INFORMATION TO USERS

While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. For example:

- Manuscript pages may have indistinct print. In such cases, the best available copy has been filmed.
- Manuscripts may not always be complete. In such cases, a note will indicate that it is not possible to obtain missing pages.
- Copyrighted material may have been removed from the manuscript. In such cases, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or as a 17"x 23" black and white photographic print.

Most photographs reproduce acceptably on positive microfilm or microfiche but lack the clarity on xerographic copies made from the microfilm. For an additional charge, 35mm slides of 6"x 9" black and white photographic prints are available for any photographs or illustrations that cannot be reproduced satisfactorily by xerography.

Order Number 8718723

**Spin-polarized metastable atom de-excitation spectroscopy:
A new probe of the dynamics of metastable atom-surface
interactions**

Hart, Mark Whitney, Ph.D.

Rice University, 1987

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy.
Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____. Text follows.
14. Curling and wrinkled pages ✓
15. Dissertation contains pages with print at a slant, filmed as received ✓
16. Other _____

University
Microfilms
International

RICE UNIVERSITY

SPIN-POLARIZED METASTABLE ATOM DE-EXCITATION SPECTROSCOPY:
A NEW PROBE OF THE DYNAMICS
OF METASTABLE ATOM - SURFACE INTERACTIONS

by

MARK WHITNEY HART

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

DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE:

F. B. Dunning
Professor of Physics and of Space Physics
and Astronomy, Chairman

G. K. Walters
Professor of Physics and of Space Physics
and Astronomy

G. M. Pharr
Associate Professor of Mechanical
Engineering and Materials Science

Houston, Texas

May 1987

Abstract

Spin-Polarized Metastable Atom De-excitation Spectroscopy: A New Probe of the Dynamics of Metastable Atom-Surface Interactions

by

Mark Whitney Hart

Metastable Atom De-excitation Spectroscopy (MDS) provides a powerful technique with which to investigate surface electronic structure with unparalleled surface specificity. In this technique a thermal energy beam of noble-gas metastable atoms is directed at the surface under study and the kinetic energy distribution of ejected electrons that result from metastable atom de-excitation is measured. Although the measured distribution contains information about the electronic structure of the outermost surface layer, its detailed analysis requires knowledge of the dynamics of the metastable atom-surface interaction. In the present work, these dynamics have been investigated directly, for the first time, by use of spin-labeling techniques. The electron spins on the incident metastable atoms are polarized and the spin-polarization of the ejected electrons is measured with a Mott polarimeter. Results are reported for Cu(100) and Ni(111) surfaces under a variety of surface conditions. The data indicate that metastable atom-surface interactions may be more complex than is generally assumed and thus suggest that assumptions inherent in earlier analyses of MDS spectra merit additional investigation. The present work further demonstrates the power of spin-resolved measurements in the study of particle-surface interactions and in surface spectroscopies in general.

Acknowledgments

It is my pleasure to thank those who have contributed significantly to the work described in this thesis. First, I would like to thank my advisor, Professor F. Barry Dunning for his invaluable guidance, his cheerful support, and his timely advice. His dedicated commitment to research and education is truly inspiring and is deeply appreciated. I would also like to thank Professor G. King Walters for the confidence he has placed in me and for his constant encouragement throughout this work. I would especially like to thank Mark Hammond for the assistance and friendship he has constantly provided. It has been a pleasure to work with him throughout these experiments. I am also quite grateful to Clyde Altemus, Bob Potter, and Mike Murphy for the assistance and expertise they have provided in the machine shop.

Finally, I would like to take this opportunity to thank my parents, my family, and my wife's family for their love, encouragement and support throughout my education. Most of all, I would like to thank my wife, Joy. Words cannot express my gratitude for the love, friendship, patience, and support she has shown me throughout my education.

Contents

Introduction	1
1. Experimental Apparatus	8
2. Mott Polarimetry	20
3. Experimental Results	39
4. Discussion	48
5. Conclusion and Future Directions	56
References	58

Introduction

Surface science is concerned with the structure and properties of the transition region between phases. It encompasses many traditional disciplines and is an important research area in biology, chemistry, materials science, and condensed matter physics. In treating most bulk properties the presence of the external surface is either ignored completely or is adequately accounted for by the introduction of convenient, although perhaps unrealistic, boundary conditions. There are, however, a great many phenomena which can only be described in a satisfactory way by considering the details of the atomic and electronic structure in the surface region. Examples include electron emission, adsorption and oxidation, adhesion, friction, nucleation and epitaxial growth, and heterogeneous catalysis.¹

The last two decades have witnessed an explosive growth of experimental and theoretical techniques used to study the surface region of crystalline samples. In particular, the importance of electron spin polarization (ESP) effects in the study of crystalline surfaces has become increasingly evident in the last few years. For example, studies of electron spin dependent effects in Low Energy Electron Diffraction (LEED) have provided new information on the geometrical properties of atoms at a surface. Indeed, calculations show that spin-polarized LEED studies provide a more sensitive test of the parameters used in a surface model than do conventional LEED intensity measurements.² Many other electron spectroscopies have also incorporated ESP measurements.³ Spin dependent measurements in field emission, photoemission, inverse photoemission, secondary electron emission, electron energy loss spectroscopy and electron capture spectroscopy⁴ have provided new insights into the electronic structure of surfaces and surface magnetism.

Information provided by these spectroscopies, while extremely valuable, often reflects the "average" behavior of the first few surface layers rather than the behavior of the topmost surface layer alone. A probe of surface electronic structure which offers

unparalleled surface specificity and thus information complementary to more conventional techniques is Metastable Atom De-excitation Spectroscopy (MDS). In MDS, a thermal energy beam of noble-gas atoms in a long-lived excited state is directed at the surface under study. The slowly moving atoms interact with the external extension of the surface electronic wavefunction and de-excite in a radiationless Auger-type interaction which can result in the simultaneous ejection of an electron. Measurements of the ejected electron energy distribution can be used to obtain information about the electronic structure of the outermost atomic layer of the surface.

MDS is a non-invasive probe in that the noble-gas atoms are chemically inert and do not physisorb at any but the lowest surface temperatures. The thermal velocity atoms move too slowly to alter the structure of the surface or cause the kinetic ejection of electrons. Electron emission results instead from the release of potential energy stored in the excited atom. Metastable helium atoms are typically used in MDS because their metastable states store the largest internal energies of the noble-gases ($\text{He}(2^1\text{S})$: 20.6 eV, $\text{He}(2^3\text{S})$: 19.8 eV).⁵ The long radiative lifetime of these states ($\text{He}(2^1\text{S})$: 0.02 sec⁶, $\text{He}(2^3\text{S})$: 9000 sec⁷) allow the metastable atoms to be formed into a beam and travel long distances at thermal speeds ($v_{\text{He}} \approx 1.5 \times 10^5$ cm/sec) before decay.

To extract the maximum information concerning the surface electronic structure from the measured electron energy distributions, the processes responsible for electron ejection must be understood. Metastable noble-gas atoms are found to undergo de-excitation with nearly unit probability at a solid surface.⁸⁻¹¹ Near the surface such atoms can undergo electronic transitions of either the resonance, Auger, or radiative type. A radiative transition is possible if the metastable level of the atom is mixed enough by its interaction with the surface to allow de-excitation of the atom by photon emission.¹² The probability for such a transition to occur, however, is very low because the typical lifetime against radiative decay ($\approx 10^{-8}$ sec) is very long compared to the time a thermal atom spends within a few angstroms from the surface ($\approx 10^{-12}$ sec). The metastable atom must therefore

undergo electronic transitions in either a resonance or Auger process.

Based on pioneering work by Hagstrum,¹³ it is widely believed that a metastable atom will de-excite in one of two ways at a surface. To illustrate these, consider the de-excitation of a metastable helium atom (He^*) in proximity to a surface. In one process, the metastable atom is first resonantly ionized by tunneling of the He^* 2s electron into an empty state at the surface. The remaining He^+ ion is subsequently neutralized in a radiationless transition involving two surface electrons. One electron drops in energy to the He^+ 1s hole as a second electron is simultaneously excited. The excited electron may be ejected from the surface if the energy transfer is sufficiently large. This two-step process, in which resonance ionization (RI) is followed by Auger neutralization (AN), is illustrated in Fig. 1. In the second process, known as Auger de-excitation (AD) or surface Penning ionization (SPI), the metastable atom undergoes a radiationless transition directly to its ground state. In the exchange AD process, shown in Fig. 2a, the 2s electron is excited as a surface electron fills the He^* 1s hole. In the direct AD process an electron from the surface is excited when the He^* 2s electron drops into the He^* 1s hole, as diagrammed in

Figure 1. Resonance Ionization-RI (a) followed by Auger Neutralization-AN (b).

Fig. 2b. In either case, the excited electron may escape into vacuum if the transfer of energy is sufficiently large.

Figure 2. Auger De-excitation-AD: exchange process (a), direct process (b).

The energy of the excited electron in the one-step AD process directly reflects the energy of the electron that fills the $\text{He}^* 1s$ hole. An energy distribution resulting solely from AD electrons thus provides a measure of the surface density of electronic states. The actual surface density of states can be determined from such a distribution if other factors such as the energy dependent transition moments and electron escape probability are known. An energy distribution resulting solely from AN electrons, however, does not provide such a direct measure of the surface electronic structure. As illustrated in Fig. 3, electrons with a given final energy can emanate from an infinite set of paired initial states within the surface. The lack of a unique energy correspondence between the initial and final states of the ejected electrons make the AN spectra quite difficult to interpret.¹⁴

Figure 3. In the AN process electrons with a given final energy can emanate from an infinite set of paired initial states.

The complexities of the metastable atom-surface interaction make it difficult to determine *a priori* which of the two processes or what relative combination gives rise to the ejected electrons. The degree of competition between the RI+AN and the AD processes depends upon a number of factors including the local work function of the surface, the presence and nature of the adsorbed species on the surface, and the dynamical changes in the atomic energy levels near the surface. It is, nonetheless, necessary to know which ejection process is occurring since the spectra resulting from the AD and AN mechanisms require a fundamentally different form of analysis. In conventional MDS only the energy distribution of the ejected electrons is measured; hence, information regarding the competition between the two processes has to come from the form of the measured distribution itself. While the shape and range of the distribution can provide some evidence as to the operative process, more direct evidence is often necessary to reliably interpret the spectrum.

Insights into the dynamics of the metastable atom-surface interactions can, however, be obtained by polarizing the electron spins of the incident metastable atom and measuring the electron-spin-polarization (ESP) of the ejected electrons. Consider the impact of

polarized $\text{He}(2^3\text{S})$ metastable atoms, i.e. $\text{He}(2^3\text{S})$ atoms in which the electron spins are aligned parallel to some quantization axis, on a surface. Applying spin labels to the electrons involved in the metastable atom-surface interaction results in the situation diagrammed in Fig. 4.

Figure 4. AD or SPI (a) and RI+AN (b) processes with spin labels.

The use of triplet state metastable atoms virtually eliminates the possibility of de-excitation in the direct AD mode, as this process is spin forbidden. The time scale for the AD and AN processes are far too short ($\approx 10^{-13}$ - 10^{-14} sec)¹⁵⁻¹⁶ for the necessary magnetic interactions to flip the electron spins on the incident metastable atoms. In consequence, measurements of the polarization of the ejected electrons provide information as to the ejection processes that occur. As illustrated in Fig. 4a, Auger de-excitation will result in the production of electrons that are spin-polarized. In Auger neutralization, however, the ejected electrons will only be spin-polarized to the extent that there is a correlation between the spins of the two surface electrons involved in the ejection process (Fig. 4b). ESP

measurements therefore provide a test for the presence of such correlation effects. Thus electron spin labels applied to the electrons on the incident metastable atom can, when coupled with ESP measurements of the ejected electrons, help resolve questions concerning the dynamics of the electron ejection processes and allow exploration of the conditions under which the AD or RI+AN ejection processes occur.

