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Spin-polarized electron emission spectroscopy (SPEES): A new and novel technique in surface science and ferromagnetism

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SPIN-POLARIZED ELECTRON EMISSION SPECTROSCOPY (SPEES):
A NEW AND NOVEL TECHNIQUE IN SURFACE SCIENCE AND
FERROMAGNETISM

by

KELLEY LYLE WATERS

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

APPROVED, THESIS COMMITTEE

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May 1989
Abstract

SPIN-POLARIZED ELECTRON EMISSION SPECTROSCOPY (SPEES): A NOVEL TECHNIQUE IN SURFACE SCIENCE AND FERROMAGNETISM

by

KELLEY LYLE WATERS

A new technique, Spin-Polarized Electron Emission Spectroscopy (SPEES), capable of investigating surface magnetism, has been successfully developed. SPEES allows us to energy- and spin- analyze electrons emitted during the interaction of a grazing-incidence ion beam with a solid surface. The energy and spin information obtained from the emitted electrons helps us to unravel the processes involved in ion-surface interactions at grazing angles.

SPEES data obtained at Ni(110) picture-frame single crystals exhibit new characteristic features in the electron energy distribution that are strikingly different from that of electron-induced spectra. For the first time, two electron capture measurements, which are sensitive to "local" magnetic order existing on an atomic scale, have been performed at low energies (15-30 keV) at surfaces of the amorphous ferromagnet Fe$_{80}$B$_{20}$; the non-zero electron spin polarization amounts to 55%.

These two new techniques open the way to study surface electronic and magnetic properties with unprecedented sensitivity.
Acknowledgments

I would like to thank many people for their support and help in completing this thesis: my advisor, Prof. Carl Rau, for his guidance and scientific insights; Changming Jin, Guoqiang Xing, Kelly Taylor, Chin-Shuang Lee, Chian Liu, Ming Lu, and Naiqun Chen for their help in the lab and some very interesting discussions.

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Most of all I would like to thank my mother for her love and confidence in me throughout my entire life. Thanks, Mom; without you this would never have happened.
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Chapter I. Introduction

Surface physics involves studies of electronic, magnetic, and chemical properties of surfaces. Different techniques are used to measure each property. In the past 20 years, the use of ion beams to obtain information about surface properties has vastly increased. Results have shown that ion-surface interaction can be used to measure many of the magnetic, electronic, and chemical properties of surfaces.

Surface magnetism is a very interesting field of investigation yielding new and fundamental insights into improved micro-chip technology and into surface catalyzed chemical processes.

Ion-surface interactions at small angles of incidence provide a powerful means to probe the magnetic and electronic properties of the topmost atomic layer of surfaces of magnetic materials. Ions which are scattered at surfaces at grazing angles of incidence can be specularly reflected, thereby not penetrating the surface. This fact shows the extreme surface sensitivity of experimental methods where ion-surface interaction is used to study surface properties.

Particle-surface interactions can also be used to study various electronic transition processes occurring near surfaces as well as the electronic structure of surfaces. If electrons emitted from surfaces are energy and spin analyzed, it is even possible to obtain information on the surface magnetic structure and on the spin dependence of various electronic transition and charge exchange processes taking place near surfaces.
There are a few surface spectroscopies that are extremely surface sensitive, among them are ECS\(^1\)(Electron Capture Spectroscopy), SLEED\(^2\)(Spin-Polarized Low-Energy Electron Diffraction), SPMDS\(^3\)(Spin-Polarized Metastable De-excitation Spectroscopy), SLEPS\(^4\)(Spin-Polarized Low-Energy Positron Spectroscopy), SPPES\(^5\)(Spin-Polarized Photoemission Spectroscopy).

We have developed a new technique, spin-polarized electron emission spectroscopy (SPEES), which uses the ion-induced emission of spin-polarized electrons from magnetic surfaces to obtain data on surface electronic and magnetic structures. The energy and spin dependence of these electrons contains information on ion-surface interactions as well as on the surface magnetic structure of ferromagnetic samples. Further, in this work, we have studied for the first time two electron capture (TEC) processes (see Chapter II A.2) at low kinetic energies (15 keV-30 keV) of the incident ions.

