinger's equation (4) for the total wave function, the equation outside the crystal ($V(\vec{r}) = 0$) becomes

$$\sum_{\vec{g}} \left[(|\vec{k}_{011} + \vec{g}|^2 - 2E) a_{\vec{g}}(z) + \frac{\partial^2}{\partial z^2} a_{\vec{g}} \right] e^{i(\vec{k}_{011} + \vec{g}) \cdot \vec{r}_{\parallel}} = 0 .$$

The orthogonality of the exponentials in this expansion requires that each Fourier component itself vanishes. Thus

$$a_{\vec{g}}(z) = b_{\vec{g}} \exp[\pm i(2E - |\vec{k}_{011} + \vec{g}|^2)^{1/2} z]$$

where $b_{\vec{g}}$ is a constant. For waves leaving the crystal the negative sign must be used. Defining

$$\vec{k}_{\vec{g}}^{\pm} = ((\vec{k}_{011} + \vec{g})_x, (\vec{k}_{011} + \vec{g})_y, \pm (2E - |\vec{k}_{011} + \vec{g}|^2)^{1/2}) ,$$

the scattered wave can be written

$$\psi_s(\vec{r}) = \sum_{\vec{g}} b_{\vec{g}} e^{i\vec{k}_{\vec{g}}^- \cdot \vec{r}} . \quad (9)$$

The expansion (9) of the scattered wave shows that the periodicity of the surface requires that the elastically scattered electrons leave the crystal only in a set of discrete beams with components of momentum parallel to the surface given by equation (3). By convention, the hk beam has $\vec{g} = h\vec{A} + k\vec{B}$ (Wood, 1964). Expression (9), furthermore, shows that a finite number of beams reach the LEED screen

(Figure I-3). Only those beams for which $2E > |\vec{k}_{011} + \vec{g}|^2$ are propagating waves; the beams for which $2E < |\vec{k}_{011} + \vec{g}|^2$ decay exponentially in the $-z$ -direction and are consequently not observed.

The surface lattice can be determined from the directions of the diffracted beams. The beam directions give the surface reciprocal lattice vectors which, in turn, can be used to calculate the surface translation vectors. Thus, the directions of the LEED beams determine the surface lattice. No information can, however, be obtained from beam directions about the locations of atoms within the surface unit cell.

3. The Coherence Area

The assumption was made in the preceding section that the incident wave has a wavevector given exactly by $\vec{k}_0$ and that it can therefore be represented by a plane wave $e^{i\vec{k}_0 \cdot \vec{r}}$. In any actual experiment, however, neither the direction nor the energy of the primary beam is precisely defined, and the incident wave consequently is a superposition of plane waves with slightly different directions and energies. Because of these uncertainties in both the magnitude and the direction of $\vec{k}_0$, the phase of the incoming wave varies over the crystal surface. For points close together on the surface, the small variation in phase is not important, but for points far apart, the phase difference is crucial. A coherence length can be defined so that atoms within a coherence length of each other can be

Figure I-3: Diffraction pattern from W(001) defining
the beam nomenclature.

•	•	20•	•	•
•	11•	10•	11•	•
02•	01•	00•	01•	02•
•	11•	10•	11•	•
•	•	20•	•	•

considered to be illuminated by an incident plane wave $e^{i\vec{k}_0 \cdot \vec{r}}$. For points more than a coherence length apart, the incident waves have arbitrary phase relations. A diffraction pattern is only formed by points within a coherence length of each other because only for these points do the amplitudes of the scattered waves add. For points separated by more than a coherence length, the arbitrary phase relation means that intensities of scattered waves add.

Following Heidenreich (1964), an expression for the coherence length of electrons normally incident on a crystal surface can be easily obtained. Assume that the incident beam has an angular spread 2β and an energy spread ΔE . The uncertainty Δk in the magnitude of the wavevector is related to ΔE by $\frac{\Delta k}{k} = \frac{\Delta E}{2E}$. There are two contributions to $\Delta k_x = \Delta k_y$. The x-component of momentum spread due to angle is $2k\beta$. The component due to energy spread is $2\Delta k\beta$. Therefore,

$$\Delta k_x = [(2k\beta)^2 + (2\Delta k\beta)^2]^{\frac{1}{2}} = 2k\beta[1 + (\Delta k/k)^2]^{\frac{1}{2}}$$

$$= 2k\beta[1 + (\Delta E/2E)^2]^{\frac{1}{2}}.$$

But, the uncertainty principle relates Δk_x to the coherence length in the x-direction $(\Delta x)_{\text{coh}}$: $(\Delta x)_{\text{coh}} \cdot \Delta k_x \sim 2\pi$

$$\Rightarrow (\Delta x)_{\text{coh}} \approx \frac{2\pi}{\Delta k_x} = \frac{\lambda}{2\beta[1 + (\Delta E/2E)^2]^{\frac{1}{2}}}.$$

For a typical LEED experiment, $\lambda \sim 2\text{\AA}$ and $\beta \sim .01$ while $\frac{\Delta E}{E} \sim .01$

$$\therefore (\Delta x)_{\text{coh}} = (\Delta y)_{\text{coh}} \approx 100\text{\AA}$$

The coherence area is therefore on the order of $10^4\text{\AA}^2$, which, for the tungsten (001) surface, means that approximately 10^3 atoms are within one coherence area. Several estimates of the coherence area have been made experimentally (Chutjian, 1967). These experiments give coherence areas in excellent agreement with the present calculation.

The coherence length parallel to the beam $(\Delta z)_{\text{coh}}$ is given by $(\Delta z)_{\text{coh}} = \frac{2\lambda E}{\Delta E}$ which, for the numbers above, is approximately $400\text{\AA}$. For a typical incident LEED beam of $1\mu\text{a}$ and beam diameter of $\sim 1\text{mm}$, it is easily calculated that the electrons in the beam act independently; i.e., their coherence volumes do not overlap. This calculation emphasizes the fact that the diffraction pattern is formed by the interaction of each electron with the crystal surface; it is not due to interference between electrons.

Since diffracted beams are due to ordered arrays of finite extent, they have an angular width given by $\Delta\theta = \frac{2\lambda}{Na \cos\theta}$ (Hecht and Zajac, 1974) where N is the number of scattering centers, a is the distance between centers, and θ is the angle the diffracted beam makes with the normal to the surface. For the LEED problem, $Na \sim (\Delta x)_{\text{coh}}$ and $\cos\theta \approx 1 \Rightarrow \Delta\theta \approx 2\lambda/(\Delta x)_{\text{coh}} \Rightarrow \Delta\theta \approx .04$. Since $\Delta\theta$ is of the same order of magnitude as the angular spread of the incident beam, diffraction broadening is not usually a problem in LEED.

The concept of a limited coherence area plays an important role in the application of LEED theory to real surfaces (Heckingbottom, 1969). A surface used in a LEED experiment is usually polished to a mirror finish. Subsequent annealing in vacuum further smooths the surface. However, defects still remain, consisting, on an atomic scale, mainly of ledges separated by steps of various heights (Sonorjai, 1972). Therefore, in a LEED experiment, the surface under study contains many discontinuities over an area as large as the incident beam cross-section ($\sim 1\text{mm}^2$). However, because of the limited coherence area, these ledges have very little effect on beam intensity since a vast majority of electrons diffract only from regions forming a perfect surface. As the density of defects is increased and the ordering of atoms within a coherence area becomes less perfect, theory predicts that the diffracted beams are both broadened and less intense. An experimental study of an ion-bombarded tungsten surface shows precisely these effects (Walls et al., 1975).

B. Intensity of the Diffracted Beams

This section is concerned with the methods used in calculating intensities of the diffracted beams and follows closely the treatments given in Pendry (1974). In particular, two distinct methods, the "kinematic" and the "dynamic" will be discussed. The kinematic method completely ignores multiple scattering of the electron in the

crystal and hence does not usually agree closely with experimental measurements. On the other hand, the dynamic method accounts fully for multiple scattering and consequently agrees well with experiment if all parameters describing the surface are accurate.

1. Scattering from Ion-Cores in a Muffin-Tin Potential

LEED calculations almost invariably use the muffin-tin approximation for modeling the solid. This approximation treats the total potential inside the crystal as a sum of spherically symmetric ion-core potentials at the positions of the atoms with a constant potential between the spheres (Figure I-4). The complicated ion-core potentials are often replaced by pseudopotentials. A surface potential barrier is included in most treatments.

The crystal potential between the ion-core spheres is usually assumed to have both a real and an imaginary component, $V = V_r + iV_i$. The real component V_r is identified with the "inner potential" and is the constant potential between the muffin tins with respect to the vacuum zero. For tungsten, V_r has a magnitude of about -15 eV. The imaginary component V_i is included to represent all inelastic scattering occurring in the crystal. Because the energy-analyzing grids of the LEED optics allow only elastically-scattered electrons to reach the LEED screen, electrons which have lost energy in the scattering process may be considered to be absorbed by the crystal since they are never detected. V_i accounts for absorption by giving

Figure I-4(a): Cross-section of a crystal divided into muffin tins. (Pendry, 1974)

(b): Cross-section of the crystal potential showing the ion-core potentials with a constant potential between ion-cores. The surface barrier is included.
(Pendry, 1974)

(a)

(b)

LEED electrons a finite lifetime in the crystal. Since the time-dependent wave function in the crystal contains a term $\exp(-i(V_r + iV_i)t) = \exp(-iV_r t) \exp(V_i t)$, the intensity of the wave decays in a characteristic time $\tau = -\frac{1}{2V_i}$. The inelastic scattering in the crystal can be divided into two kinds--absorption by the atoms and the usually dominant absorption between ion-cores. Absorption by atoms occurs through electronic excitation while absorption between ion-cores involves mainly plasmon creation. Because the possible loss processes are functions of electron energy, V_i is not constant. An estimate of V_i can be obtained from the width ΔE of features in LEED intensity profiles (VanHove, 1975b). From the uncertainty principle, ΔE is related to the electron lifetime τ by $\tau \cdot \Delta E \approx 1$. Using the expression for τ above, this implies that $-V_i \approx \frac{1}{2} \Delta E$. Studies of peak widths ΔE indicate that for energies below 15 eV, $V_i \approx -1$ eV, while for energies from 15-100 eV, $V_i \approx -4$ eV (Pendry, 1974). The jump at 15 eV is due to the onset of losses through plasmon creation.

The scattering of a plane wave from a single-ion core is determined by solving Schrödinger's equation, usually in the Hartree-Fock approximation, both inside and outside the ion-core. Standard partial wave analysis gives the amplitude of the scattered wave (Merzbacher, 1970):

$$f(\theta, k) = \frac{1}{k} \sum_{\ell=0}^{\infty} (2\ell+1) e^{i\delta_{\ell}(k)} \sin \delta_{\ell}(k) P_{\ell}(\cos \theta) .$$

θ is the scattering angle, and k is determined by the electron energy with respect to the constant potential between muffin tins, $k^2 = 2(E - V_r)$. The phase shifts $\delta_l(k)$ are determined by matching solutions inside and outside the ion-core. The total wave function after scattering is given by:

$$\psi(\vec{r}) \underset{r \rightarrow \infty}{\sim} e^{i\vec{k} \cdot \vec{r}} + f(\theta, k) \frac{e^{ikr}}{r}$$

and, hence, the differential scattering cross-section is

$$\frac{d\sigma}{d\Omega} = |f(\theta, k)|^2.$$

The scattered wave amplitude $f(\theta, k)$ is determined completely by the phase shifts $\delta_l(k)$. This observation is the basic idea behind pseudopotentials. Both in LEED and in band structure calculations, the electron wave function inside the ion-core is not of interest. For this reason, the calculations can often be simplified by replacing the actual ion-core potential by a simpler pseudopotential. The pseudopotential, through the use of adjustable parameters, is chosen to give the same scattering phase shifts as the actual potential, and consequently scattering will be the same for both potentials.

2. Kinematic Theory

Kinematic theory is the simplest LEED theory to explain variations in intensity of the diffracted beams. It is very similar to basic X-ray diffraction theory in that multiple scattering is completely ignored. As usual in

LEED theory, the crystal is divided into identical layers of atoms parallel to the surface. Such division into layers allows the calculation scheme to be easily expanded to include layers of adsorbates. The total scattered wave leaving the crystal surface is calculated by first finding the wave scattered by each atom in the unit cell. The diffracted wave from each layer is then found by summing over all atoms in a unit cell and then adding the effects of all unit cells in the layer. Finally, the wave leaving the crystal surface is calculated by summing over all layers.

Again, a simple argument can be used to explain intensity variations of a diffracted beam with changes in electron energy or angle of incidence. The argument used in Section I-A-2 to explain the origin of a set of discrete diffracted beams completely ignored interference between waves scattered from different layers of atoms. A peak in intensity should occur when waves scattered from consecutive layers of atoms interfere constructively. As shown with the help of Figure I-5, such constructive interference occurs when

$$c(\cos\psi + \cos\psi_0) = m\lambda$$

where m is an integer. This expression can be written

$$(\vec{k}_0 - \vec{k}'_0) \cdot \vec{c} = 2\pi m. \quad (10a)$$

Thus, kinematic theory predicts an intensity peak in a diffracted beam, called a Bragg peak of order m , whenever condition (10a) is satisfied.

Figure I-5: In kinematic theory, intensity maxima occur through constructive interference between waves scattered from consecutive layers of atoms. A wave with wavevector $\vec{k}_0$ is incident on the crystal while the elastically scattered wave has wavevector $\vec{k}'_0$. If $\vec{c}$ is the relative displacement of the layers, constructive interference occurs if the two rays shown have path lengths differing by an integral number of wavelengths:

$$c(\cos\psi + \cos\psi_0) = m\lambda .$$

A more rigorous derivation of a similar result--one which includes the important effects of absorption of the wave in the crystal--is given by Pendry (1974). Assume a wave of unit amplitude $e^{i\vec{k}_0 \cdot \vec{r}}$, with $|\vec{k}_0|^2 = 2E$, is incident on the crystal surface. If the reflection coefficient at the surface potential barrier is $R(\vec{k}_0)$ while the transmission coefficient is $T^+(\vec{k}_0)$, the wave actually striking the first atomic layer is given by

$$T^+(\vec{k}_0) e^{i\vec{k} \cdot \vec{r}}$$

where $|\vec{k}|^2 = 2(E-V)$ and $\vec{k}_{||} = \vec{k}_{0||}$. If an imaginary component is included in V , the absorption of the wave in the crystal is included in the calculations.

First, the wave scattered by each layer is calculated. Let the origin of the j^{th} unit cell in a particular layer be denoted by $\vec{R}_j = l\vec{a} + m\vec{b}$ with respect to some origin in the layer, and let $\vec{u}_s$ be the position of the s^{th} atom with respect to its unit cell origin. The location of the s^{th} atom in the j^{th} unit cell is then given by $\vec{R}_j + \vec{u}_s$ with respect to the origin in the layer. (Note that $\vec{u}_s$ need not be parallel to the surface plane.) The wave incident on this atom is

$$T^+(\vec{k}_0) e^{i\vec{k} \cdot (\vec{R}_j + \vec{u}_s)}$$

and hence the wave scattered by it is

$$T^+(\vec{k}_0) e^{i\vec{k} \cdot (\vec{R}_j + \vec{u}_s)} \chi_s(\vec{r})$$

where

$$\chi_s(\vec{r}) = \sum_{\ell=0}^{\infty} i^{\ell+1} (2\ell+1) e^{i\delta_{\ell}(s)} \sin \delta_{\ell}(s) P_{\ell} \left(\frac{\vec{k} \cdot (\vec{r} - \vec{R}_j - \vec{u}_s)}{|\vec{k}| \cdot |\vec{r} - \vec{R}_j - \vec{u}_s|} \right) h_{\ell}^{(1)}(|\vec{k}| \cdot |\vec{r} - \vec{R}_j - \vec{u}_s|).$$

$h_{\ell}^{(1)}$ is a Hankel function of the first kind. Summing over all atoms in the unit cell and then over all unit cells in the layer, the diffracted wave from the layer is

$$\varnothing_s = T^+(\vec{k}_0) \sum_{js} e^{i\vec{k} \cdot (\vec{R}_j + \vec{u}_s)} \chi_s(\vec{r}).$$