This thesis reports the first spin-resolved measurements with MDS. The de-excitation of spin-polarized $\text{He}(2^3\text{S})$ atoms at $\text{Cu}(100)$ and $\text{Ni}(111)$ surfaces have been used to investigate the dynamics of metastable atom-surface interactions under a variety of surface conditions. ESP measurements with this spin-polarized probe indicate that, under certain surface conditions, the interaction is more complex than is generally assumed. For example, spin-correlations between the surface electrons participating in the AN de-excitation process are observed. In addition, the data suggest that in some cases both de-excitation mechanisms may be operative in parallel and be of comparable importance. The present data thus challenge certain conventional assumptions about metastable atom-surface interactions and thereby provide valuable information necessary for reliable interpretation of MDS spectra. As an additional benefit, the use of spin-polarized incident metastable atoms provides a novel technique with which to study surface magnetic properties at both the microscopic¹⁷ and macroscopic levels.

1. Experimental Apparatus

In the present apparatus, illustrated schematically in Fig. 5, a collimated beam of polarized thermal velocity $\text{He}(2^3\text{S})$ atoms is produced¹⁸ and directed at a well characterized target surface. The spin-polarization of electrons ejected from the $\text{He}(2^3\text{S})$ atom-surface interaction is measured with a compact Mott polarimeter and the ejected electron energy distribution is determined with a retarding potential analyzer. The polarization of the $\text{He}(2^3\text{S})$ atom beam is measured with a Stern-Gerlach analyzer which also serves to monitor the purity of the beam.

Figure 5. Schematic top view of the apparatus.

A detailed diagram of the metastable atom source is shown in Fig. 6. A ground state helium atom beam is formed by effusion through a multichannel array. The array has an active area of 1.6 mm^2 comprising capillaries of 0.05 mm diameter and 0.5 mm length. A fraction of the atoms in the neutral beam are then excited to metastable levels by coaxial electron impact. This technique affords an increased electron-helium interaction volume and typically results in more efficient excitation than is possible using transverse electron impact. In addition coaxial excitation results in less transverse recoil of the atoms

following excitation¹⁹ and thus provides an increased beam flux along the forward direction. The electron gun used for the excitation combines electrostatic and magnetic elements which constrain the electrons to travel essentially coaxially with the neutral helium beam.

Figure 6. Schematic view of the metastable atom source.

Electrons are provided by a tungsten filament which is wound in a double turn (≈ 5 mm in diameter) around the neutral beam. The filament is operated at a positive potential ($\approx +40$ V) to ensure that the emitted electrons are confined to the source region. The electrons are drawn from the filament by a suitable bias ($\approx +90$ V) applied to the extraction optics and are accelerated into a three element electrostatic lens. In practice, the three elements are operated at approximately the same potential ($\approx +90$ V) and serve primarily to provide an equipotential drift region for the electrons. Further coaxial confinement is provided by an axial magnetic field (≈ 100 G) generated by a solenoid that surrounds the vacuum housing containing the electron gun. By positioning the solenoid to provide a greater magnetic field inside the lens elements than in the vicinity of the filament, electrons emitted by the

filament can be magnetically merged and focussed with the neutral beam. In addition, this field causes the electrons to execute a helical path which increases their effective interaction length with the neutral beam.

Electron impact excitation also produces 2^1S metastable atoms and these are removed from the beam by exciting transitions of the type $2^1S \rightarrow n^1P \rightarrow 1^1S$ using $2\ \mu\text{m}$ resonance radiation from a DC excited flowing helium discharge lamp wound coaxially around the beam. The 2^3S atoms are not similarly de-excited because the 2^3S state is the lowest energy state in triplet system. Charged particles present in the beam are deflected by use of a transverse electric field. Deflections of only a few millimeters are necessary to remove the charged particles from the tightly collimated beam. The transverse field also serves to ionize any long-lived highly-excited Rydberg atoms contained in the beam. With these impurities removed, the beam is then electron-spin-polarized by optical pumping with circularly polarized $1.08\ \mu\text{m}$ $2^3S \rightarrow 2^3P$ resonance radiation provided by a helium discharge lamp.

The optical pumping process can be understood by reference to Fig. 7 which shows the magnetic sublevels associated with the 2^3S and 2^3P levels. In the absence of optical pumping the 2^3S beam contains equal numbers of atoms in each magnetic sublevel, $m_j(m_s) = 0, \pm 1$. If the beam is illuminated by right hand circular polarized (RHCP) resonance radiation, $2^3S \rightarrow 2^3P$ transitions will be excited subject to the selection rule $\Delta m_j = +1$. Thus transitions from the $2^3S\ m_j = 0$ level will populate the $^3P_2\ m_j = 1$ and $^3P_1\ m_j = 1$ levels as indicated by the solid arrows in Fig. 7. These levels subsequently decay by spontaneous emission for which the selection rules are $\Delta m_j = 0, +1$ ($m_j = 0$ to $m_j = 0$ not allowed for $\Delta J=0$) resulting in the transitions indicated by the wavy lines in Fig. 7.

The net effect of each excitation-decay cycle is a transfer or "pumping" of some 2^3S atoms initially in the $m_j = 0$ to the $m_j = +1$ sublevel. Similar considerations show that optical pumping also results in a transfer of the 2^3S population from the $m_j = -1$ to the $m_j = 0$ and $+1$ sublevels. (The pumping radiation will also excite transitions from the $2^3S\ m_j =$

Figure 7. Term diagram for He(2³S) showing the levels involved in the optical pumping process.

+1 sublevel to the 2³P₂ m_j = +2 level, but these do not contribute to the pumping because the selection rules only allow them to return back to the 2³S m_j = +1 sublevel upon decay). Therefore, as illustrated in Fig. 8, repeated cycling between the 2³S and 2³P state using RHCP resonance radiation will increase the number of atoms in the 2³S m_j = +1 state at the expense of those in the 2³S m_j = 0, -1 states.

Figure 8. Optical pumping of He(2³S) with RHCP light.

Similarly, of course, use of left hand circularly polarized (LHCP) resonance radiation will increase the 2³S m_j = -1 population at the expense of the 2³S m_j = 0, +1 populations. Examination of the electronic wavefunctions corresponding to the m_j = +1(-1) sublevel

shows that optical pumping results in a spatial orientation of electron spin angular momenta with respect to the quantization axis defined by the RHCP(LHCP) radiation.²⁰ The polarization of the beam is a normalized measure of the net angular momentum along this axis and is defined as²¹

$$P = \frac{n_{+1} - n_{-1}}{n_{+1} + n_0 + n_{-1}}, \quad (1)$$

where n_i , $i=+1,0,-1$ is the population of the 2^3S $m_j=i$ sublevel.

It should be emphasized that the effect of optical pumping is simply to redistribute the 2^3S population among the magnetic sublevels. No significant beam alteration or divergence results and in principle all the 2^3S atoms can be pumped into the $m_j = +1$ or -1 sublevel. This means that by simply changing from RHCP to LHCP pumping radiation, the beam polarization can be reversed from P to $-P$ without disturbing other properties of the beam. This important capability can be used to eliminate instrumental asymmetries and/or enable the use of phase sensitive detection techniques in the measurement of signals resulting from polarization effects.

The optical pumping radiation is provided by an RF excited flowing helium discharge lamp. The lamp is excited by an RF oscillator operated at a frequency of 140 MHz and an input power of ≈ 275 W. The oscillator is coupled to the helium discharge, contained in a quartz tube of ≈ 8 mm in diameter and ≈ 130 mm in length, by a combination of capacitive and inductive coupling. The required $1.08 \mu\text{m}$ resonance radiation is selected by passing the radiation from the lamp through a combination optical filter and linear polarizer. The radiation is then circularly polarized, with a measured degree of circular polarization $\approx 96\%$, by use of a quarter wave plate. The sense of circular polarization, and hence the metastable atom beam polarization, is simply reversed by rotation of the quarter wave plate through 90° . A copper mirror located underneath the metastable atom beam serves to

collect and focus the pumping radiation back through the beam resulting in a two-to-three-fold increase in polarization. The geometry of this optical pumping configuration results in a beam that is polarized perpendicular to the plane of the apparatus shown in Fig. 5.

To prevent degradation of the beam polarization, care must be taken to provide the proper local magnetic field environment along the beamline. In the optical pumping region, an external magnetic field is applied co-linear with the quantization axis defined by the propagation direction of the pumping radiation. Without this external field a newly polarized atom would immediately begin to precess about the new quantization direction defined by the local stray magnetic field. The beam polarization relative to the original direction would therefore be reduced within a characteristic time T_L given by the Larmor period of the $\text{He}(2^3\text{S})$ electrons in the stray magnetic field ($= 2\pi m/eB$). In the earth's magnetic field $T_L \approx 0.7 \mu\text{sec}$ which means the low velocity metastable atoms ($\approx 1.5 \times 10^5 \text{ cm/sec}$) will only travel a fraction of a centimeter before suffering a degradation of their polarization. Beyond the optical pumping region, the polarization of the beam relative to the local magnetic field direction can be maintained if the directional rate of change of the local magnetic field (ω_B) experienced by the atoms is much smaller than the Larmor precession frequency ($\omega_L = 2\pi/T_L$) of the $\text{He}(2^3\text{S})$ electrons in the local field (i.e. $\omega_B \ll \omega_L$). If $\omega_B \approx \omega_L$ the atoms will no longer remain space quantized with respect to the local field direction with the same component m of their total angular momentum and non-adiabatic transitions to states $m' \neq m$ will occur.²² Consequently, to preserve the beam polarization, a magnetic guide field is applied along the entire beamline of sufficient strength to ensure that the 2^3S magnetic moments adiabatically track any local changes in the magnetic field direction.

The polarization and purity of the $\text{He}(2^3\text{S})$ beam can be measured by allowing the atoms to traverse the main experimental chamber and enter a Stern-Gerlach analyzer, which is shown schematically in Fig. 9.

Figure 9. The Stern-Gerlach analyzer.

The metastable atom beam is tightly collimated by passage through two narrow horizontal slits, resulting in a beam divergence half angle of $\approx 10^{-3}$ in the vertical plane. The beam then enters an inhomogeneous "two-wire" magnetic field²³ of length 8 cm which has a uniform field gradient of ≈ 4500 G/cm. This field spatially separates the $m_j = +1, 0$, and -1 components in the beam and these are detected by means of a movable channel electron multiplier which is located 45 cm beyond the magnet.

In Fig. 10a the channeltron count rate is shown as a function of its position for the $\text{He}(2^3\text{S})$ beam with no optical pumping. As expected three well resolved peaks are evident. The central peak comprises atoms in the $2^3\text{S } m_j = 0$ sublevel and other species which are not deflected by the field gradient. The width of this peak is characteristic of the resolution afforded by the defining apertures in front of the deflecting magnet and the electron multiplier. The two peaks on each side result from atoms in the $2^3\text{S } m_j = +1$ and -1 sublevels. The widths of these broader peaks result from the velocity distribution of atoms in the beam. Slower atoms remain in the inhomogeneous magnetic field longer and thus experience a greater deflection.

The Stern-Gerlach analyzer can also be used to investigate the purity of the $\text{He}(2^3\text{S})$ atom beam. Impurity species such as $\text{He}(2^1\text{S})$ atoms, photons, and fast neutral helium atoms (created via resonant charge exchange collisions in the source)²⁴ will pass through the magnet undeflected and contribute to the area under the central peak. If the unpolarized

$\text{He}(2^3\text{S})$ atom beam is free from impurities the area under each of the three peaks will be equal. Such a peak area analysis can demonstrate that proper source operation results in a $\text{He}(2^3\text{S})$ atom beam with an impurity content of less than 5%.

Figure 10. Stern-Gerlach profiles with and without optical pumping.

The changes in the populations among the various magnetic sublevels resulting from pumping with RHCP and LHCP radiation are illustrated in Figs. 10b and 10c. Determination of the areas under the three peaks yields quantities proportional to n_{+1} , n_0 , and n_{-1} , thereby enabling the polarization of the $\text{He}(2^3\text{S})$ atom beam to be calculated from Eq. 1. Beam polarizations of $\approx 42\%$ are routinely obtained when pumping with the radiation supplied by the RF lamp. The profiles also demonstrate the ease with which the polarization of the beam can be reversed. A simple 90° rotation of the quarter wave plate

10c. Profiles like those in Fig. 10 are generated by use of a computer based data acquisition and control system. The position of the electron multiplier is incremented with a stepper motor as the count rate at each position is recorded with a scalar-timer. A numerical evaluation of these data yields the area under each of the three peaks. The polarization and purity analysis afforded by the use of this Stern-Gerlach technique is essential for successful surface studies with this novel probe.

The surface measurements conducted with this probe are performed in a chamber which is separated from the source and optical pumping regions and is designed to maintain ultra-high vacuum conditions. To obtain such low pressures, all the components in the chamber are fabricated from stainless steel, OFHC copper, high quality ceramics, etc. - no organic materials are used. Copper gaskets are used to seal the flanges and the entire chamber is vacuum baked at $\approx 200^\circ\text{C}$ for several days to facilitate the desorption of water vapor and other gases. The chamber is pumped with a 500 L/sec turbomolecular pump, a 400 L/sec differential ion pump and a titanium sublimation pump with cryoshroud. The turbomolecular pump allows one to flow pure gases through the chamber and serves to reduce the background helium pressure resulting from introduction of the $\text{He}(2^3\text{S})$ atom beam. After the "bake-out" period the chamber pressure routinely drops to $\approx 1 \times 10^{-10}$ Torr which ensures that the surface under study will remain free of contaminant background gas molecules during the course of an extended measurement. An RF quadrupole mass spectrometer is used to periodically monitor the background gas composition and to measure the pressure and purity of gases admitted to the chamber for surface adsorbate studies.

The sample under study is attached to a precision XYZ and θ manipulator which in turn is mounted on a motorized Z-motion linear stage with an 8" stroke. This arrangement allows the sample to be accurately positioned on two different levels within the chamber. The lower level of the chamber is used to prepare and characterize the surface under study. The atomically clean and well ordered surfaces of the Cu(100) and Ni(111) crystals used in

these experiments were produced by repeated cycles consisting of argon-ion bombardment at room temperature (30 min @ 500 eV, $5 \mu\text{A}/\text{cm}^2$) followed by a comparatively brief annealing period (2-5 min @ $\approx 700^\circ\text{K}$) to restore crystallographic order to the sputter damaged surface.

The presence of impurity atoms, such as carbon, oxygen, and sulfur, is detected via Auger Electron Spectroscopy (AES). Auger electrons, resulting from the non-radiative de-excitation of core-ionized atoms, possess energies which uniquely identify the parent atom.²⁵ Using a 3 KeV electron beam to bombard the surface and to create the inner shell vacancies, the escaping Auger electrons are detected with a hemispherical retarding grid energy analyzer operated in a phase sensitive mode to suppress the large background of other secondary electrons. Since the Auger electrons have energies less than 1 KeV, they can only escape from the first few atomic layers of the surface.²⁶ Therefore, a surface is said to be clean if no Auger electrons from impurity atoms can be detected. With a retarding grid Auger electron spectrometer, impurity atoms which comprise about 1% of a monolayer can be detected.²⁷ It should be noted that while AES is a useful monitor of surface cleanliness, the MDS technique itself proves to be more sensitive to the presence of surface impurities and is thus a better probe of surface cleanliness.

To verify the existence of surface crystallographic order and the existence of ordered adsorbate overlayers on such a surface, Low Energy Electron Diffraction (LEED) is employed. Since the de-Broglie wavelengths of low energy electrons (50-500 eV) are comparable to the lattice spacing in most crystals (2-5 Å), the waves elastically scattered from different atoms on the surface will interfere and give rise to a diffraction pattern. To view this pattern the sample is placed at the center of a hemispherical grid and phosphor coated screen assembly. Low energy electrons which are elastically scattered from the sample overcome the retarding potential on the grids and are accelerated towards the positively biased screen. The incident electron energy is varied until a pattern of diffraction spots appears on the fluorescent screen which can be viewed through a window in the

vacuum chamber. The clean Cu(100) and Ni(111) samples used in this study exhibited clear and sharp diffraction patterns characteristic of their crystallographic face.

The apparatus also incorporates three SAES[®] alkali metal dispensers used to evaporate atomically clean alkali metal overlayers on the surface under study. These wire-like dispensers contain an alkali metal trapped in a Zr-Al getter material. Passage of a 4-6 A current through the dispenser heats the getter and causes the alkali metal to evaporate. Unfortunately, reactive gases like H₂ and CO are also liberated in the process. Since the metastable atom probe is extremely sensitive to changes in the alkali overlayer induced by such gases, the dispensers must be thoroughly degassed prior to use.

The surface measurements with the spin-polarized He(2³S) atom beam are conducted on the upper level of the ultra-high vacuum chamber. The energy distribution or spin-polarization of electrons ejected from the He(2³S) atom-surface interaction can be measured by positioning the surface normal at either +45° or -45° with respect to the beam. A retarding field energy analyzer is used to obtain the ejected electron energy distribution. A negative potential V_r , applied to a parallel pair of fine mesh grids, prevents electrons with energies less than eV_r from reaching a bell-mouthed channel electron multiplier which is operated in a pulse counting mode. The mouth of the multiplier is biased at +50 V to prevent positive ions from being detected. A third grid, located in front of the the retarding grids, is biased at +15 V to increase the collection efficiency for low energy electrons. A small grounded aperture in front of the grids helps to collimate the incoming electrons and thus enhance the resolution of the analyzer which is estimated to be ≈ 0.5 eV. To obtain an energy distribution, the voltage on the retarding grids is ramped under computer control from +5 V to -18 V in 0.2 V increments as a timer-scaler records the number of electrons which overcome the retarding voltage at each setting. The data is numerically differentiated and digitally filtered to yield the desired distribution.

The polarimeter used for the spin-resolved measurements in this thesis is of a unique design and was specifically developed for this apparatus. The physics underlying the

polarization measurements along with a detailed description of the polarimeter is provided in the following chapter. Since the polarimeter is too large to be positioned near the sample, a system of electrostatic lenses are used to transport electrons from the sample to the polarimeter. Electrons are extracted from the sample by a shielded conical anode which is based on a design by Koike.²⁸ Electrons emerging from the extraction anode are focussed into the polarimeter by an Einzel lens with beam steering provisions in the first and third elements. This lens was designed with a ray tracing program that incorporates a Gaussian approximation and is a modified version of a program published by Kisker.²⁹

In this chapter, only a limited description of the apparatus has been given. A quite detailed description of virtually every part of the apparatus including the physical principles underlying its design and operation is given in an earlier thesis by this author.³⁰ Since the electron spin analyzer has been incorporated into the apparatus since that time, the next chapter is devoted to a discussion of Mott polarimetry.

2. Mott Polarimetry

An electron beam is said to be polarized if there exists an axis along which the two possible spin eigenstates are not equally populated. The polarization relative to this axis is defined as

$$P = \frac{N_u - N_d}{N_u + N_d}, \quad (2)$$

where N_u and N_d are the number of electrons in the spin-up and spin-down eigenstates respectively. An ideal electron polarization analyzer would completely separate the two spin eigenstates with unit efficiency as can be accomplished with polarized atoms by use of a Stern-Gerlach magnet. Unfortunately, as first articulated by Bohr and Pauli, it is fundamentally impossible to separate the spin eigenstates of an electron beam by use of a Stern-Gerlach "type" experiment.³¹ Mott³² and Kessler³³ describe why an actual Stern-Gerlach magnet will not work and a more general discussion of why any arrangement of macroscopic electromagnetic fields fail at this task is given by Farago.³⁴

A number of techniques for electron-spin polarimetry have been developed, but they all suffer from low efficiency - orders of magnitude less than an ideal spin filter. These techniques involve Møller scattering,³⁵ inverse photoemission,³⁶ low energy electron diffraction,³⁷⁻³⁹ and spin dependencies in the current adsorbed by solid targets.⁴⁰ The most extensively used polarization analysis technique, however, involves the use of Mott scattering. In the late 1920's Mott predicted that the elastic scattering of electrons by the Coulomb field of atomic nuclei was spin-dependent.⁴¹⁻⁴³ Formidable experimental difficulties hampered the accurate characterization and use of this effect until about twenty years ago. There has since been, due in part to developments in this laboratory, significant improvements in Mott polarimeter technology.

The spin-dependence of Mott scattering results from the spin-orbit interaction which arises from the coupling of the electron spin with the magnetic field resulting from its own orbital motion. The interaction is a natural consequence of Dirac's relativistic generalization of the Schrodinger equation, but can be semi-classically understood by considering the simple Coulomb scattering of an electron by an atomic nucleus. An electron moving with velocity $\mathbf{v}$ through the electric field of the nucleus experiences a magnetic field given by,

$$\mathbf{B} = -\frac{1}{c}(\mathbf{v} \times \mathbf{E}) \propto (\mathbf{E} \times \mathbf{p}), \quad (3)$$

which is perpendicular to the scattering plane (i.e. to the plane which contains the wavevectors of the electron before and after scattering). The electron has a magnetic moment $\boldsymbol{\mu} = -(e/mc)\mathbf{s}$, interacts with this magnetic field and contributes an additional potential energy term given by

$$V_{so} = -\boldsymbol{\mu} \cdot \mathbf{B} \propto \mathbf{s} \cdot (\mathbf{E} \times \mathbf{p}). \quad (4)$$

For scattering in a central field with potential energy $V(r)$, the electric field experienced by the electron is

$$\mathbf{E} = -\nabla\phi(r) = \frac{1}{e} \frac{dV(r)}{dr} \frac{\mathbf{r}}{r} \propto \frac{1}{r} \frac{dV(r)}{dr} \mathbf{r}, \quad (5)$$

where $\phi(r)$ is the scalar potential. Substituting Eq. 5 into Eq. 4 and recalling that the angular momentum $\mathbf{L}$ is given by $(\mathbf{r} \times \mathbf{p})$ yields

$$V_{so} \propto \frac{1}{r} \frac{dV(r)}{dr} (\mathbf{s} \cdot \mathbf{L}), \quad (6)$$

from which the origin of the term spin-orbit coupling is clearly evident. Note that only electrons with a spin component perpendicular to the scattering plane experience this coupling. For a pure Coulomb potential $V(r) \propto -Z/r$ so that Eq. 6 becomes

$$V_{so} \propto \frac{Z}{r^3} (\mathbf{s} \cdot \mathbf{L}). \quad (7)$$

Since $V_{so} \propto Z/r^3$, the spin-orbit interaction is strongest in the vicinity of high- Z nuclei like W, Hg, and Au.

The inclusion of the spin-orbit term in the scattering potential causes the polarization vector $\mathbf{P}$ of an electron beam to change in both direction and magnitude upon scattering. The direction of $\mathbf{P}$ changes upon scattering because the spin-orbit magnetic field of Eq. 3 produces a torque on the magnetic moments of the electrons connected with $\mathbf{P}$. As illustrated in Fig. 11, this torque induces $\mathbf{P}$ to change its direction and precess.⁴⁴ An electron beam polarized perpendicular to the scattering plane, however, does not experience this torque and hence does not change its direction upon scattering.

Figure 11. Precession of the polarization vector about the magnetic field arising from the relative motion of the charges.

The magnitude of P is influenced by the spin-orbit coupling because the interaction corresponds to an additional scattering potential which has different signs for electrons with opposing spin components perpendicular to the scattering plane. As Fig. 12 illustrates for the Coulomb potential,⁴⁵ the resulting scattering potential ($V_{\text{coul}} + V_{\text{so}}$) will be higher or lower for spin-up electrons (e_u) than for spin-down electrons (e_d), depending on which side of the nucleus they pass.

Figure 12. Potential curves with and without spin-orbit coupling for electrons with spins up and down.