As was shown in Section I-A-2, the wave leaving the layer can also be represented as a sum over a discrete set of diffracted beams, namely those that satisfy $\vec{k}'_{\parallel} - \vec{k}_{\parallel} = \vec{g}$ where $\vec{g}$ is a reciprocal lattice vector for the layer. Therefore,

$$\varnothing_s = \sum_{\vec{k}'} \beta_{\vec{g}} e^{i(\vec{k}'_{\parallel} \cdot \vec{r}_{\parallel} + k'_z z)}$$

with $k'_z = -(2E - 2V - |\vec{k}'|^2)^{\frac{1}{2}}$. The negative sign is used because the diffracted wave now travels back toward the surface. Since this last expression for $\varnothing_s$ is just a Fourier expansion, the coefficients $\beta_{\vec{g}}$ can easily be found by integrating over the whole layer:

$$\beta_{\vec{g}} = \frac{1}{NA} \int \varnothing_s(\vec{r}) e^{i\vec{k}' \cdot \vec{r}} d^2 \vec{r}_{\parallel}$$

where N is the number of unit cells, each of area A, in the layer. Substituting

$$\beta_{\vec{g}} = \frac{T^+(\vec{k}_0)}{A} \left[\frac{1}{N} \sum_j e^{i(\vec{k}-\vec{k}') \cdot \vec{R}_j} \right] \times$$

$$\left[\sum_s e^{i(\vec{k}-\vec{k}') \cdot \vec{u}_s} \int \chi_s(\vec{r}') e^{-i\vec{k}' \cdot \vec{r}'} d^2\vec{r}'_{\parallel} \right],$$

$$\vec{r}' = \vec{r} - \vec{R}_j - \vec{u}_s$$

Since $\vec{R}_j = \ell\vec{s} + m\vec{b}$, the first sum is just N . The integral in the second term can be evaluated to give an expression for $\beta_{\vec{g}}$:

$$\beta_{\vec{g}} = M(\vec{k}; \vec{k}') T^+(\vec{k}_0)$$

where

$$M(\vec{k}; \vec{k}') = \frac{2\pi i}{A |\vec{k}'_z| |\vec{k}|} \sum_{\ell s} (2\ell+1) \sin \delta_{\ell}(s) e^{i\delta_{\ell}(s)} P_{\ell} \left(\frac{\vec{k} \cdot \vec{k}'}{|\vec{k}| |\vec{k}'|} \right)$$

$$e^{i(\vec{k}-\vec{k}') \cdot \vec{u}_s}$$

is just $\frac{2\pi i}{A |\vec{k}'_z|}$ times the scattering amplitude of a unit cell. Therefore, the scattered wave from this layer can be written

$$\phi_s = T^+(\vec{k}_0) \sum_{\vec{k}'} M(\vec{k}; \vec{k}') e^{i\vec{k}' \cdot \vec{r}}$$

Finally, the waves scattered by the different layers in the crystal need to be summed. Assume the layers are equally spaced with the top layer labeled 0 and the origin of the n^{th} layer given by $n\vec{c}$. The wave incident on the n^{th} layer with respect to the origin of this layer is

$$e^{i\vec{k} \cdot \vec{c}} T^+(\vec{k}_0) e^{i\vec{k} \cdot (\vec{r} - n\vec{c})}$$

and the wave scattered by this layer is

$$T^+(\vec{k}_0) \sum_{\vec{k}'} M(\vec{k}; \vec{k}') e^{i\vec{k}' \cdot \vec{r}} e^{in(\vec{k}-\vec{k}') \cdot \vec{c}}$$

The total scattered wave incident on the surface potential barrier is found by summing over n :

$$T^+(\vec{k}_0) \sum_{\vec{k}'} \left[M(\vec{k}; \vec{k}') \frac{e^{i\vec{k}' \cdot \vec{r}}}{1 - e^{i(\vec{k}-\vec{k}') \cdot \vec{c}}} \right].$$

Assuming the surface barrier transmission coefficient is $T^-(\vec{k}')$ and letting $\vec{k}'_0$ represent the vacuum momentum corresponding to $\vec{k}'$ (that is, $\vec{k}'_{||} = \vec{k}'_{0||}$), the total wave leaving the crystal is

$$\psi_s(\vec{r}) = \sum_{\vec{k}'} \left\{ R(\vec{k}_0) \delta_{\vec{k}_{0||}, \vec{k}'_{0||}} + \frac{T^+(\vec{k}_0) M(\vec{k}; \vec{k}') T^-(\vec{k}')}{1 - e^{i(\vec{k}-\vec{k}') \cdot \vec{c}}} \right\} e^{i\vec{k}'_0 \cdot \vec{r}}.$$

Whenever

$$\text{Re}\{(\vec{k}-\vec{k}')\} \cdot \vec{c} = 2\pi m \quad (m \text{ an integer}), \quad (10b)$$

the denominator in the second term for $\psi_s(\vec{r})$ has a minimum, and hence an intensity maximum in the diffracted beam--the Bragg peak--occurs. Condition (10b) for a Bragg peak is the same as that in equation (10a) derived using the simple interference argument. The presence of the real part in (10b) is required by the finite penetration of the electron into the crystal.

It is the difference between conditions (10a) and (10b) that primarily distinguishes X-ray diffraction from

electron diffraction. For both X-ray diffraction and LEED, the diffracted beams satisfy condition (3) for constructive interference between waves scattered from different atoms in a single layer. X-rays are not strongly scattered by the ion-cores and hence penetrate a large number of crystal layers. For this reason, X-ray diffraction beams occur only if both conditions (3) and (10a) are satisfied (Kittel, 1971). This can also be seen by noting that the expression for $\psi_s(\vec{r})$ has a singularity when (10a) is satisfied. Electrons, on the other hand, interact so strongly with the ion-cores that they penetrate only very few crystal layers. Condition (3) is therefore dominant, and it alone determines the presence of diffracted beams. Condition (10b) is of only secondary importance and determines fluctuations in intensity.

This effect can be illustrated using the Ewald sphere construction (Estrup and McRae, 1971; Kittel, 1971). The construction for the (001) surface of a simple cubic crystal of lattice parameter a is shown in Figure I-6. The reciprocal lattice for this crystal is also simple cubic with lattice parameter (the length of the unit reciprocal lattice vector) $2\pi/a$. In LEED, scattering by a single layer determines the presence of diffracted beams through condition (3). This dominant scattering by a single layer can be modeled by increasing the distance between (001) planes until only a single plane remains. As the distance between (001) planes is increased, the length of the

Figure I-6: Ewald sphere diagram for electron diffraction from the (001) surface of a simple cubic crystal. The intensity of a diffracted beam is governed by the proximity of the termination point of $\vec{k}'_0$ to a reciprocal lattice point. (Estrup and McRae, 1971).

corresponding unit reciprocal lattice vector decreases. When the (001) planes have moved infinitely far apart, these reciprocal lattice points have merged into a set of parallel rods. The wavevector $\vec{k}_0$ of the incident beam is drawn terminating at the origin of the reciprocal lattice, and the Ewald sphere is drawn with $\vec{k}_0$ as a radius vector. The intersection points of the sphere with the lattice rods determine the possible wavevectors of diffracted beams (one such $\vec{k}'_0$ is included in Figure I-6). It can be seen directly from the figure that all such diffracted beams satisfy condition (3). If interference between waves scattered from different layers is now taken into consideration, condition (10b) is interpreted in the Ewald sphere construction as stating that intensity maxima occur whenever the diffracted wavevectors terminate on a reciprocal lattice point. The proximity of the termination point of $\vec{k}'_0$ to a reciprocal lattice point strongly influences the intensity. For X-ray diffraction, on the other hand, the equal importance of conditions (3) and (10a) requires that diffracted beams occur only when the Ewald sphere passes through a reciprocal lattice point.

The penetration depth of electrons into the crystal can be estimated from the width ΔE of intensity peaks. The finite width is due to the fact that only a small number N of layers contribute to the interference causing the peaks. Diffraction theory states that $\Delta k \cdot 2Nc \approx \pi$ where Δk is the range of wavevectors which will contribute to a peak, and

c is the interlayer spacing. But $\Delta k = \Delta E / (2E)^{\frac{1}{2}}$ and therefore $N_c \approx \pi (2E)^{\frac{1}{2}} / 2\Delta E$. Using the values of $V_i = -\frac{1}{2}\Delta E$ given in the preceding section, $N_c \approx 9\text{\AA}$ for $E = 10\text{ eV}$ while $N_c \approx 5\text{\AA}$ for $E = 100\text{ eV}$. Many different experiments have studied this mean free path for inelastic scattering (e.g., Palmberg and Rhodin, 1968; Baer et al., 1970). Figure I-7 shows a compilation of experimental results. It can be seen that the penetration depths estimated above are in good agreement with experiment. The small penetration depth (on the order of two or three atomic layers) is the reason for the surface sensitivity of LEED.

The predictions of kinematic theory usually do not agree well with experimental measurements. Good agreement is found only for crystals in which elastic scattering is inhibited by the fact that the wavefield is strongly attenuated between scattering events. It is found that this condition is satisfied best by crystals of inert gases, whose experimental intensity versus energy (I-V) curves are in close agreement with kinematic theory (Ignatiev et al., 1971). In general, however, agreement between kinematic theory and experiment is not good. The reason for the failure of kinematic theory is obviously that for most crystals, electrons interact so strongly with the ion-cores that significant multiple scattering takes place. A complete theory must, therefore, include multiple scattering.

Figure I-7: Compilation of experimental determinations of the mean free path for inelastic scattering of electrons from Auger electron spectroscopy (o), X-ray photoelectron spectroscopy (+), and vacuum uv photoelectron spectroscopy (Δ). (Brundle, 1974).

3. Dynamic Theory

The presence of secondary peaks in I-V curves has a simple explanation. Again, the crystal is assumed to be divided into layers. A wave incident on the first atomic layer is diffracted not only back to the surface but also in the forward direction, and hence not one, but several, beams travel further into the crystal. At each subsequent layer, each of these beams is diffracted. This profusion of beams causes a much more complicated I-V spectrum than results from single scattering. Several complete developments of this multiple scattering theory exist (McRae, 1968a, b; McRae and Winkel, 1969; Jennings and McRae, 1970; Pendry, 1974). This overview will follow closely the clear exposition given by Pendry (1974).

In the regions between ion-core layers, where the potential V is constant with respect to position, the solutions of Schrödinger's equation are plane waves. However, as was shown in Section I-A-2, the periodicity of the atomic layers allows only plane waves whose parallel component of momentum is given by $\vec{k}_{||} + \vec{g}$. The possible wavevectors are therefore

$$\vec{k}_{\vec{g}}^{\pm} = ((\vec{k}_{||} + \vec{g})_x, (\vec{k}_{||} + \vec{g})_y, \pm (2E - 2V - |\vec{k}_{||} + \vec{g}|^2)^{\frac{1}{2}}) .$$

The total wave between the layers labeled n and $n+1$ (see Figure I-8) can be expressed as a superposition of such waves:

Figure I-8: The wavefield between layers of a crystal. A single atypical layer is shown above an ideal crystal substrate.
(Pendry, 1974)

Figure I-9: Schematic representation of the creation of a surface barrier resonance. The incident beam is refracted at the potential barrier and then partly reflected, transmitted, and diffracted at the crystal substrate. The 01 beam is totally internally reflected at the barrier but, on striking the substrate, is partly diffracted back into the 00 beam. (Jennings and Read, 1974)

$$\sum_{\vec{g}} a_{n\vec{g}}^+ e^{i\vec{K}_{\vec{g}}^+ \cdot \vec{r}} + a_{n\vec{g}}^- e^{i\vec{K}_{\vec{g}}^- \cdot \vec{r}} \quad (11)$$

Note that in this expression, both propagating and evanescent waves occur because there are an infinite number of reciprocal lattice vectors $\vec{g}$. In typical LEED calculations, only a finite number N of forward-traveling beams is included--all propagating waves and those evanescent waves which still have significant amplitude at the adjacent layer--and an equal number of backward-traveling waves.

The condition relating the wavefield between layers $n-1$ and n , and that between layers n and $n+1$ is determined by the scattering properties of the ion-cores making up the n^{th} layer, complicated by the presence of intra-layer multiple scattering. A short summary of the technique is described below, while a complete mathematical analysis can be found in Pendry (1974).

Equation (11) gives an expression for the set of plane waves incident from the left on the n^{th} layer of ion-cores:

$$\sum_{\vec{g}} a_{n-1, \vec{g}}^+ e^{i\vec{K}_{\vec{g}}^+ \cdot \vec{r}}. \quad (12)$$

If a point in one unit cell of this layer is chosen as the origin, then the j^{th} unit cell can be designated by a surface translation vector $\vec{R}_j$. Letting $\vec{r}_k$ be the coordinate of the k^{th} ion-core in the j^{th} unit cell, its position is given by $\vec{R}_{jk} = \vec{R}_j + \vec{r}_k$ with respect to the layer origin.

The set of plane waves (12) incident on the k^{th} atom in the unit cell containing the origin can be expanded in spherical partial waves:

$$\sum_{\vec{g}} a_{n-1}^+ \vec{g} e^{i\vec{K}^+ \cdot \vec{r}} = \sum_{\ell m} A_{\ell m k}^{(0)} j_{\ell}(K|\vec{r}-\vec{R}_{ok}|) Y_{\ell m}(\Omega(\vec{r}-\vec{R}_{ok}))$$

where $K = (2E-2V_0)^{1/2}$ and $\Omega(\vec{r}-\vec{R}_{ok})$ are the angular coordinates of $\vec{r}-\vec{R}_{ok}$. The partial wave amplitudes $A_{\ell m k}^{(0)}$ are given by

$$A_{\ell m k}^{(0)} = \sum_{\vec{g}} a_{n-1}^+ \vec{g} e^{i\vec{K}^+ \cdot \vec{R}_{ok}} 4\pi i^{\ell} (-1)^m Y_{\ell-m}(\Omega(\vec{K}_{\vec{g}}^+)) . \quad (13)$$

Because of the translational symmetry of the layer, the amplitudes in the spherical wave expansion of the incident wave about the k^{th} atom in the j^{th} unit cell differ by a phase factor from the amplitudes in expression (13) about the k^{th} atom in the origin unit cell:

$$A_{\ell m k}^{(0)}(j^{\text{th}} \text{ cell}) = A_{\ell m k}^{(0)} e^{i\vec{k}_{\parallel} \cdot \vec{R}_j}$$

If intra-layer multiple scattering could be ignored, the scattered wave $\varphi_{jk}^{(s)}$ from the k^{th} atom in the j^{th} unit cell could be calculated using simple scattering theory:

$$\varphi_{jk}^{(s)} = \sum_{\ell m} A_{\ell m k}^{(0)} e^{i\vec{k}_{\parallel} \cdot \vec{R}_j} \frac{1}{2} (e^{2i\delta_{\ell}(k)} - 1) h_{\ell}^{(1)}(K|\vec{r}-\vec{R}_{jk}|) \cdot Y_{\ell m}(\Omega(\vec{r}-\vec{R}_{jk}))$$

The total scattered wave $\psi_s^{(0)}$ is obtained by summing over all ion-cores and unit cells in the layer:

$$\psi_s^{(0)} = \sum_{jk} \varphi_{js}^{(s)} = \sum_{lmjk} A_{lmk}^{(0)} e^{i\vec{k}_{||} \cdot \vec{R}_j} \frac{1}{2} (e^{2i\delta_l^{(k)}} - 1) h_l^{(1)}(K|\vec{r} - \vec{R}_{jk}|) \cdot Y_{lm}(\Omega(\vec{r} - \vec{R}_{jk})) \quad (14)$$

An inverse Fourier transform then allows this wave to be expressed as a sum of discrete beams scattered both forward and backward from this layer:

$$\sum_{\vec{g}'} a_{n-1, \vec{g}'}^{-} e^{i\vec{K}_{\vec{g}'}^{-} \cdot \vec{r}} \quad \text{and} \quad \sum_{\vec{g}'} a_{n\vec{g}'}^{+} e^{i\vec{K}_{\vec{g}'}^{+} \cdot \vec{r}}$$

where $a_{n-1, \vec{g}'}^{-}$ and $a_{n\vec{g}'}^{+}$ are related to $a_{n-1, \vec{g}}^{+}$ by

$$a_{n-1, \vec{g}'}^{-} = \sum_{\vec{g}} M_{\vec{g}'\vec{g}}^{-+}(n) a_{n-1, \vec{g}}^{+}$$

and

$$a_{n\vec{g}'}^{+} = \sum_{\vec{g}} M_{\vec{g}'\vec{g}}^{++}(n) a_{n-1, \vec{g}}^{+} \quad (15)$$

Because intra-layer multiple scattering is not negligible, the above treatment must be modified to include multiple scattering. This can be done by noting that the total partial wave amplitude incident on the k^{th} atom in the origin unit cell is a sum of $A_{lmk}^{(0)}$ and the amplitude $A_{lmk}^{(s)}$ scattered from other atoms in the layer:

$$A_{lmk} = A_{lmk}^{(0)} + A_{lmk}^{(s)} \quad (16)$$

Since $A_{lmk}^{(s)}$ depends on A_{lmk} , it must be determined self-consistently. Again, translational symmetry requires that

$$A_{\ell m k}(j^{\text{th}} \text{ cell}) = A_{\ell m k} e^{i \vec{k}_{\parallel} \cdot \vec{R}_j}.$$

Using this as the wave incident on the j^{th} unit cell, the scattered wave from the k^{th} atom of this cell can be calculated in terms of $A_{\ell m k}$. The total scattered partial wave incident on the r^{th} atom of the origin unit cell is given by a sum over scattered waves from all other ion-cores in the layer and can be written symbolically:

$$A_{\ell m k}^{(s)} = \sum_{\ell' m' k'} A_{\ell' m' k'} X_{\ell' m' k', \ell m k} \quad (17)$$

where an explicit and complicated expression can be written for $X_{\ell' m' k', \ell m k}$. Equation (17) can be written as a matrix multiplication $A^{(s)} = AX$. Substituting $A^{(s)} = A - A^{(0)}$ from (16) gives

$$A = A^{(0)} (1-X)^{-1}$$

Thus, the total wave incident on a given ion-core can be calculated including all intra-layer multiple scattering. Replacing $A_{\ell m k}^{(0)}$ in (14) with the total wave $A_{\ell m k}$, the exact scattered wave ψ_s from layer n can be calculated and the scattering coefficients $M_{\vec{g}, \vec{g}'}^{\pm\pm}(n)$ in (15) are determined.