As the scattering potential becomes spin-dependent for electrons polarized perpendicular to the scattering plane, it is not surprising that the differential scattering cross-section curves for e_u and e_d are different. This is seen in the upper portion of Fig. 13 which shows experimental data for the elastic scattering of completely polarized electrons from free Hg atoms at 300 eV.⁴⁶ The differential cross-section $\sigma(\theta)$ as a function of scattering angle shows the typical interference structure determined by λ/R , where λ is the electron wavelength and R is the effective range of the scattering potential. The interference structure of $\sigma(\theta)$ is different for electrons with opposing spin-orientations because, for a given scattering angle, R depends on the sign and magnitude of the spin-orbit interaction. For electron scattering, the spin-orbit interaction is relatively weak and the deviation of σ_u and σ_d from the average differential scattering cross-section $(\sigma_u + \sigma_d)/2$ is not large. The lower portion of Fig. 13 shows, however, that the normalized difference between the two

curves ($D = (\sigma_u - \sigma_d) / (\sigma_u + \sigma_d)$) can be quite large, especially near cross-section minima. Consequently, the numbers of e_u and e_d scattered into a particular direction θ can be significantly different from each other.

Figure 13. Cross-section curves for spin-up and spin-down electrons with normalized difference between them.

To use this scattering asymmetry for polarization analysis, the relationship between the differential scattering cross-section and the incident beam polarization must be obtained. By solving the Dirac equation to obtain the appropriate scattering amplitudes and by describing the beam polarization in the density matrix formulation, which properly account for the statistical mixture of spin states in a beam with an arbitrary degree of polarization, Mott has shown that⁴⁷

$$\sigma(\theta) = I(\theta) (1 + S(\theta) \mathbf{P} \cdot \mathbf{n}), \quad (8)$$

where $\mathbf{P}$ is the polarization vector of the incident electrons and $\mathbf{n}$ is the unit vector normal to the scattering plane. If we define $\mathbf{k}$ and $\mathbf{k}'$ as the electron wavevectors before and after scattering, then

$$\mathbf{n} = \frac{\mathbf{k} \times \mathbf{k}'}{|\mathbf{k} \times \mathbf{k}'|}. \quad (9)$$

Note that only the component of the polarization vector perpendicular to the scattering plane contributes to the scattering asymmetry. The differential cross-section for an electron beam polarized in the scattering plane is simply $I(\theta)$. $I(\theta)$ and $S(\theta)$ are lengthy expressions which depend on the details of the scattering and whose exact form is not relevant to this discussion. It should be noted, however, that each expression possesses mirror symmetry about the incident beam axis (defined by $\mathbf{k}$) because parity is conserved for the electromagnetic interaction which governs electron scattering, (i.e. $I(\theta) = I(-\theta)$ and $S(\theta) = S(-\theta)$).⁴⁸

To understand the significance of $S(\theta)$ in the previous expression, consider the scattering of an unpolarized electron beam. Without any loss in generality, such a beam can be considered as a mixture of equal numbers of electrons polarized in opposite directions. One half are totally polarized in the u -direction perpendicular to the scattering plane; the other half are totally polarized in the opposite d -direction as shown in Fig. 14.⁴⁹

Figure 14. Scattering of an unpolarized electron beam.

From Eq. 8 it follows for the e_u beam that the scattering intensity to the left is proportional to $1+S(\mathbf{P} \cdot \mathbf{n}) = 1+S$, whereas the intensity to the right is proportional to $1-S$ due to the opposite vector $\mathbf{n}$. For the e_d beam the corresponding values are $1-S$ and $1+S$. In both cases the polarization vectors remain unchanged as they are perpendicular to the scattering plane and have magnitude 1 (since each beam is totally polarized). The fact that there are different numbers of e_u and e_d in the scattered beam means that this beam is polarized. Fig. 14 illustrates that for scattering to the left the polarization is

$$P = \frac{N_u - N_d}{N_u + N_d} = \frac{(1+S) - (1-S)}{(1+S) + (1-S)} = S(\theta), \quad (10)$$

whereas for scattering to the right one has $P = -S$ (as long as u and d always refer to the same reference direction). Thus, through scattering, an initially unpolarized beam acquires a polarization of magnitude $S(\theta)$ perpendicular to the scattering plane.

Now consider the scattering of a beam with a net polarization P . The total numbers of electrons scattered left (N_l) and right (N_r) are now different and one can define a normalized left-right asymmetry given by

$$A = \frac{N_l - N_r}{N_l + N_r}, \quad (11)$$

so that from Eq. 8 we have,

$$A = \frac{(1+PS) - (1-PS)}{(1+PS) + (1-PS)} = PS(\theta). \quad (12)$$

For a beam completely polarized perpendicular to the scattering plane $P=1$ and we have

$A=S(\theta)$. The function $S(\theta)$ therefore describes two important features: the extent of asymmetry in the scattering of a polarized beam and the amount of polarization produced by scattering an unpolarized beam. The first accurate calculations of the polarization acquired upon scattering were performed by Sherman^{50,51} in the late 1950's and hence $S(\theta)$ is now commonly referred to as the Sherman function.

The asymmetry described by the Sherman function forms the basis for experimental Mott polarimetry. By measuring the normalized difference in count rates for electrons scattered from a target and reaching two symmetrically placed detectors, the polarization of the incident electron beam can be determined if the Sherman function for the appropriate scattering parameters is known. Theoretical values of $S(\theta)$ which have been calculated for a single scattering from a single atom do not represent the situation in a real polarimeter. The gold foil targets utilized in most polarimeters contain so many atoms that plural or multiple scattering processes also occur. Electrons which arrive at the detectors after several scattering events usually reduce the asymmetry.⁵²

Consequently, instead of using the ideal Sherman function one must use an effective Sherman function which depends on target thickness. It also depends on other conditions of the experiment, such as the range of the scattering angle θ which is recorded by the electron detectors. Since there are rather large uncertainties in the theoretical treatment of plural scattering,⁵³ the effective Sherman function must be experimentally ascertained for each Mott polarimeter design. This can be done by calibrating the polarimeter with a beam of known polarization. The effective Sherman function can also be obtained with a beam of unknown polarization by measuring the dependence of the scattering asymmetry on foil thickness d .⁵⁴ If the amount of plural scattering is very small with the thinnest of the foils used, one can extrapolate from such a measured curve to the asymmetry for the foil thickness $d=0$. This can be related to the Sherman function for $d=0$ which is well established theoretically as well as experimentally for suitable choice of scattering angle, electron energy, and target material (e.g. for scattering from gold at 120° , $S(\theta)$ is known to

exhibit a broad maximum for 20-120 KeV electrons⁵⁵ and is known to have a magnitude of 0.37 ± 0.01 at 120 KeV⁵⁶). The extrapolated value of this asymmetry versus foil thickness curve then yields the effective Sherman function for the other foils used in the series of measurements.

To obtain significant left-right asymmetries, large values of the effective Sherman function S_{eff} are desirable. As a rule, however, at angles where the Sherman function is large, the cross-sections and thus the scattered intensities are small.⁵⁷ Therefore one must find a compromise between high scattering intensity I and high asymmetry. Kessler has shown that to minimize the statistical error, the quantity $(S_{\text{eff}})^2 I$ should be as large as possible.⁵⁸ As I also depends on the incident intensity I_0 , it is customary to use the quantity $(S_{\text{eff}})^2 I/I_0$ as a figure of merit when comparing Mott detectors. This quantity is often referred to as the efficiency of a Mott polarimeter.

Until fairly recently, Mott polarimeters tended to be of a standard design⁵⁹ in which polarized electrons are first accelerated to energies of approximately 100 KeV in a conventional accelerating column and subsequently allowed to strike a thin gold-foil target. Counting rates for electrons elastically scattered at $\theta = \pm 120^\circ$ are then measured by two energy-sensitive detectors. Such a polarimeter is rather cumbersome in part because its high voltage accelerating column is exposed and in part because its scattering chamber and detectors must be maintained at high voltage. The analyzer and the safety region around it easily occupies several cubic meters. Moreover such a polarimeter suffers from poor discrimination against inelastically scattered electrons, a consequence of the intrinsic resolution of most energy-sensitive detectors.⁶⁰

A significant simplification of this standard configuration was first developed in this laboratory. This variation has two electrodes inside the vacuum chamber such that the electrons are accelerated to the inner electrode and scattered from the gold-foil at high energy and then are decelerated as they pass again to the outer electrode which is at nominal ground potential. This configuration allows discrimination against inelastically

scattered electrons with a resolution much higher than that obtainable with energy-sensitive detectors. In addition, an analyzer of this type is much smaller than the traditional polarimeter because the electron detectors along with a major portion of the apparatus is operated at near ground potential.

The first accelerating/decelerated analyzer utilized a cylindrical geometry, with the inner cylinder operating at 120 KV and the outer cylinder near ground potential.⁶¹ The Mott analyzer developed for the polarization measurements described in this thesis is similar in concept but instead utilizes a spherical symmetry and accelerating voltages ≈ 40 KV. This analyzer provides greatly improved efficiencies and is more compact than previous designs.⁶² In fact, because of its relatively small size for a Mott analyzer, it is commonly called the "mini-Mott".⁶³ This analyzer is relatively simple to construct and operate and is fully ultra-high vacuum compatible.

Figure 15. Schematic diagram of the spherical mini-Mott analyzer.

A schematic diagram of mini-Mott, which has rotational symmetry about the horizontal axis, is shown in Fig. 15. The central components of the analyzer are two electrically isolated, concentric polished stainless-steel hemispheres. A strong radial field is established in the region between the two by application of a high potential (≈ 40 KV) to the inner hemisphere. The outer hemisphere (radius ≈ 7.5 cm) is operated near ground potential (≈ 1 KV). To minimize the electric field strength at the surface of the inner hemisphere for a given potential difference between the hemispheres, the ratio of their radii is one-half. A guard ring, biased by a resistive divider, is included to ensure that fringing fields will not significantly perturb the radial field distribution in the vicinity of the scattered electron beams. The guard ring and inner hemisphere are mounted on a machinable glass-ceramic (MacorTM) plate. The outer hemisphere, and other components of the analyzer, are electrically isolated, where necessary, using sapphire ball spacers.

The electron beam whose polarization is to be determined enters the region between the hemispheres through a circular aperture in the outer hemisphere. The beam is accelerated and focussed by the radial field and enters the inner hemisphere through a second aperture. A thin gold target foil ($\approx 193 \mu\text{g}/\text{cm}^2$, $\approx 1000 \text{ \AA}$ thickness) is located at the center of the inner hemisphere. Electrons scattered through $\pm 120^\circ$ by the foil exit the inner hemisphere through two symmetrically located apertures. The electrons are decelerated as they traverse the radial field and pass through two apertures in the outer hemisphere where they are detected by bell-mouthed channeltrons. The polarization of the beam is determined by measuring the count rates at the two detectors. Only electrons that have suffered very small inelastic energy losses on scattering are able to overcome the retarding field and be detected. Thus, the retarding field provides good discrimination against inelastically scattering electrons. The energy discrimination can be adjusted by varying the bias on the front end of the channeltrons. Indeed, if this retarding bias is larger than the initial kinetic energy of the incident electrons, no scattered electrons will reach the detectors. Electrons that pass through the gold foil are collected in a Faraday cup.

The radial field between the inner and outer hemispheres leads to a strong focusing of the input beam.⁶⁴ To check this, the area surrounding the gold foil (which is 6 mm in diameter) was phosphor coated and provision made to view this phosphor through small holes cut in the inner and outer hemispheres. However, despite the variety of input beam positions and trajectories used in this work, no fluorescence from the phosphor was detected. In addition, the measured values of S_{eff} at each energy were very reproducible. These observations indicate that the input beam is well focussed at a stable position on the gold foil.

The various apertures in the inner and outer hemispheres are rounded and carefully polished to eliminate corona discharge. No problems with electrical breakdown between the hemispheres have been experienced. The level of coronal discharge is so low that even with the inner hemisphere biased at 40 KV the background counting rates in the detectors are only ≈ 1 Hz. Ions may, however, be created in the inner hemisphere by collisional ionization of background gas (the pressure in the analyzer during testing and calibration was $\approx 10^{-6}$ Torr) or by electron bombardment desorption. Any such ions that escape will be accelerated and detected by the channeltrons resulting in a spurious background signal. To prevent this, the target foil and holder is biased at -300 V with respect to the inner cylinder. This bias is provided by a battery which floats at the inner hemisphere potential and rests on a block of teflon inside a plexiglass housing which provides a safety region around the high voltage feedthrus. With this bias applied, the background count rate due to ion production, determined by biasing the front end of the channeltrons sufficiently negative that no scattered electrons are detected, is negligible. The -300 V potential supplied by the battery relative to the inner hemisphere is also used to bias the outer electrode of the Faraday cup to suppress low-energy secondary electron ejection. The inner element of the Faraday cup is maintained at the potential of the inner hemisphere.

The degree of electron-spin polarization of the input beam, relative to an axis perpendicular to the scattering plane, is determined by measuring the asymmetry in

counting rates at two detectors. From Eq. 8 we can write the ratio of the counting rates R in the two detectors as

$$\frac{\sigma_l}{\sigma_r} = \frac{R_l}{R_r} = \frac{1 + S_{\text{eff}} P}{1 - S_{\text{eff}} P} . \quad (13)$$

In any real polarimeter the Mott asymmetry is accompanied by instrumental asymmetries which result from unequal detector response, misalignment of the incident beam, and other functions which are discussed in detail elsewhere.⁶⁵ Including the instrumental asymmetry δ , Eq. 13 becomes

$$\frac{R_l}{R_r} = \left[\frac{1 + S_{\text{eff}} P}{1 - S_{\text{eff}} P} \right] \delta . \quad (14)$$

The instrumental asymmetry δ can be determined directly by use of an unpolarized electron beam, although care must be taken to ensure that the unpolarized electron beam has the same trajectory and characteristics as the beam whose polarization is subsequently measured. However, the polarized electron source used to calibrate the mini-Mott, and the polarized He(2^3S) atom beam, permit the sign of the polarization of electrons entering the analyzer to be readily reversed (P to $-P$) without affecting the electron beam trajectory. This capability provides a simple means for instrumental asymmetry correction since, if the polarization is reversed, the new ratio of the counting rates is

$$\frac{R'_1}{R'_r} = \left[\frac{1 - S_{\text{eff}} P}{1 + S_{\text{eff}} P} \right] \delta. \quad (15)$$

Elimination of δ between Eqs. (14) and (15) yields

$$P = \frac{1}{S_{\text{eff}}} \left[\frac{X - 1}{X + 1} \right], \quad (16)$$

where

$$X = \frac{R_1 R'_r}{R_r R'_1}. \quad (17)$$

To determine S_{eff} , a beam of known polarization P_0 ($\approx 37\%$) from the Rice flowing helium afterglow polarized electron source^{66,67} was employed. This source, shown in Fig. 16 with the mini-Mott analyzer mounted in target position, incorporates the cylindrical Mott analyzer mentioned previously. The effective Sherman function for the cylindrical analyzer is known from previous measurements based on extrapolation to zero foil thickness.⁶⁸ The beam polarization P_0 is thus determined from Eq. 16 by observing electrons elastically scattered at $\pm 120^\circ$ from a gold foil located at the center of the inner cylinder. The gold scattering foil in the cylindrical analyzer is then moved to permit a beam (of known polarization P_0) to pass through the analyzer unscattered and enter the mini-Mott analyzer where the resultant scattering asymmetry X is determined. S_{eff} is then obtained from the relation

Figure 16. Schematic diagram of the apparatus used to calibrate the mini-Mott analyzer.

$$S_{\text{eff}} = \frac{1}{P_0} \left[\frac{X-1}{X+1} \right]. \quad (18)$$

Values of S_{eff} were measured as a function of the maximum inelastic energy loss an electron can suffer and still be detected. This energy loss was defined by the bias voltages applied to the front end of the channeltrons. Representative data are shown in Fig. 17 for three values of the electron accelerating voltage.

As expected, S_{eff} increases with increasing discrimination against inelastically scattered electrons. However, as illustrated by Fig. 18, this increase in S_{eff} is accompanied by a marked decrease in the scattered electron count rates and, in consequence, the efficiency of the analyzer is highest when operating with inelastic energy-loss windows of ≈ 1300 eV. Operation in this regime has the added advantage that S_{eff} is relatively insensitive to small changes in the energy-loss window.

Fig. 17 also includes values of S_{eff} obtained directly by operating the cylindrical Mott analyzer at lower electron accelerating voltages. Values of S_{eff} obtained using the two

Figure 17. Measured values of S_{eff} as a function of maximum inelastic energy loss for electron scattering energies of (a) 40 KeV, (b) 30 KeV, (c) 20 KeV. • Data obtained with the mini-Mott analyzer, × data obtained with the cylindrical Mott analyzer.

Figure 18. Electron count rate at the detectors as a function of maximum inelastic energy loss for an electron scattering energy of 30 KeV.

analyzers, both of which employ gold scattering foils of the same nominal thickness, are in good agreement. Since the two analyzers utilize different geometries, and since the scattered electron detectors subtend very different solid angles at the scattering foil in the two designs, this suggests that the values of S_{eff} in Fig. 17 may be used to calibrate any Mott analyzer similar in operation to that described here, provided a scattering foil of the same nominal thickness is used. Indeed, measurements of S_{eff} using several foils, all of the same nominal thickness, showed that the data in Fig. 17 are highly reproducible.

Values of S_{eff} obtained with inelastic energy-loss windows of 0 and 1300 eV using both Mott analyzer are shown in Fig. 19 as a function of electron energy.

Figure 19. Measured values of S_{eff} as a function of electron scattering energy. $\bullet$, $\times$ Data obtained for zero inelastic energy loss using the mini- and cylindrical Mott analyzers, respectively. Open circles and boxes represent corresponding data obtained for a maximum inelastic energy loss of 1300 eV. Solid boxes represent experimental data of Ref. 70. Solid line represents the theoretical results of Ref. 69.

Operation with a very small energy loss window discriminates very effectively against inelastically scattered electrons, and S_{eff} should approach the Mott scattering asymmetry expected for scattering from individual nuclei. The solid line shows values of the Mott

asymmetry function calculated using a relativistic Hartree potential.⁶⁹ At electron energies ≥ 60 KeV the present data are in good agreement with the theoretical values. However, at lower energies the data fall somewhat below the calculated values. This discrepancy may result from incomplete rejection of inelastically scattered electrons from multiple elastic scattering in the foil. However, as evident from Fig. 19, the present zero energy-loss values of S_{eff} are significantly higher than those obtained by Mikaelyan et. al. in a double scattering experiment.⁷⁰ The data in Fig. 19 also suggest that Mott analyzers of the present type can be calibrated, to fair accuracy, by assuming that for zero energy loss S_{eff} is equal to the calibrated Mott asymmetry.

The ratio I/I_0 of the scattered and incident currents for the mini-Mott analyzer was determined by comparing the scattered electron count rates to the incident beam current, measured by positioning a Faraday cup in the incident beam. For a 1300 eV energy-loss window this ratio varied from $\approx 2 \times 10^{-4}$ at 40 KV to $\approx 7 \times 10^{-4}$ at 20 KV. These ratios indicate that, since the background count rate is ≈ 15 Hz accurate polarization measurements are possible using input beams with currents as low as $\approx 10^{-13}$ A. The ability to use such low input currents is important since the total current generated by the metastable atom-surface interaction is only a few picoamps.

For a 1300 eV energy-loss window, the efficiency $(S_{\text{eff}})^2 I/I_0$ of the analyzer remains fairly constant at $\approx 1 \times 10^{-5}$ for all electron accelerating voltages in the range 20-40 KV. This efficiency is compatible with that obtained by high-energy Mott scattering,⁷¹⁻⁷³ low-energy scattering from a metal-atom beam,^{74,75} and by the other techniques mentioned at the beginning of this discussion. Unlike analyzers which rely on low-energy incident electrons,⁷⁶ the mini-Mott can be used to measure the polarization of an electron beam with sizable spatial extent and energy spread. The present design also permits simultaneous measurement of the scattering asymmetry in two orthogonal planes, thereby permitting, in the proper arrangement,⁷⁷ direct determination of the vector polarization $\mathbf{P}$. While the mini-Mott is relatively compact, the data indicate that scaled down versions with

hemisphere radii of ≈ 4 cm operating at 10-20 KV will provide comparable performance, and should be suitable as a movable polarization analyzer for angular resolved studies. Such a "micro-Mott" has recently been constructed and is presently being tested and calibrated.

Measurements of the spin-polarization of electrons ejected from the $\text{He}(2^3\text{S})$ atom-surface interaction are taken under computer control. With the quarter-wave plate (located under the RF excited optical pumping lamp) in the appropriate position, a timer-scaler records the count rates of electrons reaching the left and right multipliers in the analyzer. To eliminate the instrumental asymmetry, a stepper motor then rotates the quarter-wave plate by 90° (thus reversing the polarization of the $\text{He}(2^3\text{S})$ atom beam) and another set of left and right count rates are recorded. Since S_{eff} is known from the calibration procedure, these four count rates yield the polarization P of the ejected electrons (from Eq. 16). The quarter-wave plate is rotated back to its original position and the process is repeated until an acceptable statistical error in the polarization value is obtained.

Finally, it should be noted that the absolute precision of a polarization measurement with a Mott analyzer is difficult to ascertain. Published error bars usually represent statistical uncertainties and only apply to relative values of the polarization. Based upon an examination of the influence of multiple and plural scattering, Fletcher et.al. recently concluded⁷⁸ that the precision of Mott measurements is fundamentally limited by an experimental uncertainty of greater than $\pm 2.5\%$ and an absolute uncertainty of approximately 5%.

3. Experimental Results

The results of the first spin-resolved studies with MDS are presented in this section. Spin-polarized $\text{He}(2^3\text{S})$ atoms were used to investigate the metastable atom/surface interaction at $\text{Cu}(100)$ and $\text{Ni}(111)$ surfaces. Ejected electron-spin-polarization (ESP) and energy distribution measurements are reported for a variety of surface conditions.

A. $\text{Cu}(100)$ and $\text{Ni}(111)$ - Chemically Cleaned Results

For the initial measurements, the highly polished crystals were cleaned with organic solvents and studied in an ordinary vacuum environment. Ultra-high vacuum conditions were not attained and the surfaces were neither heated nor subjected to argon-ion bombardment. The observed secondary electron distributions are displayed in Fig. 20 together with the corresponding ESP of the ejected electrons.

Figure 20. Data obtained from the chemically cleaned surfaces.

Note that the ESP values, which are expressed as a percentage of that of the electrons on the incident $\text{He}(2^3\text{S})$ atoms, are similar for both surfaces and are quite large. The positive ESP values indicate that the ejected electrons, and those on the incident $\text{He}(2^3\text{S})$ atoms, were spin-polarized in the same sense. ESP values of $\approx +70\%$ were also observed from chemically cleaned polycrystalline W, Ta, Mo, Cu and stainless steel surfaces during the course of this work. Tests for systematic errors were routinely performed in this work. These tests confirmed that the measured ESP values did not change over a wide range of voltage settings on both the extraction anode and the Einzel lens used to focus electrons into the polarimeter. Additional tests revealed that if the incident $\text{He}(2^3\text{S})$ atoms were unpolarized, the ESP of the ejected electrons was, within experimental error, equal to zero. The spin-polarization effects observed in this thesis thus originate solely from the polarization of the incident metastable atoms.

For the ESP measurements, the Ni(111) sample was magnetized to saturation along the direction defined by the local magnetic guide field. To accomplish this, the crystal was mounted in the keeper position on a C-shaped electromagnet. Saturation was demonstrated by magneto-optic Kerr-effect measurements (described in the present author's M.A. thesis⁷⁹) and by ESP measurements undertaken with a variety of currents through the electromagnet. Magnetization of the crystal is required because near the surface of an unmagnetized sample there is no unique quantization axis, rather the magnetic fields associated with the various domains define local, randomly oriented quantization axes. The ejected electrons must therefore have randomly oriented spins and thus a net ESP of zero - a result confirmed experimentally. As will be discussed later, the degradation of the ESP at an unmagnetized sample may provide a novel technique with which to investigate the domain structure at a ferromagnetic surface.