These scattering coefficients can be used to relate the wavefield (11) between layers $n-1$ and n , and that between layers n and $n+1$. If distances are measured from a plane midway between ion-core layers, one component of forward-traveling waves between layers $n-1$ and n has a value

$$a_{n-1, \vec{g}}^+ e^{i\vec{K}_{\vec{g}}^+ \cdot \frac{1}{2} \vec{c}_{n-1}}$$

at layer n . This wave can be both forward and back diffracted at layer n . Forward-diffraction into the $\vec{g}'$ -beam has amplitude $\delta_{\vec{g}', \vec{g}} + M_{\vec{g}', \vec{g}}^{++}(n)$ while back-diffraction into the $\vec{g}'$ -beam has amplitude $M_{\vec{g}', \vec{g}}^{-+}(n)$.

Similarly, one component of the backward-traveling wave between layers n and $n+1$ has the value

$$a_{n\vec{g}}^- e^{i\vec{K}_{\vec{g}}^- \cdot (-\frac{1}{2} \vec{c}_n)}$$

at layer n . This wave can also be both transmitted and reflected at layer n with amplitudes $\delta_{\vec{g}', \vec{g}} + M_{\vec{g}', \vec{g}}^{--}(n)$ and $M_{\vec{g}', \vec{g}}^{+-}(n)$ respectively.

The forward-traveling wave between layers n and $n+1$ can, therefore, be written as a superposition of forward-traveling waves between $n-1$ and n transmitted through layer n and backward-traveling waves between n and $n+1$ reflected at layer n :

$$\begin{aligned} a_{n\vec{g}'}^+ e^{i\vec{K}_{\vec{g}'}^+ \cdot (-\frac{1}{2} \vec{c}_n)} &= \sum_{\vec{g}} (\delta_{\vec{g}', \vec{g}} + M_{\vec{g}', \vec{g}}^{++}(n)) a_{n-1, \vec{g}}^+ e^{i\vec{K}_{\vec{g}}^+ \cdot (\frac{1}{2} \vec{c}_{n-1})} \\ &\quad + M_{\vec{g}', \vec{g}}^{+-}(n) a_{n\vec{g}}^- e^{i\vec{K}_{\vec{g}}^- \cdot (-\frac{1}{2} \vec{c}_n)} \\ a_{n\vec{g}'}^+ &= \sum_{\vec{g}} (\delta_{\vec{g}', \vec{g}} + M_{\vec{g}', \vec{g}}^{++}(n)) a_{n-1, \vec{g}}^+ e^{i[\vec{K}_{\vec{g}}^+ \cdot (\frac{1}{2} \vec{c}_{n-1}) + \vec{K}_{\vec{g}'}^+ \cdot (\frac{1}{2} \vec{c}_n)]} \\ &\quad + M_{\vec{g}', \vec{g}}^{+-}(n) a_{n\vec{g}}^- e^{i[\vec{K}_{\vec{g}}^- \cdot (-\frac{1}{2} \vec{c}_n) + \vec{K}_{\vec{g}'}^+ \cdot (\frac{1}{2} \vec{c}_n)]} \end{aligned}$$

$$a_{n\vec{g}'}^+ = \sum_{\vec{g}} Q_{\vec{g}'\vec{g}}^I(n) a_{n-1\vec{g}}^+ + Q_{\vec{g}'\vec{g}}^{II}(n) a_{n\vec{g}}^- \quad (18)$$

Similarly, the backward-traveling wave between layers $n-1$ and n can be written:

$$a_{n-1\vec{g}'}^- = \sum_{\vec{g}} (\delta_{\vec{g}'\vec{g}} + M_{\vec{g}'\vec{g}}^{--}(n)) a_{n\vec{g}}^- e^{i[-\vec{K}_{\vec{g}}^- \cdot (\frac{1}{2}\vec{c}_n) - \vec{K}_{\vec{g}'}^- \cdot (\frac{1}{2}\vec{c}_{n-1})]} \\ + M_{\vec{g}'\vec{g}}^{+-}(n) a_{n-1\vec{g}}^+ e^{i[\vec{K}_{\vec{g}}^+ \cdot (\frac{1}{2}\vec{c}_{n-1}) - \vec{K}_{\vec{g}'}^- \cdot (\frac{1}{2}\vec{c}_{n-1})]}$$

$$a_{n-1\vec{g}'}^- = \sum_{\vec{g}} Q_{\vec{g}'\vec{g}}^{IV}(n) a_{n\vec{g}}^- + Q_{\vec{g}'\vec{g}}^{III}(n) a_{n-1\vec{g}}^+ \quad (19)$$

The Q equations (18) and (19) can be expressed in matrix form.

$$a_n^+ = Q^I(n) a_{n-1}^+ + Q^{II}(n) a_n^- \quad (20)$$

$$a_{n-1}^- = Q^{III}(n) a_{n-1}^+ + Q^{IV}(n) a_n^-$$

Since N forward-traveling beams are included, as well as an equal number of backward-traveling beams, each Q -matrix has dimensions $N \times N$ and each $a^\pm$ vector dimensions $N \times 1$.

Combining the Q -matrices into a single large matrix, an expression relating the amplitudes of the plane waves on opposite sides of layer n can be obtained:

$$\begin{pmatrix} a_n^+ \\ a_n^- \end{pmatrix} = \begin{pmatrix} Q^I(n) - Q^{II}(n) [Q^{IV}(n)]^{-1} Q^{III}(n) & Q^{II}(n) [Q^{IV}(n)]^{-1} \\ -[Q^{IV}(n)]^{-1} Q^{III}(n) & [Q^{IV}(n)]^{-1} \end{pmatrix} \begin{pmatrix} a_{n-1}^+ \\ a_{n-1}^- \end{pmatrix}$$

McRae (1968a) calls this $2N \times 2N$ matrix the "transfer matrix" for the n^{th} layer. As already explained, the explicit form of the Q-matrices is given by the scattering properties of the ion-cores making up each layer, complicated by the inclusion of intra-layer multiple scattering.

As an illustration of the use of this technique, the formalism will be developed for calculating the waves diffracted from an ideal crystal with a single surface layer ($n = 1$) which scatters differently from all the other layers (Figure I-8). This surface layer, for example, could be a monolayer of adsorbate or a surface potential barrier. Let the total wave in the vacuum above the surface (incident and diffracted) have components

$$a_{\vec{og}}^+ e^{i\vec{K}_{\vec{og}}^+ \cdot \vec{r}}$$

where

$$\vec{K}_{\vec{og}}^{\pm} = ((\vec{k}_{011} + \vec{g})_x, (\vec{k}_{011} + \vec{g})_y, \pm (2E - |\vec{k}_{011} + \vec{g}|^2)^{1/2}) .$$

An expression relating the diffracted wave amplitudes to the incident amplitudes is desired:

$$a_{\vec{og}'}^- = \sum_{\vec{g}} R_{\vec{g}, \vec{g}'}(0) a_{\vec{og}}^+$$

or, in matrix form:

$$a_{\vec{O}}^- = R(0) a_{\vec{O}}^+ . \quad (21)$$

Difficulty, however, is caused by the single atypical layer at the surface. This problem is handled by letting $R(1)$ represent the reflection matrix for the perfect crystal:

$$a_1^- = R(1)a_1^+$$

and then using the Q-equations (20) to calculate the effect of the surface layer:

$$a_1^+ = Q^I(1)a_0^+ + Q^{II}(1)a_1^-$$

$$a_0^- = Q^{III}(1)a_0^+ + Q^{IV}(1)a_1^-$$

Solving the last three equations for a_0^- in terms of a_0^+ :

$$a_0^- = \{Q^{III}(1) + Q^{IV}(1)[I - R(1)Q^{II}(1)]^{-1}R(1)Q^I(1)\}a_0^+$$

and $R(0)$ is given by:

$$R(0) = \{Q^{III}(1) + Q^{IV}(1)[I - R(1)Q^{II}(1)]^{-1}R(1)Q^I(1)\} \quad (22)$$

The reflection properties of the crystal are thus expressed in terms of the reflection and transmission matrices of the surface layer and the reflection matrix of the perfect bulk crystal. If desired, this process can be repeated to calculate $R(1)$ and all subsequent reflection matrices in terms of the scattering properties of the layers. It is much more convenient, however, to calculate $R(1)$ in terms of the normal modes of the perfect crystal. The normal modes are Bloch waves:

$$b_n^+(\vec{k}) = e^{i\vec{k} \cdot \vec{c}} b_{n-1}^+(\vec{k})$$

$$b_n^-(\vec{k}) = e^{i\vec{k} \cdot \vec{c}} b_{n-1}^-(\vec{k})$$

where $\vec{k}_{||} = \vec{k}_{011}$ and k_z is to be determined. The $b_n^\pm(\vec{k})$ are each vectors with components corresponding to the different

$\vec{g}$. Substituting these Bloch waves into the Q-equations (20), the following eigenvalue equation is obtained:

$$\left(\begin{array}{c|c} Q^I & Q^{II} \\ \hline -[Q^{IV}]^{-1} Q^{III} Q^I & [Q^{IV}]^{-1} [I - Q^{III} Q^{II}] \end{array} \right) \begin{pmatrix} b_{n-1}^+ \\ b_n^- \end{pmatrix} = e^{i\vec{k} \cdot \vec{c}} \begin{pmatrix} b_{n-1}^+ \\ b_n^- \end{pmatrix}$$

(The n -dependence of the Q -matrices has been dropped since all bulk crystal layers scatter identically.) The eigenvalues give the band structure of the crystal while the $2N$ eigenvectors give the $2N$ normal mode Bloch waves. Only N of these normal modes can be excited by the incident waves: the other N grow exponentially into the crystal or carry net flux out of the crystal. The wave incident on the perfect crystal can be expanded in terms of these N normal modes, designated by $\vec{k}$:

$$a_{\vec{g}}^+ = \sum_{\vec{k}} A(\vec{k}) b_{\vec{g}}^+(\vec{k})$$

Letting the $b_{\vec{g}}^+(\vec{k})$ be the components of an $N \times N$ matrix

$$b_{\vec{g}}^+(\vec{k}) = B_{\vec{g}\vec{k}}$$

the amplitudes of the normal modes are

$$A(\vec{k}) = \sum_{\vec{g}} (B^{-1})_{\vec{k}\vec{g}} a_{\vec{g}}^+$$

The reflected beam amplitudes are just,

$$\begin{aligned} a_{\vec{g}'}^- &= \sum_{\vec{k}} A(\vec{k}) b_{\vec{g}'}^-(\vec{k}) \\ &= \sum_{\vec{k}} \sum_{\vec{g}} b_{\vec{g}'}^-(\vec{k}) (B^{-1})_{\vec{k}\vec{g}} a_{\vec{g}}^+ \end{aligned}$$

and hence the components of the perfect crystal reflection matrix $R(1)$ are:

$$R(1)_{\vec{g}'\vec{g}} = \sum_{\vec{k}} b_{\vec{k}}^{-1}(\vec{k}) (B^{-1})_{\vec{k}\vec{g}} .$$

In conjunction with (21) and (22), this last expression completes the LEED problem.

The expansion of the incident waves in terms of the Bloch waves of the crystal reveals a close connection between LEED intensities and the band structure of the crystal. Namely, if the electron energy corresponds to a band gap, no Bloch waves can carry electron flux into the crystal. Instead, an intensity peak in the diffracted electrons occurs.

4. Effects of the Surface Potential Barrier

The surface potential barrier can have several effects on the diffracted LEED beams (McRae, 1971; Jennings, 1971a; 1973; Jennings and Read, 1974; VanHove, 1975a). All LEED calculations assume a potential barrier dependent only on the distance from the first atomic layer, although physically it is expected that the barrier has some periodic structure parallel to the surface. The only effects of such a smooth barrier are to reflect and refract electron beams incident on it.

The main effect of the surface barrier is to refract electron beams as they enter and leave the crystal. However, at energies just below the emergence energy of a new beam,

the diffracted beam is incident on the barrier at a grazing angle and is totally internally reflected back into the bulk of the crystal. The flux in this beam is then redistributed among the other beams, thus changing the intensities of the beams leaving the crystal.

In some special cases, a further effect can occur after total internal reflection. If, at this energy, the substrate also reflects strongly, because of the presence of a band gap, the beam can become trapped between the surface barrier and the substrate, and a quasi-stable surface state exists in the surface region (see Figure I-9). This surface state is not stable because diffraction into beams that can escape from the crystal occurs at the substrate atoms. The effect is to produce a "surface barrier resonance" in the I-V profiles of the diffracted beams in the energy range between the emergence of the new beam from the substrate and its emergence in the vacuum. The exact location of the resonance feature, however, is determined by the requirement that the phase difference between each of the wavelets contributing to the beam containing the resonance is an integral multiple of 2π (McRae, 1971).

Because of their localization at the surface, resonance features are especially sensitive to the precise form of the surface potential barrier and to the presence of adsorbates.

C. Spin Polarization in Atomic Scattering

1. Introduction

It is well-known that, as a result of a small spin-orbit interaction, substantial electron spin polarization can result when electrons are scattered from free atoms of large atomic number (Kessler, 1969; 1976; Walker, 1971). Using the fact (to be proved in the next section) that a spin-orbit interaction does not change the electron spin if it is aligned perpendicular to the scattering plane, Kessler (1969) has given a simple argument to explain spin polarization in atomic scattering. The unpolarized incident beam can be considered to be made up equally of electrons with spins parallel and antiparallel to the normal of the scattering plane. The spin-orbit interaction has opposite signs for electrons with spin up and with spin down and, hence, the effective radius R of the scattering potential is different for the two spins. Using a simple optical model, electrons with the two different spin orientations will be diffracted differently since the location of the maxima and minima is determined by λ/R . The scattering cross-sections will also be affected by the small difference in the potentials themselves. The net result of these two effects is that the cross-sections for scattering into a certain angle will usually be different for the two spins. If $(\frac{d\sigma}{d\Omega})^\uparrow$ and $(\frac{d\sigma}{d\Omega})^\downarrow$ are the cross-sections for spin up and spin down, respectively, then the polarization of the scattered electrons is

$$P = \frac{(\frac{d\sigma}{d\Omega})_{\uparrow} - (\frac{d\sigma}{d\Omega})_{\downarrow}}{(\frac{d\sigma}{d\Omega})_{\uparrow} + (\frac{d\sigma}{d\Omega})_{\downarrow}} .$$

Figure I-10 shows that, because the difference in scattering for the two spins is usually small, high polarizations will be observed only with low intensity, and vice versa.

2. The Density Matrix Formalism of Spin-Dependent Scattering

A more sophisticated treatment of spin polarization in scattering can be given by use of spinors and the density matrix. The formalism developed in this section can be used both to analyze the polarization produced in an unpolarized beam by a spin-orbit interaction, and to determine asymmetries, such as the Mott-asymmetry, when a polarized beam is scattered.

Assume a monoenergetic, collimated beam of electrons is incident on a spherically symmetric scattering center. If the Hamiltonian contains a spin-orbit interaction term $W(\vec{r})\vec{L}\cdot\vec{\sigma}$, spin-dependent scattering occurs. Following Merzbacher (1970), spin can be included in the formalism by writing the incident wave as

$$e^{ikz}\chi_{\text{inc}} = e^{ikz} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} , \quad \chi_{\text{inc}}^+ \chi_{\text{inc}} = 1 .$$

The scattered wave will then be

$$\psi_{\text{sc}} \sim e^{ikz}\chi_{\text{inc}} + h(\theta, \varphi, k) \frac{e^{ikr}}{r}$$

where $h(\theta, \varphi, k)$ is a two-component spinor.

Figure I-10: Illustration of the relationship between the spin polarization and the cross-sections for scattering of electrons with spins "up" and "down" with respect to the scattering plane. In this example, 300 eV electrons are scattering from mercury (Kessler, 1969).

$$P = \frac{\left(\frac{d\sigma}{d\Omega}\right)_{\uparrow} - \left(\frac{d\sigma}{d\Omega}\right)_{\downarrow}}{\left(\frac{d\sigma}{d\Omega}\right)_{\uparrow} + \left(\frac{d\sigma}{d\Omega}\right)_{\downarrow}}$$

Since Schrödinger's equation is linear, the scattering can be completely described by finding solutions for two particular incident polarizations: $\chi_{\text{inc}} = \alpha$ and $\chi_{\text{inc}} = \beta$, which are beams longitudinally polarized parallel and anti-parallel to the direction of the incident momentum, taken as the z-axis. Then

$$\begin{aligned}\psi_1 &\sim e^{ikz} \alpha + (S_{11}\alpha + S_{21}\beta) \frac{e^{ikr}}{r} \\ \psi_2 &\sim e^{ikz} \beta + (S_{12}\alpha + S_{22}\beta) \frac{e^{ikr}}{r}\end{aligned}\tag{23}$$

Multiplying the first equation by c_1 and the second by c_2 , superposition gives the general solution:

$$\begin{aligned}\psi_{\text{sc}} &\sim e^{ikz} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} + \frac{e^{ikr}}{r} \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \\ \psi_{\text{sc}} &\sim \left(e^{ikz} + \frac{e^{ikr}}{r} S \right) \chi_{\text{inc}}\end{aligned}$$

The scattering amplitude is thus given by $S\chi_{\text{inc}}$ and, hence, the scattering problem is solved once the 2×2 scattering matrix S , with the elements dependent on θ , φ , and k , is determined.

The general form of S can be deduced from some simple invariance arguments, although the exact dependence on θ and k is governed by the form of the scattering potential and can only be derived by a detailed phase shift analysis. Since the scattering potential is assumed spherically symmetric, the Hamiltonian H is invariant under rotations.

Consequently, the incident waves in equation (23) are eigenstates of the z-component of the total angular momentum J_z with eigenvalues $+\hbar/2$ and $-\hbar/2$, respectively. The fact that J_z is a constant of the motion requires that ψ_1 and ψ_2 must also be eigenfunctions of J_z :

$$J_z \psi_1 = (L_z + S_z) \psi_1 = \hbar \left(\frac{1}{i} \frac{\partial}{\partial \varphi} + \frac{1}{2} \sigma_z \right) \psi_1 = \frac{\hbar}{2} \psi_1$$

$$J_z \psi_2 = (L_z + S_z) \psi_2 = \hbar \left(\frac{1}{i} \frac{\partial}{\partial \varphi} + \frac{1}{2} \sigma_z \right) \psi_2 = -\frac{\hbar}{2} \psi_2$$

Substituting the explicit expressions for ψ_1 and ψ_2 shows that S_{11} and S_{22} are independent of φ , while the off-diagonal elements of S have the form

$$S_{12} = e^{-i\varphi} \cdot \text{function of } \theta$$

$$S_{21} = e^{i\varphi} \cdot \text{function of } \theta$$

Furthermore, H is invariant under reflection with respect to any coordinate plane. Under a reflection in the yz plane, $\varphi \rightarrow \pi - \varphi$ and $e^{ikz}_\alpha \rightarrow e^{ikz}_\beta$ while $\frac{e^{ikr}}{r}$ remains invariant. Applying this reflection to the first wave function in (23) results in the second wave function and hence

$$S_{11} = S_{22} = f(\theta, k)$$

$$-S_{21}(-\varphi, \theta, k) = S_{12}(\varphi, \theta, k) = -e^{-i\varphi} g(\theta, k) \cdot$$

S must therefore have the form

$$S = \begin{pmatrix} f(\theta, k) & -g(\theta, k)e^{-i\varphi} \\ g(\theta, k)e^{i\varphi} & f(\theta, k) \end{pmatrix} \quad (24)$$

or

$$S = f(\theta, k)I + ig(\theta, k)(\sigma_x \sin\varphi - \sigma_y \cos\varphi)$$

where $\vec{\sigma}$ are the Pauli matrices. But $\hat{n} = (-\sin\varphi, \cos\varphi, 0)$ is the normal to the plane of scattering. Therefore

$$S = f(\theta, k)I - ig(\theta, k)\hat{n} \cdot \vec{\sigma} . \quad (25)$$

It is evident from expression (25) that a spin-orbit interaction does not change the spin if it is aligned parallel or anti-parallel to $\hat{n}$. This result is a consequence of the fact that for the spin parallel to $\hat{n}$, no torques are exerted on the spin.

The intensity and polarization of the scattered beam can be evaluated in terms of $f(\theta, k)$ and $g(\theta, k)$. The differential scattering cross-section is given by

$$\frac{d\sigma}{d\Omega} = (S\chi_{\text{inc}})^+ (S\chi_{\text{inc}}) = \chi_{\text{inc}}^+ S^+ S \chi_{\text{inc}} .$$

If the density matrix ρ for a definite spinor state χ is defined by $\rho = \chi\chi^+$ and, for an ensemble of N spinors, by $\rho = \frac{1}{N} \sum_i \chi_i \chi_i^+$, then, in both cases, the expectation value of an operator A is given by $\langle A \rangle = \text{trace}(\rho A)$. Hence

$$\frac{d\sigma}{d\Omega} = \text{trace}(\rho_{\text{inc}} S^+ S) .$$

Writing $\rho_{\text{inc}} = \frac{1}{2}(I + \vec{P}_O \cdot \vec{\sigma})$, where $\vec{P}_O$ is the polarization of the incident beam, and using the form (25) for S :

$$\frac{d\sigma}{d\Omega} = (|f|^2 + |g|^2) \left(1 + i \frac{fg^* - f^*g}{|f|^2 + |g|^2} \vec{P}_o \cdot \hat{n} \right) \quad (26)$$

The polarization $\vec{P}$ of the scattered beam can be calculated from the expression

$$\vec{P} = \frac{\text{trace}(\rho_{sc} \vec{\sigma})}{\text{trace}(\rho_{sc})} \quad (27)$$

where ρ_{sc} is the density matrix of the scattered beam

$$\rho_{sc} = \chi_{sc} \chi_{sc}^+ = (S \chi_{inc}) (S \chi_{inc})^+ = S \rho_{inc} S^+ .$$

If the incident beam is assumed unpolarized, then (27) shows that the scattered beam has polarization

$$\vec{P} = i \frac{fg^* - f^*g}{|f|^2 + |g|^2} \hat{n} \quad (28)$$

The polarization is perpendicular to the scattering plane.

The Sherman function $\mathfrak{J}$ is defined by $\mathfrak{J} = i \frac{fg^* - f^*g}{|f|^2 + |g|^2}$ and, hence, the scattered intensity can be written:

$$\frac{d\sigma}{d\Omega} = (|f|^2 + |g|^2) (1 + \mathfrak{J} \vec{P}_o \cdot \hat{n}) . \quad (29)$$

Expression (29) is basic to the technique of polarization analysis by Mott scattering. In this technique, electrons scattered in the plane perpendicular to their polarization vector are recorded by symmetrically placed detectors. Because $\hat{n}$ points in opposite directions for scattering into the left and right detectors, the ratio of counts in the detectors is

$$\frac{N_L}{N_R} = \frac{1 + \sum P_o}{1 + \sum P_o} . \quad (30)$$

Explicit expressions for $f(\theta, k)$ and $g(\theta, k)$ can be obtained by solving the relativistic Dirac equation (Mott and Massey, 1965):

$$\begin{aligned} f(\theta, k) &= \frac{1}{2ik} \sum_{\ell} \left\{ (\ell+1) \left[e^{2i\delta_{\ell}(k)} - 1 \right] + \ell \left[e^{2i\delta_{-\ell-1}(k)} - 1 \right] \right\} P_{\ell}(\cos\theta) \\ g(\theta, k) &= \frac{1}{2ik} \sum_{\ell} \left\{ e^{2i\delta_{-\ell-1}(k)} - e^{2i\delta_{\ell}(k)} \right\} P_{\ell}^1(\cos\theta) . \end{aligned} \quad (31)$$

For any scattering potential, the phase shifts can be determined, and the polarization calculated from (28). As shown in Figure I-11, excellent agreement exists between theoretically predicted and experimentally measured polarizations. The calculations have been extended to many elements, including tungsten (Fink and Yates, 1970; Fink and Ingram, 1972; Gregory and Fink, 1974).

D. Spin Polarization in LEED

1. Introduction

Since the diffracted beams in LEED result from interactions between the electrons and the atoms at the surface, spin polarization of the LEED beams is expected from crystals with atoms of large atomic number. In analogy with atomic scattering, the polarization of a LEED beam is usually determined by the difference between the numbers

Figure I-11: Energy dependence of the polarization for electrons scattered through 90° from mercury atoms. The solid circles are experimental values with their statistical errors while the dashed line is given by theory. The pseudologarithmic energy scale is defined by $\log(1 + E(\text{eV})/100 \text{ eV})$. (Kessler, 1969)

of spin "up" and spin "down" electrons with respect to the scattering plane in the beam:

$$P = \frac{N^{\uparrow} - N^{\downarrow}}{N^{\uparrow} + N^{\downarrow}} .$$

In scattering from free atoms, both polarization and intensity are determined solely by the nature of the atomic potential. In LEED, however, the scattering process is also influenced by several other factors: the periodicity of the crystal lattice through the Bragg conditions, modifications in the electronic wave functions in the crystal structure, multiple scattering, the surface potential barrier, the top interlayer spacing, and the inelastic processes.

Two theoreticians, Jennings and Feder, have made extensive calculations of spin polarization in LEED, using different modifications of the dynamic method. The calculations predict strong polarization features. As in atomic scattering, the highest polarizations occur at intensity minima. Because crystal structure has previously been deduced mainly from the positions of intensity maxima, features such as polarization, which are large at intensity minima, complement intensity data in surface structure determinations. Furthermore, calculations indicate spin polarization to be a sensitive probe of the crystal surface. In particular, theory predicts polarization to be more sensitive than intensity to certain features of the surface such as the top interlayer spacing and the shape of the surface potential barrier.

2. Description of Jennings' and Feder's Calculations

Both Jennings and Feder have independently developed dynamical LEED calculations incorporating spin (Jennings, 1970; 1971b,c; Jennings and Sim, 1972; Jennings, 1974; Feder, 1971; 1972; 1973a,b; 1974; 1975; 1976; 1977; Feder, Jennings, and Jones, 1976; Feder, private communication). Their theoretical techniques have undergone transformations since their early calculations and, as a consequence, their methods have become increasingly sophisticated. Only the latest techniques used in their calculations will be discussed here.

Both models are relativistic formulations of the dynamic method discussed in Section I-B-3. Both make the usual assumptions of electron plane waves incident on a crystal with perfect two-dimensional periodicity parallel to the surface. The scattering potentials are of the muffin-tin form and inelastic scattering processes are represented by a constant imaginary term in the crystal potential. In the Pauli-spinor formalism, every plane wave beam becomes a spinor. For example, the incident beam is

$$\psi_{\text{inc}} = e^{i\vec{k}_0 \cdot \vec{r}} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix}.$$

The inclusion of spin in the plane wave basis doubles the dimensions of all vectors and matrices in Section I-B-3. In particular, the basis vectors in the crystal are now of the form

$$e^{i\vec{K}_{\vec{g}}^{\pm} \cdot \vec{r}} \quad \alpha \quad \text{and} \quad e^{i\vec{K}_{\vec{g}}^{\pm} \cdot \vec{r}} \quad \beta$$

The effect on the final reflection matrix $R(0)$ is to replace each single matrix element $R_{\vec{g}'\vec{g}}(0)$ by four:

$$R_{\vec{g}'\vec{g}}(0) \rightarrow \begin{pmatrix} R_{\vec{g}'\alpha \vec{g}\alpha}(0) & R_{\vec{g}'\alpha \vec{g}\beta}(0) \\ R_{\vec{g}'\beta \vec{g}\alpha}(0) & R_{\vec{g}'\beta \vec{g}\beta}(0) \end{pmatrix}$$

where, for example, $R_{\vec{g}'\beta \vec{g}\alpha}(0)$ is the amplitude that an incoming wave with spin α and wavevector $\vec{K}_{\vec{g}}^+$ leaves the crystal with spin β and wavevector $\vec{K}_{\vec{g}'}^-$.

The full $R(0)$ will thus have its dimensions doubled by inclusion of spin, and can be divided into 2×2 matrices, each representing a scattering matrix S_{hk} describing the transformation of the incident beam into the hk diffracted beam. For example, the diffraction into the 00 beam will be described by a matrix

$$S_{00} = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix}$$

which can be used to calculate the intensity and polarization of the 00 beam by the methods described in Section I-C-2. Namely, for an unpolarized incident beam, the density matrix of the 00 beam is

$$\rho_{00} = \frac{1}{2} S_{00} S_{00}^+ = \frac{1}{2} \begin{pmatrix} |R_{11}|^2 + |R_{12}|^2 & R_{11}R_{21}^* + R_{12}R_{22}^* \\ R_{21}R_{11}^* + R_{22}R_{12}^* & |R_{21}|^2 + |R_{22}|^2 \end{pmatrix}.$$

The intensity is

$$I_{00} = \text{trace}(\rho_{00}) = \frac{1}{2}(|R_{11}|^2 + |R_{12}|^2 + |R_{21}|^2 + |R_{22}|^2)$$

and the polarization is

$$\vec{P}_{00} = \frac{\text{trace}(\rho_{00} \vec{\sigma})}{\text{trace}(\rho_{00})} = \frac{\text{trace}(\rho_{00} \vec{\sigma})}{I_{00}}$$

which gives, for example,

$$P_{00}^z = \frac{1}{2I_{00}} (|R_{11}|^2 + |R_{12}|^2 - |R_{21}|^2 - |R_{22}|^2) .$$

Some details of the methods of Jennings and Feder will be discussed next (Feder, Jennings, and Jones, 1976). Each method solves the LEED problem in three stages. First, the relativistic scattering phase shifts are determined for the muffin-tin potential by numerically solving the radial Dirac equation. Both methods are identical in this respect. The second stage of the calculations, the treatment of intra-layer scattering, however, is handled differently in the two formalisms. Although both use essentially the method outlined in Section I-B-3, the manner in which the X-matrix in (17) is obtained by summing the scattered waves from all other ion-cores in the layer is treated differently by Jennings and Feder. The difficulty lies in the convergence of this sum. Feder sums directly and relies on the absorption of electrons by the imaginary part of the potential to cause the sum to converge. Jennings, on the other hand, uses an Ewald summation

technique (Ziman, 1972) as modified by Kambe (Pendry, 1974) to ensure convergence. The Kambe formalism is valid even in the limit of zero absorption. If N is the number of beams under consideration, both methods produce a $4N \times 4N$ transfer matrix for the layer relating the $2N$ outgoing wave spinor amplitudes to those incident on the layer. Because of the inclusion of spin, the dimensions of this transfer matrix are twice as large as in nonrelativistic calculations.

The third stage of the LEED problem, interlayer scattering, is also treated differently by Jennings and Feder. Jennings uses the relativistic generalization of the normal mode method outlined in Section I-B-3: amplitudes of the back-scattered waves are found from the normal modes of the perfect crystal. Feder, however, uses an approximation technique called "layer doubling." Because of electron absorption, all electron wave functions die away with distance in the crystal. Therefore it is possible to approximate the semi-infinite crystal by a slab of finite thickness since electrons incident on one surface cannot sense the presence of the second surface if the slab thickness is much greater than the extinction length. The transfer matrix for this slab can be found by multiplication of the single-layer transfer matrices until numerical convergence of reflection coefficients is achieved.

To test the numerical methods used in these two programs, the results of the programs have been compared for

runs using the same diffraction conditions, atomic phase shifts, and reciprocal lattice vectors. Figure I-12 shows agreement to be excellent.

3. Theoretical Results

Both Feder and Jennings have used their programs to investigate the relative sensitivities of intensity and polarization to various parameters. These parameters include effects of relativistic terms in the scattering potential, modifications of the electronic wave functions in the crystal structure, multiple scattering, inelastic processes, top interlayer spacing, and the surface potential barrier. The theoretical results for each of these effects will be discussed in turn.

The effects on intensity and polarization of the inclusion of relativistic corrections in LEED calculations have been investigated by both Feder and Jennings (Feder, 1971; 1972; 1973a; 1974; Jennings, 1970, 1971a). Some typical results are shown in Figure I-13 where the intensity of the 10 beam from W(001) at normal incidence is calculated both for a nonrelativistic potential (a) and with the inclusion of relativistic terms (b). Significant differences are seen in the intensity profiles. Whereas nonrelativistic potentials scatter spin "up" and "down" electrons equally, part (c) of Figure I-13 shows that the inclusion of relativistic corrections causes the two spins to be scattered differently. Finally (d) presents

Figure I-12: 00 beam intensities and polarizations as functions of energy from a W(001) surface. The upper curve in each case uses Feder's program while the lower curve is the result of Jennings' program. The intensities and polarizations shown in this figure should not be compared to experiment because parameters used are not necessarily optimal for convergence of intensities and polarizations (Feder, Jennings, and Jones, 1976).

Figure I-13: Effects of relativistic corrections on LEED intensities of the 10 beam for normal incidence from W(001).

- (a) Nonrelativistic I-V curve
- (b) Relativistic I-V curve for an unpolarized primary beam
- (c) Relativistic I-V curves for a totally polarized primary beam. The solid curve is for spin "up" while the dotted curve is for spin "down."
- (d) Polarization of the 10 beam as determined from

$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} .$$

The results presented in this figure cannot be compared to experiment because only elastic scattering of electrons was considered; inelastic effects were neglected (Jennings, 1971a).

the polarization of the 10 beam as calculated from

$$P = \frac{N_{\uparrow} - N_{\downarrow}}{N_{\uparrow} + N_{\downarrow}} . \quad \text{Large polarization features are obvious.}$$

Modification of the electronic wave functions in the crystal structure also has an effect on polarization. Figure I-14 shows the polarizations resulting from elastic electron scattering from atomic tungsten (Fink, private communication, 1975) and from a single tungsten muffin-tin atom (Feder, 1977). The parts of these potentials near the nucleus are virtually identical; the major modifications are in the regions distant from the nucleus. Nevertheless, polarizations differ greatly indicating that polarization, although originating from the coulombic part of the potential in the vicinity of the nucleus, is strongly affected by the shape of the potential further away from the nucleus.