The ejected electron energy distributions were measured using unpolarized $\text{He}(2^3\text{S})$ atoms. The magnetic guide field in the experimental chamber and the voltage on the front grid of the energy analyzer were adjusted to optimize the collection efficiency for low

energy electrons. The energy distributions from the chemically cleaned surface are characterized by a large low energy peak and are strikingly similar to published MDS spectra from contaminated stainless steel and polycrystalline tungsten surfaces.⁸⁰

B. Cu(100) and Ni(111) - Atomically Clean Results

Data obtained from the atomically clean and well-ordered Cu and magnetized Ni surfaces are shown in Fig. 21.

Figure 21. Data obtained from the atomically clean surfaces.

The ESP values obtained are substantially lower than those obtained at chemically cleaned surfaces. Dramatic changes in the secondary electron energy distribution are also observed. The distributions exhibit a smooth and relatively structureless form which is characterized by a predominance of higher energy electrons and a fairly sharp high energy cut-off. Note that the ESP values measured at the two surfaces are, within experimental

error, equal, and that both electron energy distributions are qualitatively similar. The ESP values and energy distributions from both clean surfaces were observed to be independent of sample temperature over the range from 30°C to 450°C. Note that temperatures within this range exceed the Curie temperature of Ni which is $\approx 354^\circ\text{C}$.⁸¹ The energy distributions shown in Fig. 22 are in excellent agreement with published MDS spectra from clean Cu(110)⁸² and Ni(111)^{83,84} surfaces.

As mentioned earlier, the surface cleanliness was verified by Auger Electron Spectroscopy (AES). The extreme surface specificity afforded by the metastable atom probe, however, makes the MDS spectrum very sensitive to the presence of surface impurities. Figure 22 shows an MDS spectrum from an initially clean Ni surface after a two hour exposure to background gases in an ultra-high vacuum environment at room temperature.

Figure 22. MDS spectrum obtained from an initially clean Ni surface after a two hour exposure to background gases in an ultra-high vacuum environment.

Even though the total background gas pressure was only $\approx 2 \times 10^{-10}$ Torr, the MDS spectrum shows a pronounced increase in the number of low energy electrons relative to those with higher energy as compared to the clean surface data. In contrast, AES measurements did not indicate the presence of any surface contaminants under either

condition. It was observed that changes in the MDS spectrum, like those evident in Fig. 22, could be avoided if the sample was maintained at $\approx 80^\circ\text{C}$. The higher surface temperature apparently reduces the sticking probability for background gases like H_2 or CO . Consequently, prolonged measurements on clean Cu and Ni surfaces were performed at this slightly elevated temperature.

C. O_2 on Cu(100) - Atomic Adsorbate Results

It is well known that oxygen adsorbs in a dissociative manner on a Cu(100) surface at room temperature.⁸⁵ The oxygen atoms form a well-ordered, chemisorbed overlayer on the Cu substrate which can be investigated via Low Energy Electron Diffraction (LEED).^{86,87} Before the spin-polarized MDS measurements were performed on the O/Cu system, LEED studies were undertaken to characterize the room temperature adsorption of oxygen on Cu(100). The LEED pattern from an initially clean and well-ordered Cu(100) surface was monitored as the surface was exposed to pure oxygen. With exposures up to ≈ 180 L ($1\text{L}=1\text{Langmuir}=1\times 10^{-6}\text{Torr-sec}$), the LEED pattern was that characteristic of a clean Cu(100) surface. Higher exposures (≈ 1500 L), however, produced a sharp LEED pattern associated with a $(\sqrt{2}\times\sqrt{2})\text{R}45$ adsorbate structure. A more complex LEED pattern, representative of a $(\sqrt{2}\times 2\sqrt{2})\text{R}45$ adsorbate structure, appeared as the oxygen exposure approached ≈ 5500 L. Exposures beyond this point produced no further changes in the pattern, but flashing this heavily exposed surface to $\approx 150^\circ\text{C}$ did improve the quality of the $(\sqrt{2}\times 2\sqrt{2})\text{R}45$ pattern. These observations are in accord with a number of other recent reports.⁸⁸⁻⁹³ In contrast, spin polarized MDS studies revealed that the ESP of the ejected electrons was essentially unchanged by oxygen exposure, remaining close to the clean surface value even after exposures $>10,000$ L. Figure 23 shows the ESP value and energy distribution for both a $(\sqrt{2}\times\sqrt{2})\text{R}45$ and a $(\sqrt{2}\times 2\sqrt{2})\text{R}45$ oxygen covered surface.

Figure 23. Data obtained from the O/Cu(100) atomic adsorbate system.

Both energy distributions are significantly different from the distribution obtained with a clean Cu surface. They exhibit a predominance of low energy electrons, which is a characteristic of adsorbate covered surfaces. Note that the two distributions are quite similar even though they correspond to very different oxygen exposures.

D. CO on Ni(111) - Molecular Adsorbate Results

The behavior of the ESP and energy distributions for the magnetized Ni(111) surface were studied as a function of exposure to pure CO. Reversible molecular adsorption of CO on Ni(111) is known to occur at room temperature.⁹⁴ Previous studies have shown that CO exposures of ≈ 5 L at room temperature produce a saturation coverage of $\Theta_{\text{CO}} \approx 0.5$.⁹⁵⁻⁹⁸ Measurements showed that the ESP values rose from the clean surface

value of $\approx 25\%$ to only $\approx 35\%$ after a 6 L exposure at room temperature. To ensure that this exposure produced saturation, additional measurements were performed while the background gas pressure of CO was maintained at $\approx 1 \times 10^{-8}$ Torr. Figure 24 shows the results of such a measurement after an initial 10 L exposure.

Figure 24. Data obtained from the CO/Ni(111) molecular adsorbate system.

Note that the ESP of the ejected electrons has not changed from the 6 L value. The energy distribution is again skewed towards low energies, but shows additional peaks not present in the O/Cu(100) spectrum. The distributions obtained from the CO covered Ni(111) surface are in good agreement with published MDS spectra for this system.⁹⁹⁻¹⁰¹

E. K on Cu(100) - Low Work Function Results

Spin-resolved MDS measurements on an atomically clean, low work function surface were performed by evaporating a potassium overlayer on the Cu(100) surface under ultra-high vacuum conditions. It is well known that the work function of a metal such as copper can be significantly reduced by surface adsorption of alkali atoms.¹⁰² Such a

reduction, however, also lowers the threshold for photoelectron ejection from the surface. Photoelectron ejection can be caused by photons produced in conjunction with the metastable atom excitation, and by radiation emanating from the white-hot filament in the metastable atom source. A time-of-flight technique, in which the accelerating voltages in the metastable atom source were pulsed, was used to discriminate against photoelectrons connected with the metastable atom excitation. Photoelectrons associated with radiation from the filament were accounted for by measuring the ejected electron signal when the accelerating voltages in the metastable atom source were off.

Figure 25. Data obtained from the K/Cu(100) low work function surface.

MDS data obtained in this manner after a successful overlayer evaporation at room temperature are shown in Fig. 25. Comparison with the clean Cu(100) data (Fig. 22) shows that no features characteristic of the Cu substrate remain following K deposition. Previous studies of K adsorption on a Cu(110) surface demonstrate that the absence of substrate features in the MDS spectrum is associated with a drop in work function, $-\Delta\phi$, of at least 2.2 eV.¹⁰³ Such a drop is almost equal to the difference in work function between the bulk surfaces of clean Cu(100) and clean K ($\phi_{\text{Cu}(100)} - \phi_{\text{K}} \approx 4.6 \text{ eV} - 2.3 \text{ eV} = 2.3 \text{ eV}$).¹⁰⁴ Note, however, that deposition of K does not significantly change the ESP of the

ejected electrons from its clean surface value. The larger statistical error associated with the K data is due to the lower count rate resulting from the reduced duty cycle of the pulsed He(2^3S) atom source, and the need to subtract background counts due to filament radiation-induced photoemission.

The low work function of the Cu/K surface is reflected by the increased width of the observed energy distribution. The large high energy peak results from the potassium 4s valence level located just below the Fermi energy of the K/Cu system.¹⁰⁵⁻¹⁰⁷ The extreme surface sensitivity of MDS is again illustrated by noting that this 4s-level feature, while clearly seen with MDS, is extremely difficult to observe with ultra-violet photoelectron spectroscopy (UPS).^{108,109} Below this 4s-level feature the spectrum is relatively smooth, gradually rising to a peak at the lowest electron energies. Such characteristics are indicative of an atomically clean alkali overlayer.¹¹⁰

4. Discussion

A. Cu(100) and Ni(111) - Chemically Cleaned Case

The observation of large ESP values (of $\approx 70\%$) at chemically cleaned surfaces is consistent with earlier measurements conducted with the Rice flowing helium afterglow apparatus, which is used to study ESP effects in gas-phase Penning ionization reactions. Large ESP values ($\approx 80\%$)¹¹¹ are observed in this apparatus when spin-polarized $\text{He}(2^3\text{S})$ atoms impact chemically cleaned metal parts within the flow tube. As explained in the introduction, a large ESP is indicative of the one-stage Auger de-excitation (AD) or surface Penning ionization (SPI) process (Fig. 4a). On the heavily contaminated metal surface, layers of physi- and chemi-sorbed gas molecules can shield the $\text{He}(2^3\text{S})$ atoms from the metal. As illustrated in Fig. 26, this shielding prevents the He 2s wavefunction from significantly overlapping with the vacant metallic states above the Fermi level and thus makes the probability for energy resonant tunneling of the He 2s electron very low. Since resonance ionization (RI-Fig. 1a) of the $\text{He}(2^3\text{S})$ atom is effectively blocked, de-excitation of the atom can only proceed via surface Penning ionization.

Figure 26. Schematic illustration of a metal surface shielded by adsorbed gas molecules.

Although the spin-polarization of the ejected electrons from the SPI process is large, it is not 100%. Possible explanations for this include the dilution of the ESP by low energy secondary electrons liberated by those electrons produced in the $\text{He}(2^3\text{S})$ atom/surface interaction that are initially directed into the bulk. Such an explanation is prompted by the large low energy peak observed in the energy distributions for chemically cleaned surfaces (Fig. 20). It should be noted, however, that the relative size of this peak clearly requires that not all the low energy electrons be unpolarized as this would result in an ESP value much less than 70%. The reduced polarization could also be due to surface Penning ionization reactions in which spin is not conserved. Measurements with spin-polarized $\text{He}(2^3\text{S})$ atoms in the flowing helium afterglow demonstrate that some gas phase targets do not completely conserve spin angular momentum during Penning ionization.^{112, 113} For example, CO and Cl_2 are observed to conserve $\approx 73\%$ of the incident spin-polarization of the $\text{He}(2^3\text{S})$ atoms. Non-singlet reactant gases such as O_2 and NO exhibit a more dramatic effect, with O_2 conserving only $\approx 30\%$ of the incident spin-polarization.

B. Cu(100) and Ni(111) - Atomically Clean Case

The ESP values obtained from the atomically clean Cu and Ni surfaces are substantially lower than the values obtained after chemical cleaning alone. As explained in the introduction, low ESP values are indicative of the two-step resonance ionization-Auger neutralization (RI+AN) process illustrated in Figs. 1 and 4b. At a clean surface, there are no adsorbed molecules to block or shield the $\text{He}(2^3\text{S})$ atoms from the bare metal surface. Consequently, the He 2s wavefunction can overlap with the empty metallic states above the Fermi level and the 2s electron can tunnel into such a state if He^+ formation is energetically favorable. The energetics of the RI process can be understood by reference to Fig. 27 which schematically illustrates the relevant potential energies as a function of the

particle-surface separation. The zero energy reference is chosen as the combined energy of the ground state, n electron metal $n_e(M)$ and the $\text{He}(2^3\text{S})$ atom at infinite separation. For simplicity, only the attractive portions of the He^+ -metal curves are shown which represent the image-force interaction between the ion and the metal. The potential energies for the neutral He and $\text{He}(2^3\text{S})$ atoms are assumed to be constant until they become repulsive at particle-surface separations comparable to the atomic radii.

Figure 27. Schematic diagram of the potential energy curves for the $\text{He}(2^3\text{S})$ -metal system.