The calculations of Feder and Jennings illustrate the effects of multiple scattering in several different ways. Figure I-15 shows the intensity and polarization of the 00 beam as calculated using the kinematic and dynamic LEED methods but for the same incidence conditions and surface parameters (Jennings and Sim, 1972). Because the kinematic method assumes single-scattering whereas the dynamic method accounts for multiple scattering, the large differences between the curves illustrate the great importance of multiple scattering in determining both intensity and spin-polarization profiles. A more direct

Figure I-14: Polarization as a function of atomic scattering angle for elastic electron scattering: ● ● ● ● Single W muffin-tin atom, $E = 82$ eV (Feder, 1977).
● — ● Free W atom, $E = 95$ eV (Fink, private communication, 1975). The difference in energy is due to the inclusion in the muffin-tin result of an inner potential correction of ~ 12 eV.

Figure I-15: Illustration of the effects of multiple scattering in determination of intensity and polarization. All profiles are for the 00 beam from W(001) at an angle of incidence of 10° . A square potential barrier of height 1.09 Ryd is situated 3 a.u. above the surface layer. Inelastic scattering of electrons by electronic excitation of atomic cores is introduced into the model by use of complex phase shifts determined from an imaginary term in the scattering potentials. The solid curve refers to weak absorption ($V_i = 0.04$ Ryd) while the dotted curve refers to strong absorption ($V_i = 0.4$ Ryd).

(a) Kinematic intensity and spin polarization

(b) Dynamic intensity and spin polarization

The square barrier in these calculations probably scatters too strongly to permit meaningful comparison to experiment (Jennings and Sim, 1972).

(a)

ENERGY (Ry)

(b)

test of the effects of multiple scattering is shown in Figure I-16. Feder (1977) has calculated the polarization of the specularly reflected beam for constant energy = 82 eV as a function of angle of incidence for three different situations--a single tungsten muffin-tin atom, a monolayer of tungsten muffin-tins, and a W(001) surface. Only single scattering occurs in the first situation while intra-layer multiple scattering is included in the second. The third curve shows the effects of both intra- and inter-layer multiple scattering. The changes in polarization with increased multiple scattering illustrate clearly the necessity for accurately including all multiple scattering in LEED calculations.

A final indirect demonstration of the necessity of including multiple scattering in LEED calculations is shown in Figure I-17. Jennings (1974) has calculated the dependence of both intensity and polarization of the 00 beam on the azimuthal angle of incidence ϕ . If scattering were purely kinematic, intensity and polarization would both be independent of ϕ . The changes in the profiles evident in this figure indicate the necessity for including multiple scattering effects. It should be noted that polarization is not necessarily perpendicular to the LEED scattering plane unless this plane is a symmetry plane of the crystal surface. Electrons multiply scattered only in the scattering plane are polarized perpendicular to this plane.

Figure I-16: Calculations of polarization of the specular beam for constant energy = 82 eV as a function of angle of incidence illustrating the effects of increased multiple scattering.

(a) A single tungsten muffin-tin atom

(b) A monolayer of tungsten muffin-tins

(c) A W(001) surface

(Feder, 1977).

Figure I-17: Azimuthal dependence of the intensities and polarizations of the 00 beam from W(001) for $\theta = 45^\circ$. φ is measured from the 10 azimuth. The solid lines are intensity profiles and the dashed lines are polarizations (Jennings, 1974).

However, electrons scattered out of the scattering plane can attain spin polarizations in other directions. If the scattering plane is a symmetry plane, scattering up and down with respect to this plane cancels the components of polarization parallel to this plane. Such cancellation does not occur if the scattering plane is not a symmetry plane and consequently the total polarization is not necessarily perpendicular to the scattering plane. Since the Mott polarization analyzer in this experiment measures only the component of the total polarization perpendicular to the scattering plane, the polarization measured for an arbitrary φ is not necessarily the total polarization. For this reason, the polarizations shown in Figure I-17 are the components of the total polarization perpendicular to the scattering plane.

Jennings and Sim (1972) emphasize the use of spin in determining the kinds of inelastic scattering occurring in the crystal. They point out that inelastic scattering by electronic excitation of the atomic cores is accounted for in the calculations by an imaginary component in the atomic scattering phase shifts. But, from equations (31) for $f(\theta, k)$ and $g(\theta, k)$ such an imaginary component will introduce an exponential damping factor in g while affecting f less strongly. The difference between g and f will significantly influence the polarization given by (28). On the other hand, phonon and plasmon losses between the ion

cores have little effect on either f or g and hence should not greatly affect polarization directly. Such losses, however, will reduce the distance an electron travels before absorption and hence will limit multiple scattering. It is predicted that measurements of polarization should give information of the relative strengths of these two inelastic processes. The effect of electronic excitation on spin polarization is illustrated in Figure I-18 where intensity and polarization of the 00 beam are shown for both very weak and very strong absorption by electronic excitation of the atom cores.

Calculations indicate that spin polarization is more sensitive than intensity to contraction of the top interlayer spacing (Feder, 1976; private communication, 1977). An example illustrating the relative sensitivity of intensity and polarization to this parameter is shown in Figure I-19. Although some differences exist between the intensity profiles for no contraction and 10% contraction, the peak structure is shifted in energy about 7 eV but otherwise is essentially unchanged. The lack of sensitivity of intensity to top interlayer spacing is evidenced by the poor agreement of three recent investigations, all based on intensity measurements, of contraction of the W(001) surface. The studies report contractions of 11% (Lee et al., 1977), 6% (VanHove and Tong, 1976), and 4.4% (Debe et al., 1977). On the other hand, the polarizations

Figure I-18: Intensity and spin polarization profiles for the 00 beam from W(001) at an angle of incidence of 10° . An inner potential correction of 1.09 Ryd is applied. Inelastic scattering of electrons by electronic excitation of atomic cores is introduced into the model by use of complex phase shifts determined from an imaginary term in the scattering potentials. The solid curve refers to weak absorption ($V_i = 0.04$ Ryd) while the dotted curve refers to strong absorption ($V_i = 0.4$ Ryd) (Jennings and Sim, 1972).

Figure I-19: Intensity and polarization of the 01 beam from W(001) at normal incidence.
-- No surface contraction; — 10% contraction of the top interlayer spacing (Feder, private communication, 1977).

calculated for no contraction and 10% contraction and shown in Figure I-19 are strikingly different. This great sensitivity of the polarization indicates that spin polarization measurements, in conjunction with calculations for a greater number of surface contractions, can accurately determine the top interlayer spacing of the W(001) surface.

Spin polarization measurements may also be useful in a detailed investigation of the structure of the surface potential barrier. Figure I-20 shows the effect on intensity and polarization of three different surface potential barriers (Feder, Jennings, and Jones, 1976). These barriers are:

- (a) Non-reflecting barrier: a square barrier that does not reflect waves but only refracts transmitted waves. Nonrelativistic LEED intensity calculations above 50 eV commonly use this barrier.
- (b) Modified step barrier: a square barrier that both reflects and transmits electrons leaving the crystal. Transmitted beams are refracted.
- (c) Exponential barrier: a reflecting and transmitting barrier of the exponential type which provides a smoother, more realistic continuation of the crystal potential into the vacuum.

Figure I-20: Intensity and polarization profiles of the 00 beam from W(001) at $\theta = 11^\circ$ calculated for three different surface potential barriers.

(a) Non-reflecting barrier

(b) Modified step barrier

(c) Exponential barrier

The results presented in this figure are illustrative but not considered accurate enough to be compared to experiment (Feder, Jennings, and Jones, 1976).

The intensity profiles in Figure I-20 are almost identical indicating that intensity measurements are insensitive to the shape of the surface potential barrier. On the other hand, large changes are evident in the polarization curves for the three barriers. Figure I-20 shows that the polarizations are largest for reflecting barriers. These large polarizations are probably caused by the reflection back into the bulk of the crystal of a highly polarized beam. The spin-polarized electrons in this reflected beam are then redistributed among the other beams causing the observed polarizations. A specific example of the effect of a surface barrier resonance on intensity and polarization is shown by a comparison of Figures I-18 and I-15b (Jennings and Sim, 1972). The model used in Figure I-15b assumes a square surface potential barrier not included in the model of Figure I-18. The intensity profile in the presence of the barrier exhibits a well-defined surface barrier resonance at 0.75 Ryd. The corresponding polarization profile shows a strong feature associated with this resonance. The negative polarization feature just above 1 Ryd. is due to a redistribution of the flux in the 01 and 01 beams which are strongly polarized and totally internally reflected at this energy. These results all indicate that spin polarization may be more useful than intensity in studies of the surface potential barrier.

The reason for the sensitivity of spin polarization to surface parameters is probably the relationship between polarization and intensity. As in atomic scattering, the largest polarizations in LEED occur at intensity minima. The polarization is thus determined by small differences in the scattering of spin "up" and spin "down" electrons. Hence, any process such as reflection at a surface potential barrier that causes changes in the relative numbers of spin "up" and "down" electrons affects the polarization. Whereas the intensity of a LEED beam is determined by the sum of the numbers of spin "up" and "down" electrons, an accurate polarization calculation at an intensity minimum requires the difference between these two small quantities.

II. EXPERIMENTAL CONSIDERATIONS

A. Experimental Apparatus

The experimental apparatus is contained within two stainless steel ultrahigh vacuum chambers connected by an accelerating column. LEED is performed in the first chamber while the second chamber is used for Mott polarization analysis (Figure II-1).

1. The Vacuum System

Ultrahigh vacuum is required for experimental work on atomically clean surfaces. This is demonstrated by the fact that an initially clean metal surface at atmospheric pressure is covered with a monolayer of adsorbates in about 10^{-9} seconds. The vacuum required to maintain a well-defined surface for experimental work is easily calculated. The number ϕ of gas molecules striking a unit area of the surface per unit time is given by (Reif, 1965):

$$\phi = \frac{P}{\sqrt{2\pi mkT}} .$$

If less than one monolayer of adsorbates is desired for 2000 seconds and if every gas molecule that strikes the surface sticks to it, then the required pressure is calculated to be 10^{-9} Torr.

Such a pressure is in the ultrahigh vacuum (UHV) region, and hence the vacuum system was designed using exclusively UHV techniques. The UHV requirements were met

Figure II-1: Overview of the experimental apparatus.

LEAD CHAMBER

MOTT ANALYSIS CHAMBER

by constructing the vacuum chambers from No. 304 low-carbon stainless steel, by using only UHV-compatible materials inside the chamber, by sealing all flanges with gaskets fabricated from oxygen-free high conductivity (OFHC) copper, and by using only valves and pumps specially designed for UHV work. The complete LEED chamber is designed so that it can be baked to 200°C to outgas impurities from the chamber walls. Bakeout of the LEED system is accomplished by a marinite oven which can be lowered over the chamber.

The LEED chamber is evacuated by using a combination of three liquid nitrogen sorption pumps for the initial pumping from atmospheric pressure to about 5×10^{-4} Torr, a 100 l/sec differential ion (D-I) pump for reducing the pressure further to approximately 10^{-7} Torr, and finally two 400 l/sec D-I pumps, one on the LEED chamber and the other on the Mott chamber. The D-I pumps utilize two different yield sputtering elements (titanium and tantalum) in order to overcome the poor inert gas pumping capability of single element ion pumps. The ultimate pressure is about 10^{-10} Torr in the LEED chamber and about 10^{-8} Torr in the Mott chamber. The difference in final pressure in the two chambers has a simple explanation: it is not possible to bake the Mott chamber since the surface barrier detectors in this chamber are destroyed at temperatures above 35°C. The Mott system was baked to 150°C for several days before insertion of the detectors. Installation of the detectors, however, allowed impurities to enter the chamber, thus limiting the ultimate pressure.

The pressure in the LEED chamber can be independently monitored by three different gauges. First, the D-I pumps are essentially large Penning-type cold cathode gauges (Tom and James, 1969; Tom, 1972). Since the current from the pump cathode is caused by gas ions incident on it, the cathode current is pressure-dependent and calibration curves are provided by the pump manufacturer. Secondly, a nude Bayard-Alpert type gauge is mounted in the LEED chamber. Finally, a partial pressure analyzer, which is essentially a small mass spectrometer, can be used both to analyze the gas components and to estimate the total pressure in the LEED chamber.

The partial pressure analyzer is designed to work in conjunction with an x, y plotter to record partial pressures of gases in the vacuum system. Figure II-2 shows a scan of the unbaked system at a pressure of about 10^{-7} Torr. The major contaminants are hydrogen, water, inert gases (He and Ne), carbon monoxide, and carbon dioxide. Figure II-3 shows the effect of bakeout on the gas constituents. At 10^{-9} Torr, no neon is present and the amount of water has been reduced dramatically. The major contaminants are those typical of a clean UHV environment, namely hydrogen and carbon monoxide.

The Mott chamber has its own 400 ℓ /sec D-I pump. A copper glow discharge screen has been installed over the mouth of this pump to prevent the glow discharge present when the pump is started from damaging the delicate surface

Figure II-2: Mass spectrometer scan of the partial pressures of gases in the unbaked system at a pressure of about 10^{-7} Torr. The major contaminants are H_2 , H_2O , CO , CO_2 , and inert gases.

Figure II-3: Mass spectrometer scan of the partial pressures of gases in the baked system at a pressure of about 10^{-9} Torr. The major contaminants are H_2 and CO.

barrier detectors in the Mott chamber. Pressure in the Mott chamber is monitored using a bakeable Thermocouple gauge (10 - 10^{-3} Torr) and a nude ion gauge ($< 10^{-4}$ Torr). When the Mott system is biased to 100 kV, pressure is measured using the cathode current of the D-I pump. This current indicates a pressure of about 1×10^{-8} Torr.

2. The Gas Handling System

A completely bakeable, UHV-compatible gas handling system has recently been installed to admit to the LEED chamber accurately metered quantities of clean gases (Figure II-4). Gases are required for two purposes: oxygen is needed to clean the crystal (see Section II-A-4), and O_2 , CO, and H_2 are admitted to study the effects of adsorbates on the crystal surface on intensity and polarization.

The research-grade gases are purchased in 1 l glass flasks at a pressure of 1 atmosphere. The flasks are attached to glass-metal transition tubes and can then be mounted on the gas handling system. Withdrawal of gas from each flask is controlled by the UHV valve (1) positioned at the mouth of the flask.

The operation of the gas handling system is straightforward. Initially the gas handling line is evacuated using a sorption pump, followed by the 100 l/sec roughing ion pump, to a pressure of less than 10^{-8} Torr. With valve (2) closed, the line is then charged with gas by

Figure II-4: Schematic of the Roughing/Gas Handling System. The system is completely bakeable and all valves are UHV-compatible.

opening and subsequently closing valve (1) for the appropriate gas flask. Valve (2) is then cracked to admit gas to a pressure of about 10^{-1} Torr to the reservoir immediately preceding the UHV leak valve. This valve, which has a conductance continuously variable between 10^{-14} l/sec and 1 l/sec, is used to smoothly admit the required amount of gas to the LEED chamber. Purity of the gas admitted to the LEED chamber is monitored by use of the partial pressure analyzer.

3. The LEED System

The LEED chamber contains a conventional commercial LEED optics assembly and electron gun (Figure II-5). This entire assembly is mounted on a rotary drive and can be turned about a vertical axis through the center of the hemispherical LEED screen. The tungsten crystal is positioned at the center of the LEED optics mounted on a manipulator which allows independent rotation of the crystal about a vertical and a horizontal axis. LEED is performed in the usual manner. The LEED assembly is shielded from stray magnetic fields by use of a mu-metal can and from stray electric fields produced by nearby biased components by use of several electrostatic screens. The crystal manipulator, in conjunction with the movable LEED optics, enables any one of several LEED beams to be directed through a narrow horizontal slit cut in the phosphor screen and into the small, fixed entrance aperture of

Figure II-5: Schematic of the LEED chamber in a horizontal plane through the center of the chamber. The electron gun, screen, and grids are mounted from the chamber bottom and can be rotated about an axis perpendicular to the plane of the figure. The crystal is mounted from the chamber top on a manipulator which allows independent rotation of the crystal about two axes, one in the plane of the figure and the other normal to the figure plane.

a system of electron lenses. The area surrounding this entrance aperture is phosphor-coated to aid in centering the chosen beam on the aperture.

In the electron gun, electrons are emitted at a resistively heated hair-pin filament biased negatively to the desired energy of the electron beam (Figure II-6). With the normal 3A current through the filament, the voltage drop across the filament is 8.3 V. The electron energy is taken as the average of the voltages on each side of the filament. Energies measured using this procedure are in good agreement with values obtained using the retarding grids. Three anodes draw electrons from the filament, focus, and then direct the electron beam at the grounded tungsten crystal at the center of the hemispherical LEED optics. The beam diameter at the crystal is estimated at 1 mm on the basis of the LEED spot diameters on the phosphor screen.