At large atom-surface separations, the energy required to transfer an electron from the 2s level of the He(2^3S) atom to the Fermi level of the metal is given by $E_i^* - \phi$, where E_i^* is the ionization energy of the free He(2^3S) atom and ϕ is the work function of the surface. If $E_i^* - \phi < 0$, as in the case of Ni(111), RI of the atom is energetically favorable at all He(2^3S) atom-surface separations. If $E_i^* - \phi > 0$, as in the case of Cu(100), RI of the atom is energetically favorable only at separations less than some critical separation given by the appropriate curve crossing. Figure 27 shows that this critical separation for Cu(100) is ≈ 20 Å, which is much larger than the radius of the He(2^3S) atom (≈ 1.5 Å). Therefore, RI is energetically favorable at separations where the metastable atom/surface interaction is significant, which is consistent with the observed low ESP values of the ejected electrons.

Although the spin-polarization of the ejected electrons is low, it is not zero, and this has interesting implications. If the ejection results solely from the RI+AN mechanism, then the two surface electrons which participate in the AN process must be of opposite spin, as is evident from the inset of Fig. 21. The spin correlation between the two AN electrons can be explained if the metastable atom/surface interaction is viewed as a localized process and if, as expected from the exclusion principle, there is a higher probability of finding electrons of opposite spin in proximity to each other than of finding electrons with the same spin. Alternatively, the non-zero ESP values could indicate that a fraction of the ejected electrons result from de-excitation in the AD mode. This is considered unlikely, however, because the AD process can only occur at small distances from the surface, where there is significant overlap between the surface electronic wavefunction and the 1s hole of the He(2^3S) atom. In contrast, the RI process, which involves the overlap of the excited 2s orbital with the surface, will occur at larger atom-surface separations. Since the transition rate associated with RI ($\approx 10^{15}$ - 10^{16} sec $^{-1}$)¹¹⁴⁻¹¹⁹ is much larger than that for AD ($\approx 10^{13}$ - 10^{14} sec $^{-1}$),¹²⁰ the RI process should dominate whenever it can occur. If, in fact, ejection results solely from the RI+AN mechanism, it is interesting to note that the

observed surface electron spin-correlation is the same for both Cu and magnetized Ni samples and is independent of sample temperature, even above the Curie temperature of Ni. It should also be noted that the observed spin-correlation value (of $\approx 23\%$) must include any dilution due to unpolarized secondary electrons and thus represents a lower bound on the true correlation.

C. O₂ on Cu(100) - Atomic Adsorbate Case

Subjecting the clean Cu(100) surface to saturation exposures of oxygen at room temperature did not significantly change the spin-polarization of the ejected electrons. The secondary electron energy distribution, however, changed dramatically (Fig. 24). In contrast to the distribution obtained from the chemically cleaned surface, the predominance of low energy electrons in the present case is not associated with a large ESP. The clean surface ESP value obtained from the oxygen saturated surface indicates that the RI+AN de-excitation mechanism remains dominant. This is consistent with the fact that oxygen adsorption at room temperature results in a small increase in the work function of the Cu(100) surface.^{121,122} It has been reported that the $(\sqrt{2}\times\sqrt{2})$ R45 and $(\sqrt{2}\times 2\sqrt{2})$ R45 O/Cu(100) LEED patterns are associated with an increase in work function, $+\Delta\phi$, of approximately 0.3 eV.¹²³ In the context of the potential energy diagram shown in Fig. 27, this small increase in work function makes $E_i^* - \phi < 0$ and thus makes the RI process energetically favorable at all atom-surface separations.

The apparent dominance of the RI+AN process may indicate that the oxygen atoms do not shield the vacant metallic states above the Fermi level from the incident He(2^3S) atoms. This is consistent with azimuthal photoelectron spectroscopy data from the $(\sqrt{2}\times\sqrt{2})$ R45 O/Cu(100) surface which show that the oxygen atoms occupy hollow sites on the Cu surface and are coplanar with the Cu surface atoms.¹²⁴⁻¹²⁶ Although the oxygen atoms

may not act as a shield, their presence on the surface is clearly evident from the changes in the secondary electron energy distribution. If, as the present data suggest, the RI+AN process is dominant, the observed ESP value indicates that the surface electron spin-correlation is unchanged from the clean surface value by the presence of adsorbed oxygen.

D. CO on Ni(111) - Molecular Adsorbate Case

The ESP value obtained at the CO saturated, magnetized Ni(111) surface was $\approx 40\%$. Saturation exposure to CO at room temperature is known to increase the work function of Ni(111) by ≈ 1.3 eV.¹²⁷ Thus, as is evident from Fig. 27, this increase makes the RI process even more energetically favorable than it was before. This fact, combined with the relatively small increase in the observed ESP value, immediately suggests that the RI+AN process remains dominant. Under these conditions, however, it is not unreasonable to expect the adsorbed CO molecules to act as a "molecular blanket" and thus shield the vacant metallic states above the Fermi level from the incident He(2^3S) atoms. With the probability for resonance tunneling of the He 2s electron reduced, the SPI de-excitation mechanism should become more important. Based on the spatial extent of the adsorbed CO molecule (≈ 3.7 Å), it has recently been suggested that saturation CO adsorption effectively suppresses the resonance ionization of the incident metastable atoms.¹²⁸

The present data, nonetheless, indicate that there is a significant contribution from the RI+AN process. Were the SPI process entirely dominant, the spin-polarization of the ejected electrons would have to be substantially diluted to obtain the present value of $\approx 40\%$. Such a dilution could result from unpolarized true secondary electrons and/or from SPI reactions in which spin is not conserved. The CO/Ni(111) energy distribution is, indeed, somewhat peaked toward low energies indicating the presence of true secondaries.

The large ESP value obtained at the chemically cleaned surface, however, indicates that even if a large number of secondary electrons are present, a significant fraction of these must be polarized. The ESP of the ejected electrons can also be diluted by non-spin-conservation in SPI reactions between the He(2^3S) atoms and the adsorbed CO molecules. The possible dilution from such an effect is difficult to estimate, but as stated earlier, CO is known to conserve $\approx 73\%$ of the incident spin-polarization of the He(2^3S) atoms in gas phase Penning ionization reactions. Since it appears unlikely that these effects can account for the required spin degradation, the ESP value obtained from the CO saturated Ni(111) surface strongly suggests a mixture of both the RI+AN and SPI de-excitation processes. Based on less direct evidence, other investigators have reached a similar conclusion.¹²⁹

E. K on Cu(100) - Low Work Function Case

The ESP value obtained at the atomically clean, low work function K/Cu(100) surface ($\phi \leq 2.4$ eV) is only slightly higher than the value obtained from the clean Cu(100) surface alone. Such a small rise would initially suggest that de-excitation of the incident metastable atoms remains dominated by the RI+AN process. The low work function of the K/Cu(100) surface, however, makes this result rather surprising. As illustrated by the K curve in Fig. 27, the large drop in the work function makes the RI process energetically favorable only at atom-surface separations less than ≈ 1.5 Å, which is comparable to the radius of the He(2^3S) atom itself. At these separations, it would not be unreasonable to expect the one-step Auger de-excitation (AD) process to be operative, since it becomes probable when the surface electronic wavefunction overlaps with the 1s hole of the He(2^3S) atom. In light of this, it is sensible to re-examine the K/Cu data in more detail.

Since the width of the 4s valence band in bulk potassium is only ≈ 2.4 eV,¹³⁰ the smooth, rising portion of the observed energy distribution (Fig. 25) at energies below the large 4s peak must be due to true secondary electrons. Comparing the area under this portion of the distribution to the area under the 4s peak shows that the lower energy electrons comprise almost two-thirds the total yield. If these secondary electrons are unpolarized, the ESP associated with the 4s peak would be almost three times the observed average ESP value, i.e. almost 100%, and would be consistent with dominance of the AD process. Clearly, the question as to which mechanism is responsible for de-excitation at the low work function, alkali covered surface hinges on the ESP value associated with the potassium 4s peak. The final resolution of this question must await energy-resolved polarization measurements that discriminate against the low-energy electrons.

6. Conclusion and Future Directions

This thesis reports the first spin-resolved MDS measurements. The present results demonstrate that use of spin-polarized metastable atoms, in conjunction with analysis of the ESP of the ejected electrons, provides a novel and valuable technique with which to study the dynamics of metastable atom-surface interactions. The data indicate that such interactions are more complex than is generally assumed. For example, the results for atomically clean surfaces suggest the existence of spin-correlations between the two surface electrons that participate in the Auger neutralization process. In analysis of MDS spectra from atomically clean surfaces such correlations are ignored and it is assumed that the matrix element characterizing the AN process is independent of the exchange interaction between the two participating surface electrons.¹³¹⁻¹³³ The present data also suggest that, under certain surface conditions, the two de-excitation mechanisms, i.e. RI+AN and SPI, may be operative in parallel. Since the relative contribution from each process cannot be determined from the energy distribution alone, ESP measurements offer the only real hope for detailed interpretation of the MDS spectra obtained under such conditions. The data also clearly indicate, however, that energy-resolved ESP measurements are necessary to answer questions regarding the relative contributions from each process.

Improved energy-resolution can be obtained using a number of different approaches. The first involves use of noble-gas metastable atoms other than He(2^3S) that store less internal energy. We have recently demonstrated that highly polarized ($P > 95\%$) metastable argon (Ar^*) and neon (Ne^*) atom beams can be produced by laser optical pumping with a frequency-modulated multimode dye laser.¹³⁴⁻¹³⁷ Since Ar^* atoms, for example, possess an excitation energy of only ≈ 11.6 eV,¹³⁸ they will produce a narrower ejected electron energy distribution than is generated by the He(2^3S) atoms. This means, in particular, that the total width of the K/Cu(100) energy distribution (Fig. 25) would be reduced by ≈ 8 eV suggesting that true secondary electrons would comprise a much smaller fraction of the

total ejected electron signal. It should be remembered, however, that Ar^* and Ne^* atoms have non-zero orbital angular momentum and even though this moment is initially polarized by optical pumping, it may affect the spin-polarization of the ejected electrons. In addition, thermal energy Ar^* and Ne^* atoms travel at much lower velocities than $\text{He}(2^3\text{S})$ atoms and this may also influence the dynamics of the metastable atom-surface interaction.

A more direct and versatile way to obtain energy-resolved ESP measurements is, of course, to place an energy analyzer between the target sample and the polarimeter. Unfortunately, the efficiency of the present mini-Mott polarimeter is too low to accommodate the transmission losses associated with an in-line energy analyzer. As mentioned previously, a smaller, lower-voltage, "micro-Mott" polarimeter has recently been developed that has an efficiency of $\approx 3 \times 10^{-5}$. This is approximately three times that of the present polarimeter and suggests that energy-resolved ESP measurements may be possible in the near future. Even with energy-resolution, however, it may still not be possible to separately identify the contributions to the total ejected current that result from each de-excitation process and from true secondary electrons.

As noted previously, the spin-polarization of the electrons ejected from an unmagnetized $\text{Ni}(111)$ crystal was observed to be equal, within experimental error, to zero. This interesting effect appears to be due to the random magnetic field directions associated with the domain structure of the unmagnetized sample. Spin-resolved MDS measurements may therefore provide a novel means with which to study surface domain structure and its temperature dependence. Preliminary measurements show, for example, that the spin-polarization of electrons ejected from a chemically-cleaned, unmagnetized $\text{Ni}(111)$ sample, increases rapidly in the immediate vicinity ($\pm 30^\circ\text{C}$) of the Curie temperature. The present measurements clearly demonstrate the considerable potential of spin-resolved MDS studies in probing the dynamics of metastable atom-surface interactions and thus the electronic and magnetic properties of surfaces.

References

1. Blakely, *Introduction to the Properties of Crystal Surfaces*, Pergamon (1973).
2. Feder, J. Phys. C **14**, 2049 (1981).
3. Feder, *Polarized Electrons in Surface Physics*, World Scientific (1985).
4. Rau, J. Magn. and Mag. Mat. **30**, 141 (1982.)
5. Moore, *Atomic Energy Levels*, Vols. I-III, National Bureau of Standards, Circular No. 467, U.S. Government Printing Office (1971).
6. Van Dyck, Johnson, and Shugart, Phys. Rev. A **4**, 1327 (1971).
7. Woodworth and Moos, Phys. Rev. A **12**, 2455 (1975).
8. Roussel, Physica Scripta **T4**, 96 (1983).
9. Conrad, Doyen, Ertl, Kuppers, Sesselmann, and Haberland, Chem. Phys. Lett. **88**, 281 (1982).
10. Conrad, Ertl, Kuppers, Sesselmann, and Woratschek, Surf. Sci. **117**, 98 (1982).
11. Roussel, Boizau, Nuvolone, and Reynaud, Surf. Sci. **110**, L634 (1981).
12. Boizau, in *Inelastic Particle-Surface Collisions*, Taglauer and Heiland, eds., Springer-Verlag (1981), p.49.
13. See for example,
Hagstrum, Phys. Rev. Lett. **43**, 1050 (1979),
Hagstrum, J. Vac. Sci. Technol., **12**, 7 (1975),
Hagstrum, in *Electron and Ion Spectroscopy of Solids*
Fiermans, Vennick, and Dekeyser, eds., Plenum (1978), pp. 273-323.
14. Hagstrum and Becker, Phys. Rev. B **4**, 4184 (1971).
15. Haberland, Lee, and Siska, Adv. Chem. Phys. **45**, 487 (1981).
16. Hagstrum, J. Vac. Sci. Technol., **12**, 7 (1975).
17. Onellion, Hart, Dunning, and Walters, Phys. Rev. Lett. **52**, 380 (1984).
18. Riddle, Onellion, Dunning, and Walters, Rev. Sci. Instrum. **52**, 797 (1981).
19. Rundel, Dunning, and Stebbings, J. Phys. B **4**, 116 (1974).
20. Powell and Craseman, Quantum Mechanics, Addison-Wesley, (1965) pp. 365-367, 454-462.
21. Goldfarb, Nucl. Phys. **7**, 622 (1958).

22. Rabi, Phys. Rev. **49**, 324 (1936).
23. Ramsey, *Molecular Beams*, Oxford (1956), pp.397-402.
24. Onellion, Riddle, Dunning, and Walters, Rev. Sci. Instrum. **53**, 257 (1982).
25. Grant, Surf. Sci. **13**, 35 (1982).
26. Chang, Analytical Auger Electron Spectroscopy,
in *Characterization of Solid Surfaces*, Kane and Larrabee, eds.,
Plenum, (1974).
27. Ertl and Kuppers, *Low Energy Electrons and Surface Chemistry*,
Verlag-Chemie (1974), p. 21.
28. Koike and Hayakawa, J. Appl. Phys. **57**, 4244 (1985).
29. Kisker, Rev. Sci. Instrum. **53**, 114 (1982).
30. Hart, M.A. Thesis, Rice University (1985), unpublished.
31. Farago, in *Advances in Electronics and Electron Physics*,
Vol. 21, L. Marten, ed., Academic Press (1965), p. 24.
32. Mott and Massey, *The Theory of Atomic Collissions*, 3rd ed.,
Oxford (1965), pp. 214-219.
33. Kessler, Polarized Electrons, 2nd ed., Springer-Verlag (1985), pp. 2-6.
34. See ref. 31, pp. 24-30.
35. See ref. 33, pp. 137-141.
36. Eminyan and Lampel, Phys. Rev. Lett. **45**, 1171 (1980).
37. Kirschner and Feder, Phys. Rev. Lett. **42**, 1008 (1979).
38. Kirschner, *Polarized Electrons at Surfaces*, Springer-Verlag (1985), p. 62.
39. Kirschner, in ref.3, pp. 276-282.
40. Pierce, Girvin, Unguris and Cellotta, Rev. Sci. Instrum. **52**, 1437 (1981).
41. Mott, Proc. Roy. Soc. **A124**, 425 (1929).
42. Mott, Proc. Roy. Soc. **A135**, 429 (1932).
43. See ref. 32, Chapter IX.
44. See ref. 33, p. 49.
45. See ref. 33, p. 51.

46. See ref. 33, p. 51.
47. See ref. 32, Chapter IX.
48. See ref. 32, Chapter IX.
49. See ref. 33, p. 57.
50. Sherman, Phys. Rev. **103**, 1601 (1956).
51. Sherman and Nelson, Phys. Rev. **114**, 1541 (1959).
52. See ref. 33, p. 239.
53. See ref. 33, p. 239.
54. J. Van Klinken, Nucl. Phys. **75**, 161 (1966).
55. Campell, Hermann, Lampel, and Owen, J. Phys. E **18**, 663 (1985).
56. See ref. 54, p. 186.
57. See ref. 33, p. 52.
58. See ref. 33, p. 242.
59. Wainwright, Alguard, Baum, and Lubell, Rev. Sci. Instrum. **49**, 571 (1978).
60. Fletcher, Gay, and Lubell, Phys. Rev. A **34**, 911 (1986).
61. Hodge, Moravec, Dunning, and Walters, Rev. Sci. Instrum. **50**, 5 (1979).
62. Gray, Hart, Dunning, and Walters, Rev. Sci. Instrum. **55**, 88 (1984).
63. Unguris, Pierce, and Cellotta, Rev. Sci. Instrum. **57**, 1314 (1986).
64. See ref. 61.
65. See ref. 33, pp. 233-243.
66. See ref. 61.
67. Gray, Giberson, Cheng, Keiffer, Dunning, and Walters,
Rev. Sci. Instrum. **54**, 271 (1983).
68. See ref. 61.
69. Holzwarth and Meister, Nucl. Phys. **59**, 56 (1964).
70. Mikaelyan, Borovoi, and Denisov, Nucl. Phys. **47**, 328 (1963).
71. Heinzmann, J. Phys. B. **11**, 399 (1978).

72. Kisker, Clauberg, and Gudat, *Rev. Sci. Instrum.* **53**, 1137 (1982).
73. Kalisvaart, O'Neil, Riddle, Dunning, and Walters,
Phys. Rev. B **17**, 1570 (1978).
74. Jost, Kaussen, and Kessler, *J. Phys. E* **14**, 735 (1981).
75. Deichsel, Reichart, and Steidl, *Z. Phys.* **189**, 212 (1966).
76. See refs. 38,39, 63, 74,75.
77. See ref. 33, p. 231 and ref. 63, p. 1321.
78. See ref. 60.
79. See ref. 30, pp.130-136.
80. Allison, Dunning, and Smith, *J. Phys. B* **5**, 1175 (1972).
81. Ashcroft and Mermin, *Solid State Physics*, Saunders College (1976), p. 697.
82. Woratschek, Sesselmann, Suppers, Ertl, and Haberland,
Phys. Rev. Lett. **55**, 1231 (1985).
83. Bozso, Arias, Hanrahan, Martin, Yates, and Metiu, *Surf. Sci.* **136**, 257 (1984).
84. Roussel, Boiziau, Nuvolone, and Reynaud, *Surf. Sci.* **110**, L634 (1981).
85. Spitzer and Luth, *Surf. Sci.* **118**, 121 (1982).
86. Papageorgopoulos, *Phys. Rev. B* **251**, 3740 (1982).
87. Mayer, Zhang, and Lynn, *Phys. Rev. B* **33**, 8899 (1986).
88. McDonnell and Woodruff, *Surf. Sci.* **46**, 505 (1974).
89. McDonnell, Woodruff, and Mitchell, *Surf. Sci.* **45**, 1 (1975).
90. Hoffman, Unwin, Wyrobisch, and Bradshaw, *Surf. Sci.* **72**, 635 (1978).
91. Onuferko and Woodruff, *Surf. Sci.* **95**, 555 (1980).
92. Richter and Gerhardt, *Phys. Rev. Lett.* **51**, 1570 (1983).
93. Yang, Jona, and Marcus, *Phys. Rev. B* **27**, 1394 (1983).
94. Netzer and Madey, *J. Chem. Phys.* **76**, 710 (1982).
95. See ref. 94.
96. Erley and Wagner, *J. Chem. Phys.* **72**, 2207 (1980).
97. Conrad, Ertl, Kuppers, and Latta, *Surf. Sci.* **57**, 475 (1976).

98. Christmann, Schober, and Ertl, *J. Chem. Phys.* **60**, 4719 (1974).
99. Bozso, Yates, Arias, Metiu, and Martin, *J. Chem. Phys.* **78**, 4256 (1983).
100. Bozso, Arias, Yates, Martin, and Metiu, *Chem. Phys. Lett.* **94**, 243 (1983).
101. Roussel, Boiziau, Nuvolone, and Reynaud, *Surf. Sci.* **110**, L634 (1981).
102. Decker, *Solid State Physics*, Prentice Hall (1957), pp.228-230.
103. See ref. 82.
104. Holzl, Schutte, and Wagner, *Solid Surface Physics*, Springer-Verlag (1979), p.28.
105. See ref. 82.
106. Lee, Hanrahan, Arias, Bozso, Martin, and Metiu, *Phys. Rev. Lett.* **54**, 1440 (1985).
107. Hagstrum, *J. Vac. Sci. Technol.* **20**, 626 (1982).
108. Woratschek, Sesselmann, Kuppers, Ertl, and Haberland, *Surf. Sci.* **180**, 187 (1987).
109. Heskett, Strathy, Plummer, and dePaola, *Phys. Rev. B* **32**, 6222 (1985).
110. See refs. 82, 106-108.
111. L.G. Gray, private communication.
112. Keliher, Dunning, O'Neill, Rundel, and Walters, *Phys. Rev. A* **11**, 1271 (1975).
113. Gray, Keiffer, Ratliff, Dunning, and Walters, *Phys. Rev. A* **32**, 1348 (1985).
114. Remy, *J. Chem. Phys.* **53**, 2487 (1970).
115. Janev, *J. Phys. B* **7**, 1506 (1974).
116. Janev and Nedeljkovic, *J. Phys. B* **14**, 2995 (1981).
117. Grimly, Jyothi, Bhasu, and Sebastian, *Surf. Sci.* **124**, 305 (1983).
118. Lang, Williams, Himpfel, Reihl, and Eastman, *Phys. Rev. B* **26**, 1728 (1982).
119. Avouris, Demuth, and DiNardo, *J. Phys. (Paris) Colloq.* **44**, 451 (1983).
120. See refs. 15 and 16.
121. See refs. 85, 90, and 102.
122. Delchar, *Surf. Sci.* **27**, 11 (1971).

123. See ref. 86.
124. Kono, Fadley, Hall, and Hussain, *Phys. Rev. Lett.* **41**, 117 (1978).
125. Kono, Goldberg, Hall, and Fadley, *Phys. Rev. Lett.* **41**, 1831 (1978).
126. Kono, Goldberg, Hall, and Fadley, *Phys. Rev. B* **22**, 6085 (1980).
127. Christman, Schober, and Ertl, *J. Chem Phys.* **60**, 4719 (1974).
128. Sesselmann, Woratschek, Ertl, and Kuppers, *Surf. Sci.* **146**, 17 (1984).
129. Bozso, Arias, Hanrahan, Martin, Yates, and Metiu, *Surf. Sci.* **136**, 257 (1984).
130. Moruzzi, Janak, and Williams, *Calculated Properties of Metals*, Pergamon (1978), p. 57.
131. Sesselmann, Woratschek, Kuppers, and Ertl, *Phys. Rev. B* **35**, 1547 (1987).
132. Hood, Bozso, and Metiu, *Surf. Sci.* **161**, 491 (1985).
133. Hagstrum, *Phys. Rev.* **150**, 495 (1966).
134. Lynn, Hart, Jeys, and Dunning, *Applied Optics* **25**, 2154 (1986).
135. Giberson, Hammond, Hart, Lynn, and Dunning, *Optics Letters* **10**, 119 (1985).
136. Giberson, Johnson, Hart, Hammond, Jeys, and Dunning, *Optics Communications*, **52**, 103 (1984).
137. Giberson, Hart, Hammond, Dunning, and Walters, *Rev. Sci. Instrum.* **55**, 1357 (1984).
138. See ref. 5.