The crystal is mounted on a UHV manipulator (O'Neill and Dunning, 1974). This manipulator allows both the angle between the axis of the analysis system and the normal to the crystal surface, and the azimuthal angle between a fixed axis in the plane of the crystal surface and the scattering plane, to be varied independently. The 100A current required to resistively heat the crystal are provided through two flexible, braided copper straps.

Figure II-6: Electronic schematic of the LEED optics.

The electron gun consists of the filament and three anodes V_1 , V_2 , and V_3 . The crystal is grounded and electron energy is controlled by biasing the filament negatively to the desired energy. The LEED pattern is displayed on the phosphor screen which is biased by V_c to about 2 kV. The hemispherical grids prevent inelastically-scattered electrons from reaching the phosphor screen.

Positioned immediately adjacent to the crystal is a 10 mil diameter tungsten filament. Electrons thermionically emitted from this filament are used to check operation of the Mott system (see Section II-A-6).

Elastically diffracted electrons leave the tungsten surface in discrete beams while those inelastically scattered leave in all directions. The four wire grids on the LEED optics are used to prevent the inelastics from reaching the phosphor screen (Figure II-6). The outermost grid is grounded to maintain a field-free region in which the electrons travel. The two middle grids are operated near filament potential to discriminate against the inelastically scattered electrons. During this experiment, electrons that have lost more than 2 eV are prevented from reaching the collector. The fourth grid is grounded to shield the discriminating grids from the collector. The phosphor-coated collector is biased several kilovolts positive to provide sufficient energy for the electrons to excite the phosphor. Voltages biasing the electron gun and LEED optics are provided through flexible cables insulated by 3/4" lengths of pyrex capillary tubing.

Initial polarization measurements were badly affected by bending of electron beams by magnetic and electric fields in the LEED region. The source of the magnetic field is the earth and the ion pumps, and the electric field is due to the biased elements in the LEED chamber.

The magnetic field was reduced from .400 gauss to .020 gauss by completely enclosing the LEED region in a 40 mil thick mu-metal cylinder with ends, placed inside the LEED chamber. Holes made as small as possible are cut in this can where required. Because the LEED ion pump is a major source of the magnetic field, the hole facing the adapter between the LEED chamber and the LEED ion pump is shielded by a 6"-long mu-metal extension to inhibit penetration of magnetic field into the beam region. After construction, the mu-metal can was annealed by the manufacturer. No deterioration of vacuum capability has been noted due to the presence of the mu-metal can.

To shield against electric fields, a fine wire grid was constructed and placed across the front of the hemispherical LEED optics so as to enclose the crystal and the beam region. Further shielding is provided by stainless-steel screens positioned in front of biased feedthroughs and around electron lens elements.

Shielding has completely alleviated field problems. Beams are only slightly bent even at energies below those for which data are reported.

4. Preparation and Cleaning of the Crystal

The tungsten crystals used in this experiment were grown at the Materials Science Center of Cornell University using zone refining in the melt. When obtained by the Rice LEED group, the tungsten blanks were rectangular

slices $\frac{1}{2}$ " x $\frac{1}{4}$ " x .020" oriented $\pm 0.5^\circ$ on the (001) face. Both sides of the crystals are polished by hand using instructions provided by C. Brucker of Cornell. Coarse polishing is done on a $\frac{1}{4}$ " thick pyrex glass plate using progressively finer grits of alumina (Al_2O_3) in a water slurry. Fine polishing is done on a revolving cloth-covered wheel using microgrits of diamond and alumina. During polishing, the crystal is glued to the flat stainless steel plug of a toroidal keeper. The grits used are:

1. #400 alumina
2. #600 alumina
3. #800 alumina
4. #1200 alumina
5. #3200 alumina
6. 1.0μ diamond paste on matching cloth
7. 0.05μ alumina on matching cloth

Polishing is continued until the crystal thickness is .005" and both sides have a mirror finish: no irregularities can be seen under the microscope. The final orientation of the crystal face is checked using a Laue back-reflection x-ray camera and has always shown a (001) face accurate to better than $\pm 0.5^\circ$.

The tungsten crystal is electron-beam welded to the two .08" diameter tungsten support rods of the manipulator. The diameter of these rods was increased when the initial rods of .04" diameter melted during a heat treatment. The tungsten crystal is then mounted in the LEED chamber where an atomically clean surface is obtained preparatory to the taking of data.

Surface cleanliness is monitored by use of Auger electron analysis (Chang, 1971; Bouwman, 1973; O'Neill, 1975). Auger analysis detects atoms by measuring the kinetic energy of electrons ejected in certain autoionization processes. A high-energy electron (2 keV in this experiment) incident on an atom can eject an inner-shell electron. The resultant inner-shell vacancy can be filled by an outer-shell electron with the energy released in this transition being used to eject a second electron from the ion. The energy of this second electron is characteristic of the autoionizing atom and can therefore be used for identification. Auger electrons from different atoms form small distinct peaks in the back-scattered electron spectrum (Figure I-1).

Auger electron analysis is extensively used to detect contaminants on a surface because the LEED optics are easily adapted to working in the Auger mode (Figure II-7). The LEED electron gun provides the 2 keV primary electron beam, and the two retarding grids of the hemispherical grid system are used to energy-analyze the secondary electrons from the surface. The collector is biased positively and the electron current passing through the retarding grids is recorded. With a voltage V on the retarding grids, the current $i(V)$ striking the collector is given by:

$$i(V) = e \int_V^{E_0} N(E) dE \quad (31)$$

Figure II-7: Schematic of the circuit used with the
LEED optics in the Auger analysis mode.

where E_0 is the primary electron energy and $N(E)$ is the back-scattered secondary electron spectrum. Equation (31) shows that it is difficult to detect a small Auger electron peak using this technique since the feature is superimposed on a large background of electrons with energies between V and E_0 .

To overcome this difficulty, the back-scattered spectrum is electronically differentiated by applying a small modulation voltage on the linear retarding sweep applied to the retarding grids. If the retarding voltage is changed from V_0 to $V_0 + \Delta V$ by the modulation voltage, the change in collector current can be found from a Taylor series:

$$i(V_0 + \Delta V) = i(V_0) + \left[\frac{di(V)}{dV} \right]_{V=V_0} \Delta V + \left[\frac{d^2 i(V)}{dV^2} \right]_{V=V_0} \frac{(\Delta V)^2}{2!} + \dots$$

Substituting the expression for $i(V)$ from (31):

$$i(V_0 + \Delta V) = i(V_0) + eN(V_0)\Delta V + \frac{e}{2} N'(V_0) \cdot (\Delta V)^2 + \dots$$

If the AC modulation voltage on the grids is given by

$$\Delta V = k \sin \omega t, \text{ then}$$

$$i(V_0 + \Delta V) = i(V_0) + eN(V_0)k \sin \omega t - \frac{e}{4} N'(V_0)k^2 \cos 2\omega t + \dots$$

The derivative $N'(V)$ of the secondary electron spectrum is therefore proportional to the coefficient of the second harmonic of the modulation frequency and can be obtained using a lock-in amplifier. In the present experiment, the

Auger signal is enhanced through the use of a narrow-band preamplifier between the collector and the phase-sensitive detector (Dunning, private communication, 1976).

Auger analysis of the tungsten crystal before cleaning showed carbon to be the major contaminant (O'Neill, 1975). The cleaning procedure, based on heating the crystal in an oxygen atmosphere, is designed to remove this carbon (Joyner et al., 1973; Hopkins et al., 1976). This cleaning cycle consists of several steps. First, the crystal is resistively heated to 1500 K in 10^{-7} Torr of research-grade oxygen. At this temperature, carbon in the crystal migrates relatively freely. A carbon atom reaching the surface can combine there with an oxygen atom to form carbon monoxide which is subsequently pumped. This step can only be continued for periods of about 6 minutes because the large currents (45A) required to heat the crystal also cause significant heating and outgassing of other components. During this step, care should be taken to prevent excessive heating of the crystal which could cause the formation of a tungsten oxide surface. During the second step of the cycle, the crystal cools while the oxygen is pumped from the system. About one-half hour is required for the pressure in the LEED chamber to fall below 10^{-9} Torr. In the third step, the crystal is "flashed" by heating to 2700 K for approximately 4 seconds to remove residual carbon monoxide. The crystal is then allowed to cool before the

whole cycle is repeated. Temperatures are measured using an optical pyrometer and an infrared telephotometer.

Between cycles, the surface condition is monitored using Auger analysis which, for the present crystal, showed a very slow decrease in carbon contamination. After hundreds of cycles, so that the total time of heating in oxygen was tens of hours, the Auger scan showed no carbon feature immediately after flashing the crystal (Figure II-8). Carbon, however, slowly returns to the surface. The source of this carbon is probably the Mott chamber, there being a straight line path through the electron lens apertures from the Mott chamber to the crystal.

To ensure a clean surface while data are taken, an oxygen treatment cycle is performed every two hours, and the crystal is flashed prior to every intensity or polarization measurements.

5. Electron Lens and Accelerating Column

Electrons enter the electron lens system and accelerating column by being directed through the narrow horizontal slit cut in the phosphor LEED screen and into the fixed 2mm entrance aperture of the first cylindrical lens element V_1 which is at 2900 V (Figure II-9). The next three elements, V_2 , V_3 , and V_4 , form an Einzel lens system. During this experiment, both V_2 and V_4 were biased to 3800 V while V_3 was at 960 V. Steering of the beam is also possible because, instead of being completely cylindrical, V_2 is actually

Figure II-8: Auger scan of the clean tungsten surface. Positions of the characteristic tungsten, carbon, and oxygen features are indicated. A modulation voltage of 6V peak-to-peak and frequency 400 Hz was used.

Figure II-9: The lens system.

divided into four quadrants. A steering potential of up to 250 V can be applied to the upper and lower quadrants for steering in the vertical plane. Similarly, the left and right quadrants can be used for horizontal steering. The exit angle from V_4 is defined by a 2mm aperture. V_4 is followed by a final cylindrical lens element V_5 , again consisting of four steering quadrants. V_5 is normally biased at 3700 V, 100 V less than V_4 to prevent low-energy secondaries emitted at the exit aperture of V_4 from passing into the Mott chamber.

V_5 is followed immediately by the accelerating column, which consists of ten equally-spaced electrodes in the shape of frustums of cones with vertices pointing toward the Mott chamber. A corona ring outside the vacuum wall is attached to every other electrode. The electrodes are biased through a cascade of resistors ($150\text{ M}\Omega \pm 10\%$) in equal steps from 10 kV to 100 kV. Although the column was rated at only 75 kV, it has worked well at 100 kV with mylar sheets between the corona rings to prevent sparking. The last accelerating electrode (at 100 kV) ends immediately in front of the first collimator leading into the Mott chamber.

6. The Mott Scattering System

The spin polarization of the electrons is measured in the Mott chamber (Figure II-10). Electrons entering the chamber first pass through a series of three collimating

Figure II-10: The Mott chamber.

apertures to produce a well-defined beam. This beam is then incident on a thin gold foil (approximately 1×10^{-5} cm thick). The beam current passing through the foil is monitored by a Faraday cup positioned at the end of the chamber. Two symmetrically placed silicon surface barrier detectors count electrons scattered through angles of 120° in the same plane as the LEED scattering plane (and hence perpendicular to the polarization direction expected from expression (28) for atomic scattering). The scattering angles are accurately defined by a series of three collimators in front of each detector. The detectors are mounted on an aluminum cylinder almost completely enclosing the scattering foil. The purpose of the cylinder is to prevent multiply scattered electrons from reaching the detectors, and aluminum was used because of its large forward-scattering cross-section.

The detectors produce pulses proportional to the energy of the electrons striking them. The pulses from the two detectors are analyzed in two separate channels, one for each detector (Figure II-11). The signals are amplified and pulse-height-analyzed to eliminate inelastically scattered electrons, and the pulses from elastically scattered electrons are counted on scalars. The polarization of the electron beam can be deduced from the small Mott asymmetry in the scattering. Curves showing the actual resolution of 100 keV elastic peaks with gold and

Figure II-11: Block diagram of the Mott analysis counting electronics. The detectors are positioned inside the Mott chamber while all other components are outside the vacuum system (O'Neill, 1970).

aluminum foils in the beam reveal that the peaks are nearly identical for both foils and for both channels (Figure II-12). Furthermore, the detector outputs have been stable over periods of years.

Whenever small asymmetries are being measured, care must be taken to eliminate the effect of instrumental asymmetries. These are determined by rotating an aluminum foil (approximately 1×10^{-4} cm thick) into the position initially occupied by the gold foil. The aluminum foil exhibits only a very small known Mott scattering asymmetry because of its low atomic number (Sherman, 1956). Both foils are positioned on a movable foil vane which can be controlled from outside the chamber. The true scattering asymmetry, and hence also the instrumental asymmetry and the electron-spin polarization, can be deduced from consecutive measurements of the scattering asymmetry at the gold and aluminum foils.

Care is taken to ensure that electrons strike only the 3/4" diameter foils and not the aluminum vane on which they are mounted. The incident beam diameter at the foils can be measured experimentally in two ways. First, one position on the foil vane is occupied by a phosphor disk which can be rotated into the beam path. The incident-beam light spot is a disk about 1/4" diameter positioned at the center of the phosphor. Secondly, the incident beam can be probed by sweeping the edge of the foil vane across the

Figure II-12: Curves showing the actual resolution of 100 keV elastic peaks for the gold and aluminum foils. Note that the peaks are nearly identical for both foils and for both channels.

beam. Such measurements indicate a diameter of about .3". These results are both in excellent agreement with the .31" diameter of the last collimation aperture less than two inches before the foil. To ensure that electrons scattered toward the detectors by the foils are not intercepted by the foil vane, the vane edges have been cut back. Finally, the foil vane is mounted on a precision rotary drive which enables foil positions to be reproducibly set to better than 0.1° .

Since the accelerating column, Mott scattering chamber, Mott D-I pump, and the associated electronics are all at high voltage (most at 100 kV), they are all completely enclosed in a grounded wire screen.

B. Measurement Technique

1. Polarization

The polarization of the electrons is measured using standard Mott scattering techniques (van Klinken, 1966). The measurement procedure is designed to satisfy two requirements. The first requirement is that all data be taken soon after flashing the crystal to ensure that the tungsten surface is clean while the second is that the instrumental asymmetry of the Mott analyzer be determined. A two-step procedure was adopted. First, the crystal is flashed to 2700K in vacuum. During the subsequent 3 minutes, the electrons scattered by the aluminum foil into the two detectors is recorded, with counting rates being

typically 50 counts/sec. The gold foil is then rotated into the beam; the crystal is flashed again; and for 3 minutes repeated measurements of the scattering asymmetry from gold are recorded. With the gold counting rate about ten times the aluminum counting rate, gold asymmetries are recorded approximately every 20 seconds to give the same number of gold counts as aluminum counts. The short data acquisition time for the gold foil enables any change in polarization with time after flashing to be noted. Although the polarization is in fact observed to be time-dependent, only in exceptional cases are changes observed over the 3 minutes used for data-taking. Since all measurements are made within 3 minutes after flashing the crystal, its temperature is between 600K and 500K.

The polarization of the electrons is then calculated. For each foil, expression (30) gives the Mott asymmetry. Including an instrumental asymmetry δ , the ratio of counts in the two detectors is given by

$$\frac{N_L}{N_R} = \left(\frac{1 + \mathcal{S} P_O}{1 - \mathcal{S} P_O} \right) \delta \quad (32)$$

where P_O is the spin polarization of the beam and $\mathcal{S}$ is the Sherman function for the foil used. Assuming δ remains constant, and letting the ratio of counts for the aluminum foil be denoted by A, while that for the gold foil is G, a quadratic equation is obtained which can be solved to give

$$P_O = - \frac{(\delta_G - \delta_A)(A+G) - \sqrt{(\delta_G - \delta_A)^2(A+G)^2 + 4\delta_G\delta_A(G-A)^2}}{2\delta_G\delta_A(G-A)}.$$

Only the negative square root gives the correct value for the electron polarization. The following values for the Sherman function were used (McCusker, 1967; Hodge, private communication, 1976):

$$\delta_G = - .25 \pm .02$$

$$\delta_A = - .015 \pm .05$$

These values of the Sherman function were determined experimentally and differ from the values calculated theoretically because of multiple scattering in the foils. δ is then calculated from

$$\delta = \frac{G(1 - \delta_G P_O)}{(1 + \delta_G P_O)}$$

δ is typically within 3% of unity.

Using the one aluminum asymmetry, the polarization is computed for each gold asymmetry. The polarization reported is the mean of the polarizations obtained from all gold asymmetries.

2. Intensity

Intensity-energy profiles of the diffracted beams are obtained by using a spot photometer to record the light emitted by the phosphor of the LEED optics. The absolute intensities of the beams are not measured in this experiment. As the electron energy is increased, the anode

voltage of the electron gun is continuously adjusted to maintain optimal focusing of the primary beam on the crystal. For the 01 and 11 beams, the spot photometer is tracked to follow the motion of the spots on the phosphor screen. For the 00 beam, intensities are determined by positioning the beam immediately adjacent to the aperture of the first electron lens element and recording the light-output from the phosphor surrounding this aperture. The angles reported have been corrected for this angular adjustment. The 00 spot is partially buried in the reflected light from the electron gun filament. Since the P1 phosphor used in this experiment has its emission peak at 525 nm, filters are used in front of the spot photometer to allow only light in the range 500-550 nm to be recorded. Because, as in polarization measurements, intensity data are taken within 3 minutes after flashing, crystal temperature is between 600K and 500K.

3. Sources of Error

Several possible sources of error, both statistical and systematic, are present in this experiment. The Mott scattering measurement is the major source of statistical error. Possible systematic errors result from instrumental asymmetries in the Mott analyzer, errors in the measurement of electron energy, and incorrect angular determinations. These different possible sources of error will be discussed in turn and estimates will be made of their magnitudes.

Counting statistics contribute a statistical error to Mott analysis, and an estimate of the standard deviation of the resulting polarization measurements is easily given (Bevington, 1969). Using the notation of Section II-B-1, a measure of the gold asymmetry $G = N_L/N_R$ has a standard deviation

$$\frac{\sigma_G^2}{G^2} = \frac{\sigma_{N_L}^2}{N_L^2} + \frac{\sigma_{N_R}^2}{N_R^2} .$$

But, for counting statistics, $\sigma_{N_L}^2 = N_L$ and $\sigma_{N_R}^2 = N_R$, and to a good approximation, $N_L \approx N_R = N$. Thus $\sigma_G^2/G^2 = 2/N$. With aluminum foil in the beam, approximately N counts are recorded in each channel also, and a similar expression applies: $\frac{\sigma_A^2}{A^2} = \frac{2}{N}$. Because the Sherman function for aluminum is so small, the instrumental asymmetry δ is given approximately by A , and $\sigma_\delta^2 \approx \sigma_A^2 = 2A^2/N$. From expression (32),

$$\frac{\sigma_P^2}{P^2} = \frac{\sigma_G^2 + \sigma_\delta^2}{(G-\delta)^2} + \frac{\sigma_G^2 + \sigma_\delta^2}{(G+\delta)^2} - \frac{2(\sigma_G^2 - \sigma_\delta^2)}{(G-\delta)(G+\delta)} .$$

For $P = 1$ and a typical $\delta = 1$, $G = 1.67$ and $A \approx 1$. The resultant standard deviation of the polarization is $\sigma_P^2 = 14/N$. Typically, $N \approx 8000$ implying $\sigma_P \approx 4\%$. Because a reported polarization is a mean of about 10 individual measurements, the standard deviation of the mean is about 1.5%. It should be noted that σ_P^2 varies inversely with N . Therefore, at intensity minima, where N may be only 2000, standard devia-

tions of the mean polarizations can range up to 3%. These estimates of statistical error in polarization measurements are in good agreement with experiment in that polarizations are regularly repeatable to within these limits.

Possible systematic errors in Mott polarization analysis, which generally take the form of instrumental asymmetries, are discussed by McCusker (1967) and Kessler (1976). As previously stated, the two-foil technique used in this experiment determines instrumental asymmetries directly. Several additional checks of the polarization measurement are possible. First, Mott analysis can be checked by measuring the polarization of electrons scattered from a crystal that has not been cleaned over a period of days. No polarization is expected from a thick adsorbate layer consisting primarily of hydrogen, carbon, and oxygen. Theoretical calculations (Fink and Yates, 1970; Fink and Ingram, 1972) show that, because of their low atomic numbers, polarizations of much less than 1% are expected for atomic scattering from these elements. Furthermore, because of the random ordering of the adsorbed atoms, it is not possible for a small polarization to be enhanced by surface state resonances. Consequently, no significant polarization is expected from such contaminants, and, in fact, polarizations were always measured to be within 3% of zero. A similar test makes use of the tungsten filament positioned immediately adjacent to the crystal in the LEED chamber. Electrons thermionically emitted from this

filament, and obviously unpolarized, are directed into the Mott chamber. The polarization of these electrons was always measured to be within a few percent of zero.

A distinct possibility for systematic errors in the reported polarizations lies in the uncertainties in the values of the Sherman functions of gold and aluminum used in the polarization calculations. Because the Sherman function for aluminum is so small, its relatively large uncertainty affects polarization measurements minimally. On the other hand, an actual Sherman function for gold which differs from that used in this experiment by .02 causes all polarizations to be changed by about 5% of their stated values. Such changes, however, affect only the polarization magnitudes and not the relative polarizations.

Uncertainties exist as to the energy of the electrons incident on the crystal. This uncertainty comes in two forms: the average energy of the beam is not precisely known and the electron energies have some variation about this average value. As discussed in Section II-A-3, electrons are emitted by a resistively-heated hairpin filament across which exists a voltage drop of 8.3V. The assumption is made that electrons are emitted from the midpoint of the filament, and an energy reported here is the average of the voltages at each end of the filament. Furthermore, because the filament temperature is about 2500K, the thermal spread of the emitted electrons is

$$\Delta E = 2kT \approx 0.5 \text{ eV} .$$

A simple experimental test, consisting of measuring the current into the Faraday cup at the back of the Mott chamber as a function of the retarding voltage on the LEED optics grids, was used to estimate the parameters of the electron beam. The results for a beam with an electron energy of 63.5 eV, as determined from filament voltages, is shown in Figure II-13. This figure shows an average electron energy of about 64.4 eV with the elastic peak having a full-width at half-maximum of about 1 eV. Because contact potentials can easily have effects of about 1 eV, the agreement between the two methods of determining electron energy parameters is good. It is therefore estimated that electron energies reported in this work are accurate to ~ 1 eV and, furthermore, that the energy spread of the electron beam is of the order of 1 eV.

Angles of incidence reported are determined by measuring the angle between the axis of the electron gun and the axis of the Mott analysis system. Because of uncertainties as to the precise directions of these axes, a systematic offset of $\pm \frac{1}{2}^\circ$ in all angles is possible. Repeated measurements of angle settings, however, show them to be reproducible to about $.2^\circ$.

Figure II-13: Mott chamber Faraday cup current and its derivative as a function of retarding voltage on LEED optics grids. The derivative curve shows the elastic peak centered on 64.4 eV with a FWHM of about 1 eV.

III. RESULTS AND DISCUSSION

In order to investigate the usefulness of electron-spin polarization measurements in LEED, the experimental program was designed to attain several goals. The first goal was the collection of many measurements of intensity and polarization as functions of electron energy for LEED beams from a clean tungsten (001) surface. This goal has been accomplished with measurements for the 00 beam at a large number of angles of incidence and for both the 10 and the 11 beams at normal incidence. The second goal was to use these experimental data to investigate the extent to which polarization measurements complement intensity studies in more accurately testing LEED model calculations and in determining the structure of the crystal surface. A full realization of this second goal requires close comparisons between theoretical calculations with a variety of surface parameters and experimental data. However, at present only limited theoretical results exist because of the great calculational complexity of dynamical LEED models incorporating spin. For this reason, only preliminary conclusions exist concerning the usefulness of polarization measurements. The third goal was to investigate the relative sensitivities of intensity and polarization to adsorbates on the surface. Only a few results have been obtained toward this goal, and research is continuing on this subject.

A. The Clean Tungsten (001) Surface

1. The 00 Beam

Experimental data of both spin polarization and intensity of the 00 beam as functions of electron energy for angles of incidence θ (i.e., the angle between the axis of the electron gun and the normal to the crystal surface) from 10° through 18° in 1° steps are shown in Figure III-1. The primary electron beam is incident along the [10] direction in the tungsten (001) surface. The angular correction required when the beam is positioned adjacent to the aperture in the first lens element for intensity measurements resulted in the intensity curve for $\theta = 9^\circ$ and the polarization curve for $\theta = 19^\circ$. Intensity profiles have been corrected for changes in incident beam current; polarization measurements do not require such a correction. Finally, since all measurements are made within 3 minutes after the crystal is flashed to 2700K, its temperature is between 500K and 600K.

It is obvious from this figure that both intensity and polarization are sensitive to changes in electron energy and angle of incidence. For example, the intensity peak at $E \approx 70$ eV at $\theta = 9^\circ$ gradually diminishes in size as θ increases and disappears altogether at $\theta = 17^\circ$. Gradual changes with θ in the structure of the large polarization feature between $E \approx 70$ eV and 80 eV are evident.

Figure III-1: Measured intensity-energy (I-V)
and polarization-energy (P-V)
profiles for the 00 beam from
W(001) for angles of incidence
from $\theta = 10^\circ$ through $\theta = 18^\circ$.

The sensitivity of polarization to both variations in electron energy and changes in angle of incidence can be seen more clearly in Figure III-2 for $\theta = 17^\circ$, 18° , and 19° . The sensitivity to electron energy is shown by the sharp feature at $E \approx 26$ eV in the curve for $\theta = 17^\circ$ where the polarization drops from +45% to -35% over an energy range of only 2 eV. A similar change occurs at about the same energy at $\theta = 19^\circ$. The sensitivity of polarization to angle of incidence is shown by the dramatic change in polarization at $E \approx 75$ eV. The large negative polarization peak (-80%) at $\theta = 17^\circ$ becomes a large positive peak (+55%) at $\theta = 19^\circ$.

In Figure III-3, the sensitivity of polarization and intensity to electron energy and angle of incidence can be compared for $\theta = 11^\circ$, 12° , and 13° . Polarization changes most dramatically with energy at $E \approx 75$ eV for $\theta = 13^\circ$ where an energy change of 2 eV results in a polarization change from +15% to -75%. Several significant changes in polarization can be seen for this 2° change in angle of incidence. While the polarization peak at $E \approx 55$ eV drops from +45% to zero, the feature at $E \approx 75$ eV increases in size by about a factor of 2. These large changes in polarization are not accompanied by any obvious corresponding changes in intensity. For example, the intensity minimum at $E \approx 55$ eV remains unchanged although variations occur in the relative magnitudes of the peaks bordering this minimum. It is interesting that the main

Figure III-2: P-V profiles for the 00 beam from
W(001) for $\theta = 17^\circ$, 18° , and 19° .

Figure III-3: I-V and P-V profiles for the 00
beam from W(001) for $\theta = 11^\circ$,
 12° , and 13° .

changes in the intensity profiles occur above 80 eV. For these energies, the number of intensity features increases with the angle of incidence. It is in this region that polarizations are least interesting.

A direct comparison of intensity and polarization is made in Figure III-4 for the 00 beam at $\theta = 11^\circ$. As discussed in Section I-C-2 for atomic scattering, large polarizations are observed only at intensity minima. Figure III-4 shows that a rough correlation of this kind can also be made in LEED. At $E = 55$ eV, the polarization exhibits a large positive peak directly on an intensity minimum. Similarly, the intensity minimum at $E = 80$ eV has a large negative polarization peak associated with it. A slightly different, but related correlation, exists between intensity maxima and polarizations near zero. Examples in this figure occur at $E = 44$ eV, $E = 68$ eV, and $E = 116$ eV. However, several obvious exceptions to these correlations exist. The polarization peak at $E = 107$ eV is not situated at an intensity minimum, and the intensity peak at $E = 85$ eV has a rather large negative polarization associated with it. Detailed study of the correlation of polarization with intensity shows similar effects at all angles of incidence. The very largest polarization features are usually situated on intensity minima, and the largest intensity features are usually at energies where polarization is near zero. Exceptions, however, occur and polarizations can have large values at energies and angles where intensities are not small. Crystal structure has been deduced

Figure III-4: Comparison of the magnitudes of
intensity and polarization for
the 00 beam from W(001) at $\theta = 11^\circ$.

mainly from the positions of intensity maxima with little importance attached to intensity minima. Large polarizations, however, often occur at intensity minima. The whole energy scale is thus used more effectively if both intensity and polarization measurements are considered in surface analyses.

Since intensity profiles are sensitive to the presence of contaminants on the crystal surface, it is of interest to compare the intensity scans for the 00 beam of this experiment with those reported in other studies of the tungsten (001) surface. Such a comparison is shown in Figure III-5 for two angles of incidence. In general, the agreement is good. Discrepancies, however, exist among all three I-V profiles at each angle. For $\theta = 14^\circ$, two real differences seem to exist. At $E = 60$ eV, Wei (1970) has a peak which is seen neither in this experiment nor in that of Debe et al. (1977). At $E = 105$ eV, Debe et al. observe a small peak which is not present in the I-V curve of this experiment. The agreement at $\theta = 18^\circ$ is better. Although exact peak positions and magnitudes differ, every feature is present in all three profiles. Similar comparisons (not reproduced here) can be made between our results and those published by other workers for all angles of incidence except $\theta = 13^\circ$ and $\theta = 17^\circ$. The agreement is consistently good and is taken as further proof of the cleanliness of the surface used in this experiment.

Figure III-5: Comparison of the I-V profiles for the 00 beam from W(001) at two different angles of incidence. The curves are from this experiment; from Debe et al. (1977); and from Wei (1970).

2. The 00 Beam - Azimuthal Dependence

The dependence of intensity and polarization on the azimuthal angle of incidence φ (i.e., the angle between a fixed axis in the plane of the crystal surface and the scattering plane) is shown in Figure III-6 for $\theta = 13^\circ$. Polarizations are measured by using the manipulator to turn the crystal about the φ axis. As explained in Section I-D-3, the polarization vector need not be perpendicular to the scattering plane for arbitrary azimuthal angle. The results shown in Figure III-6 are therefore the components of the total polarization along the normal to the scattering plane. As pointed out in Section I-D-3, for purely kinematic scattering both intensity and polarization are independent of the azimuthal angle. In agreement with the predictions of Jennings from a dynamical model calculation, the intensities and polarizations in Figure III-6 are very sensitive to changes in φ . The intensity curves show large changes as the azimuthal angle is increased with only the intensity peak at $E \approx 43$ eV remaining constant. Changes in polarization are even greater with no resemblance at all between the P-V profiles for $\varphi = 0^\circ$ and $\varphi = 45^\circ$.

3. The 10 Beam

The 10 beam is one of a set of four beams--10, 01, $\bar{1}0$, $0\bar{1}$ --that, at normal incidence, exhibit the same intensity and the same polarization with respect to the appropriate scattering plane (Figure I-3). The normal

Figure III-6: Azimuthal dependence of intensity and polarization for the 00 beam from W(001) at $\theta = 13^\circ$. The azimuthal angle φ is measured between a fixed axis in the plane of the crystal surface and the scattering plane. The polarization reported in this figure is the component of the total polarization perpendicular to the scattering plane.

00 $\theta = 13^\circ$

ENERGY, eV

incidence condition is determined by directing the 00 beam back into the LEED electron gun and by checking that the LEED pattern is symmetrical about the electron gun. While polarization measurements are made on the 10 beam, intensity measurements are most easily obtained for the $\bar{1}0$ beam because of the slit cut in the phosphor screen.

The intensity and polarization profiles for the 10 beams at normal incidence are presented in Figure III-7. The range of energies accessible for polarization study is limited by the geometry of the apparatus. Furthermore, the scatter evident in the measured polarizations results primarily from the requirement that both the crystal and the LEED optics assembly be independently repositioned for each energy. Nonetheless, polarization features are clearly discernible.

The correlation between intensity minima and polarization maxima so prevalent for the 00 beam is not as clear for the 10 beam. Although the largest polarizations seem to occur at intensity minima, definite statements are difficult to make on the basis of these data.

At least three other I-V profiles have been reported for the 10 beam. A comparison is made in Figure III-8 between the profile obtained in this work and these other three. Agreement is excellent.

4. The 11 Beam

Many of the comments made about the 10 beam apply equally to the 11 beam. Again, by symmetry, it is one of

Figure III-7: The I-V and P-V profiles for the 10
beam at normal incidence from W(001)
obtained in this experiment.

Figure III-8: Comparison of the I-V profiles for the 10 beam from W(001) at normal incidence. The curves are from this experiment; from Debe et al. (1977); from Lee et al. (1977); and from Wei (1970). Note that an energy shift of -2 eV has been applied to the last two profiles.

10 Beam, Normal Incidence

four beams-- 11 , $\bar{1}1$, $1\bar{1}$, $1\bar{1}$ --which, at normal incidence, have identical intensities and polarizations. The 11 beam is directed into the Mott chamber by a 45° rotation of the crystal about the φ -axis, while normal incidence is determined as for the 10 beam. Intensity measurements are made on the $1\bar{1}$ beam.

The intensity and polarization profiles for the 11 beams at normal incidence are presented in Figure III-9. Again, the scatter in the measured polarizations is a result of repositioning of the crystal and LEED optics at each energy. Very little correlation is evident between polarization maxima and intensity minima. In fact, the polarization peak at $E \approx 70$ eV is centered almost directly on an intensity maximum.

Figure III-10 shows a comparison between the I-V profiles obtained for the 11 beam in four different experiments. Although agreement is not as good as in Figure III-8, peaks match well though fine structure varies widely.

5. Comparison between Experiment and Theory

Dynamical LEED model calculations incorporating spin have been developed independently by Feder and by Jennings. As discussed in Section I-D-2, a recent comparison of their model calculations show excellent agreement. A comparison can also be made between intensity and polarization profiles predicted by theory and those measured by this experiment. Figure III-11 shows results of Feder (private communication, 1977) for the 00 beam with $\theta = 11^\circ$ for two

Figure III-9: The I-V and P-V profiles for the 11
beam at normal incidence from W(001)
obtained in this experiment.

Figure III-10: Comparison of the I-V profiles for the 11 beam from W(001) at normal incidence. The four curves are from the present experiment; from Debe et al. (1977); from Lee et al. (1977); and from Wei (1970). An energy shift of -3 eV has been applied to the last two profiles.

Figure III-11: Comparison of theoretical (Feder, private communication, 1977) and experimental I-V and P-V profiles for the 00 beam from W(001) for $\theta = 11^\circ$. ● measured polarizations; — theoretical results, 10% contraction of the top interlayer spacing; -- theoretical results, no surface contraction. An energy shift of -5 eV has been applied to all theoretical profiles.

00 Beam, $\theta = 11^\circ$

different spacings of the top interlayer, one being the bulk interlayer spacing and the other a 10% contraction. A non-reflecting surface barrier is used in these calculations. Superimposed are the experimentally measured profiles. It is immediately obvious that virtually no agreement exists between the experimental I-V curve and either of the theoretical curves. Because Ignatiev (private communication, 1976) has independently obtained an experimental I-V profile very similar to that of this experiment, it is believed that the fault for this lack of agreement between theory and experiment lies with the theoretical calculations. On the other hand, some agreement exists for polarizations. Both theoretical polarization calculations show the same feature seen experimentally between $E \approx 65$ eV and $E \approx 115$ eV. Although no definite conclusions can be drawn from this energy region, the experimental curve seems to lie closer to the theoretical profile for a surface contracted by 10% than to that for an uncontracted surface. No agreement between theory and experiment, however, exists at either lower or higher energies. This lack of agreement is not surprising considering the poor comparison of intensity profiles.

A second comparison between theory and experiment is shown in Figure III-12 for the 10 beam at normal incidence (Feðer, private communication, 1977). The agreement between theoretical and measured intensity profiles is significantly

Figure III-12: Comparison of theoretical (Feder, private communication, 1977) and experimental I-V and P-V profiles for the 10 beam from W(001) at normal incidence. ● measured polarizations; — theoretical results, 10% contraction of the top interlayer spacing; -- theoretical results, no surface contraction. An energy shift of -5 eV has been applied to all theoretical profiles.

IO Beam, Normal Incidence

better than for the 00 beam in the previous figure. Although the double peak at $E \approx 100$ eV calculated theoretically has never been observed experimentally (Figure III-8), there is good agreement between experiment and theory for a surface 10% contracted. Notice, however, that the theoretical intensity results are very similar: except for a peak at $E \approx 135$ eV in the 10% contraction curve, peak structure is the same in both profiles except displaced about 6 eV along the energy axis.

The polarizations predicted by theory are rather dramatic with sharp, large features. Furthermore, in contrast to the intensity results, the calculated polarizations for the two values of top interlayer spacing are completely different. It is on the basis of calculations such as this that Feder concludes that polarization is more sensitive than intensity to the top interlayer spacing (Feder, 1976). A comparison of the experimental polarization profile with the theoretical ones shows better agreement for a 10% contraction. The agreement, however, is obviously not perfect.

These comparisons of the present intensity and polarization data with the results of theoretical calculations show reasonable agreement with respect to gross features. This agreement between experiment and theory is encouraging, especially considering that the theoretical calculations were made with virtually no experimental polarization measurements to guide the choice of surface parameters.

6. Estimate of the Top Interlayer Spacing

A comparison of the I-V profiles obtained in this experiment with those calculated theoretically for different top interlayer spacings allows an estimate to be made of this spacing. Such comparisons are most commonly made visually although a variety of numerical tests have been developed. A clear explanation and critique of visual evaluation and of several numerical tests is given by Zanazzi and Jona (1977). To illustrate the simplest of these numerical tests but one often utilized, the intensity results of this experiment will be used to estimate the top interlayer spacing by comparison to theoretical intensity curves calculated by other workers (VanHove and Tong, 1976; Lee et al., 1977; Debe et al., 1977).

The method used in this analysis, as described by Debe et al. (1977), is based solely on a comparison of intensity peak positions with no regard to relative intensities. The justification for ignoring both peak shapes and relative sizes in the analysis is that these are very sensitive to parameters such as electron absorption and temperature whereas peak positions, on the other hand, are relatively insensitive to these parameters. Since the theoretical calculations have not optimized these parameters, comparisons more detailed than peak positions are not warranted.

The approach used is to first calculate intensity-energy profiles for various values of the top interlayer

spacing, as shown for the 00 beam at $\theta = 9^\circ$ in Figure III-13 (Debe et al., 1977). The experimental intensity curve shown at the bottom of the figure is then compared to each theoretical curve in turn. If a theoretical peak can be associated with an experimental peak, the energy deviation $\Delta E_i = E_i^{\text{exp}} - E_i^{\text{theor}}$ is recorded, where E_i^{exp} is the energy of the i^{th} experimental peak and E_i^{theor} is the energy of the corresponding theoretical peak. For a peak present in theory but not in experiment, or vice versa, a penalty value of $|\Delta E_i|$ is assessed depending on the prominence of the feature. For each of the calculated spectra in Figure III-13, the mean of the absolute deviations is found:

$$\overline{|\Delta E|} = \frac{1}{N} \sum_i |\Delta E_i| \quad (33)$$

where N is the numbers of features considered. This process is then repeated for all beams under consideration. A mean total deviation for each interlayer spacing $\langle \overline{|\Delta E|} \rangle$ is then calculated by averaging the results (33) for a particular interlayer spacing over all beams under consideration. The top interlayer spacing is taken as the value that minimizes $\langle \overline{|\Delta E|} \rangle$.

Using theoretical calculations for various interlayer spacings by VanHove and Tong, 1976; Lee et al., 1977; and Debe et al., 1977, for the 00 beam at $\theta = 9^\circ$, 14° , and 18° and the 10 and 11 beams at normal incidence, this method

Figure III-13: Theoretical I-V calculations with various interlayer spacings for the 00 beam at $\theta = 9^\circ$ (Debe et al., 1977). The experimentally measured I-V profile is also shown.

was applied for the five corresponding I-V curves from this experiment. The result is an interlayer spacing of about $1.50\text{\AA}$ corresponding to a 5% contraction of the surface. Values previously reported are 11% (Lee et al., 1977), 6% (VanHove and Tong, 1976), and 4.4% (Debe et al., 1977). The present result tends to support the lower values of interlayer spacing. A similar analysis using spin polarization with its increased sensitivity may ultimately determine this interlayer spacing unambiguously.

B. Effects of Adsorbates on the Tungsten (001) Surface

1. Changes in I-V Profiles with Time

Both intensity and polarization data have been observed to undergo time-dependent changes. It is because of these changes that all data are taken within 3 minutes after the crystal is flashed. A study was made of time-dependent changes in intensity profiles for the 00 beam at several angles of incidence. A typical result at an angle of incidence of 11° is shown in Figure III-14. Significant changes are observed with time after flashing, the most prominent being the growth of a peak at $E = 51\text{ eV}$ and the rapid decay of the peak at $E = 70\text{ eV}$.

Several possible explanations exist for these changes. One possibility is reconstruction of the clean tungsten surface as the crystal cools. In fact, very recent work (Felter et al., 1977; Debe and King, 1977) has concluded

Figure III-14: Repeated I-V curves of the 00 beam from W(001) for $\theta = 11^\circ$. The time after flashing the crystal for each profile is recorded.

that, at a temperature between 300K and 400K, the tungsten (001) surface undergoes a phase transition from the 1×1 structure observed at high temperature to a $c(2 \times 2)$ structure. Two facts, however, argue against this being the explanation for the changes observed in this experiment. First, at least ten minutes are required after flashing for the crystal to cool to 400K while Figure III-14 shows large changes in intensity occurring within these ten minutes. Second, Debe and King (1977) observe no changes in the I-V spectrum of the 00 beam accompanying surface reconstruction. A second possible explanation for time-dependent intensity changes is a variation in some other surface parameter such as, for example, the top interlayer spacing. However, within 1 minute after flashing to 2700K, the crystal cools to below 650K and from then on, continues cooling very slowly. Therefore, although temperature effects may account for some very early changes in I-V profiles, they cannot explain the continuing changes over long time periods. The final possible explanation for the intensity changes is contamination of the crystal surface since the presence of adsorbates has been shown to result in significant changes in I-V curves (Estrup and Anderson, 1967; Pendry, 1974).

Two techniques were used to test for the presence of these adsorbates. The first was Auger analysis while the second attempted to reproduce the observed changes in I-V

profiles by exposing the crystal to various gases. The Auger scan shows a gradual increase in carbon and oxygen on the crystal surface. Such a build-up is expected on the basis of the partial-pressure analysis of the gas in the LEED chamber (Figure II-3). A second method for analysis of adsorbates is to use the gas handling system described in Section II-A-2 to admit known quantities of research-grade gases to the LEED chamber and to investigate the effects of these adsorbates on the I-V profiles. The procedure used consisted of flashing the crystal to 2700K, waiting 10 seconds to let it cool to about 1000K, and then admitting a gas for 45 seconds at different pressures. The UHV leak valve is then closed, the gas is pumped out for 5 seconds, and the I-V profile is started. The resulting I-V curves are presented in Figures III-15, 16, 17 for oxygen, carbon monoxide, and hydrogen, respectively. Assuming a sticking coefficient of unity, the exposures used correspond to the formation of about .1, .2, and .4 monolayer of adsorbate on the surface.

Figures III-15, 16, 17 show that different gases have characteristic effects on the I-V profiles. For example, the effect of hydrogen is minimal other than causing the shoulder at $E \approx 62$ eV to become more prominent. The effects of oxygen are significantly greater. In addition to causing the shoulder at $E \approx 62$ eV to become the dominant peak, a deep minimum is formed at $E \approx 68$ eV.

Figures III-15, 16, 17: I-V profiles of the 00 beam from W(001) for $\theta = 11^\circ$ with various exposures of different gases. Curve (a) in each case is the clean crystal; curve (b) is an exposure corresponding to a coverage of .1 monolayer; curve (c) corresponds to a coverage of .2 monolayer; curve (d) corresponds to a coverage of .4 monolayer.

Figure III-15: Oxygen

Figure III-16: Carbon monoxide

Figure III-17: Hydrogen

00 Beam, $\theta = 11^\circ$
OXYGEN

OO Beam, $\theta = 11^\circ$
CARBON MONOXIDE

00 Beam, $\theta = 11^\circ$

HYDROGEN

The effects of carbon monoxide are somewhat similar to those of oxygen except that the minimum at $E \approx 68$ eV is not nearly as deep. A comparison of these profiles with those shown in Figure III-14 indicates that the major adsorbate is possibly carbon monoxide since it seems to produce changes in intensity most similar to those shown in the time-dependent series.

The next investigation attempted to determine the source of this carbon monoxide. One possibility is diffusion of carbon from the bulk of the crystal. This is in fact the source of the carbon removed by the original oxygen treatments described in Section II-A-4. The amount of carbon in the bulk, however, is not infinite and tens of hours of oxygen treatments should have depleted this source significantly. Also, crystal temperatures below 1000K preclude significant diffusion of the remaining carbon. The second possible source of carbon monoxide is the background gas. The pressure in the LEED chamber, however, is too low to explain the rate of carbon build-up observed by Auger analysis. For these reasons, it is suspected that the major source of contaminant is the Mott chamber. The Mott chamber, at a pressure of about 10^{-8} Torr because it cannot be baked, limits the base pressure in the LEED chamber because of conductance through the electron lens apertures. Furthermore, these 2 mm diameter apertures direct any impurities from the Mott system exactly at the

crystal surface. The only way to test whether the Mott system is indeed the source of the contaminants is to close off the connection between the two chambers. This was not feasible at this stage of the experiment.

2. Effects of Adsorbates on Polarization

Because of the polarization data-taking technique in which a series of about ten gold asymmetries are measured over a period of three minutes, changes in polarization within time periods of 1 minute can be detected. For a vast majority ($\sim 90\%$) of the polarization measurements, no variation in polarization is detected during this 3 minute period. Over longer periods, the polarization is observed to degrade slowly with time after flashing. A typical example of this degradation is shown in Figure III-18 for the 00 beam at $\theta = 11^\circ$ and at an energy of 79.5 eV. Also shown in this figure is the electron current passing through the gold scattering foil and into the Faraday cup at the back of the Mott chamber. The slow drop of polarization toward zero is attributed to adsorption on the crystal surface of layers of contaminants with low atomic number.

At some energies, however, polarizations show a much more marked change with time. An example is shown in Figure III-19 for $E = 54.5$ eV where, $3\frac{1}{2}$ minutes after the crystal is flashed, the polarization has dropped to less than half its original value. At the energy of 54.5 eV, the I-V profile (Figure III-14) shows an intensity minimum.

Figure III-18: Polarization as a function of time after flashing the crystal for the 00 beam from W(001) at $\theta = 11^\circ$ and electron energy 79.5 eV. Also shown is the electron current passing through the gold foil and measured by the Faraday cup in the Mott chamber.

Figure III-19: Polarization as a function of time after flashing the crystal for the 00 beam from W(001) at $\theta = 11^\circ$ and electron energy 54.5 eV. Also shown is the electron current passing through the gold foil and measured by the Faraday cup in the Mott chamber.

Furthermore, over the same period of $3\frac{1}{2}$ minutes, not much change is apparent in the region of this minimum although a small feature is appearing at $E \approx 52$ eV. The change in the I-V curve does not seem to be able to account for the large observed polarization change. Appearances are deceiving, however, as is shown in Figure III-19 by the electron current into the Faraday cup. Although the I-V profile does not appear to have changed much at $E = 54.5$ eV, the intensity has in fact increased by a factor of about four. Thus polarizations can be used effectively to investigate energy regions, primarily intensity minima, where no changes in intensity are apparent from I-V curves although relative intensity changes are in fact quite large. This is a further example of the way in which intensity and polarization measurements complement each other, small changes in I-V profiles being more easily detected and investigated through polarization studies rather than intensity measurements alone.

This preliminary study of the effects of adsorbates on polarization is being continued in greater depth.

IV. CONCLUSIONS AND RECOMMENDATIONS

Improvements made in the experimental apparatus have enabled the completion of the first systematic measurements in LEED of both intensity and electron-spin polarization. Data were obtained for the 00 beam at a large number of incidence angles and for the 10 and 11 beams at normal incidence.

For the 00 beam at 11° angle of incidence and for the 10 beam at normal incidence, comparisons of the present intensity and polarization data with the results of recent theoretical calculations show reasonable agreement. This agreement between experiment and theory is encouraging, especially considering that the theoretical calculations were made with virtually no experimental polarization measurements to guide the choice of surface parameters.

Preliminary studies of intensity and polarization indicate both to be sensitive to the presence of adsorbates on the tungsten (001) surface. In certain energy regions, primarily at intensity minima, spin polarizations show much larger changes than intensities upon even small exposures of adsorbates.

Experimental results show that the largest polarization features occur at energies where intensities are small. This observation is probably the reason for the sensitivity of polarization to surface structure. The polarization is

determined by small differences in the scattering of spin "up" and spin "down" electrons. Hence, any process such as reflection at a surface potential barrier that causes changes in the relative numbers of spin "up" and "down" electrons in a LEED beam affects the polarization. Whereas an intensity calculation requires the sum of the spin "up" and spin "down" currents, an accurate polarization calculation at an intensity minimum requires the difference between these two small quantities. Because crystal structure has previously been deduced mainly from the positions of intensity maxima, polarization, which is especially sensitive at intensity minima, should complement intensity measurements in more accurately testing LEED model calculations and in determining the structure of the crystal surface. Such a use of spin polarization measurements will require a significant increase in the number of theoretical calculations for a large assortment of surface parameters.

Because the experiment is continuing, recommendations can be divided into categories. The first category concerns changes to improve the experimental apparatus while the second provides some suggestions for future experiments. The experimental apparatus can be improved in several ways. First, the addition of a sputter-ion gun would possibly enable faster cleaning of the crystal surface. Second, the mounting of the LEED optics assembly on a precision rotary drive would allow angles of incidence to be measured much more quickly. Furthermore, such a drive would enable the

study of angles of incidence above 19° , the present limit because the electron-gun axis must be determined through the viewport. Finally, the addition of a titanium-sublimation pump to the system would increase pumping speed and enable oxygen to be pumped from the system much more quickly after crystal-cleaning treatments.

Some recommendations for future experiments are also possible. First, a more detailed study of polarization in the presence of adsorbates could provide information about the relative sensitivities of intensity and polarization to the condition of the surface. Investigation of the polarization of half-order beams due to adsorbates could be a direct test of the effects on polarization of the adsorbates. Finally, a study of spin polarization from magnetic materials may be used to investigate exchange effects in scattering.

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