In the following chapters, we discuss various measurements and procedures used to perform these experiments along with a review of different experimental techniques. In Chapter II, we review the principles of ECS and SPEES. Chapter III discusses sample preparation. The experimental apparatus and techniques of the various measurements are examined in Chapters IV and V. In Chapter VI, we review the theoretical background on various methods of electron emission. In Chapter VII, the experimental results will be discussed and in Chapter VIII, we present our conclusions.
Chapter II. Review of Electron Capture Spectroscopy (ECS) and Spin-Polarized Electron Emission Spectroscopy (SPEES)

A. Introduction to Electron Capture Spectroscopy

Electron Capture Spectroscopy (ECS)\(^6\) is an interesting and relatively new approach into probing the electron spin-polarization (ESP) at the surface of magnetic crystals under ultra high vacuum (UHV) conditions. Electron spin-polarization refers to the measure of the spin of an electron oriented along a certain direction. The electron spin-polarization can be described by a polarization vector, \( \mathbf{P} \),

\[
\mathbf{P} = \langle \sigma_x \rangle \mathbf{i} + \langle \sigma_y \rangle \mathbf{j} + \langle \sigma_z \rangle \mathbf{k}
\]

(1)

where \( \sigma_x, \sigma_y, \) and \( \sigma_z \) are the Pauli spin matrices.\(^7\) If we examine one component of this polarization by magnetizing a sample in a particular direction, the \( z \) direction for instance, we can characterize the polarization, \( P_z \), as follows,

\[
P_z = \frac{N^\uparrow - N^\downarrow}{N^\uparrow + N^\downarrow}
\]

(2)

where \( N^\uparrow \) and \( N^\downarrow \) are the fractional occupational densities of electrons oriented anti-parallel and parallel to an external magnetic field (see Figure 1). The polarization, \( P_z \), varies between -1 and 1 using \( N^\uparrow + N^\downarrow = 1 \).
Fig. 1. Definition of ESP in solid state physics (upper part) and in atomic physics (lower part). B is the external magnetic field applied along the +z-axis.\textsuperscript{8}
In ECS, we use the capture of one [one electron capture (OEC)] or two [two electron capture (TEC)] spin-polarized electrons from a sample surface by a beam of D$^+$ or H$^+$ reflected at a small angle. Typically, the scattering angles are less than 3°, mostly around 0.2°. The energy, $E_\perp$, of an ion normal to the surface is given by

$$E_\perp = E_0 \sin^2 \alpha = E_0 \alpha^2$$

(3)

where $E_0$ is the initial ion energy and $\alpha$ the angle of incidence. For ECS, we keep $E_\perp$ small (< 20eV), to avoid the penetration of the ion into the surface. An example of a typical ion beam reflection in ECS can be seen in Figure 2.

The figure shows an ion beam of H$^+$ scattering off of a sample with angle of 2°. The ions scattered off the surface having captured either one, two, or no electrons are represented by the H$^0$, H$^-$, and H$^+$ beam fractions. Further details are given in the following sections.

A.1. Electron Capture Spectroscopy (ECS) using One Electron Capture (OEC) processes

One or two electron capture can occur when a hydrogen or deuteron ion reflects off of a crystal surface. The hydrogen or deuteron ion can be neutralized by the transfer of one electron from the surface to the ion. In the case of a ferromagnetic surface, the electron may be spin polarized. Electron capture will therefore result in the formation of deuterium or hydrogen atoms having a net spin polarization. The spin polarization of the captured electron can be transferred to a nuclear polarization by the hyperfine interaction.
Fig. 2. Scheme of the ion trajectory for a reflection angle of 2° and surface potential plotted on a plane perpendicular to the reflecting surface.⁹
The determination of the nuclear polarization (of the deuterium or hydrogen atom) will provide a measure of the net spin polarization, \( P \), of the captured electrons.

The development of a theory of electron capture is difficult and requires a knowledge of the wave functions of the surface electrons. A description of some of the methods used to describe the electron capture process can be found in a review of ECS by C. Rau.\(^{10}\)

By looking at the distance of closest approach for \( D^+ \) ions on a sample, we can see where the capture of electrons can occur. A calculation using a Thomas-Fermi-Molière potential\(^ {11,12,13}\) on a reflection of \( D^+ \) on Ni(110) and Co(0001) (Figure 3) shows that the distance of closest approach for 150 keV \( D^+ \) is about 2 Å for a scattering angle 0.2°. Therefore, the ions probe in real space only the exponential tail of the electronic wave functions at the surface. This again shows the extreme surface sensitivity of ECS.

This supports the fact that electron capture is a unique method of probing the electron spin polarization at surfaces. As seen in table I-1, we see a very good agreement between the theoretical and experimental electron spin polarization values, \( P \). Table I-1 gives a comparison of theoretical values derived from various band structure calculations to the experimental results of ECS. For further details on the results in Table I-1, see the review article by C. Rau.\(^ {14}\) The agreement is best for Ni.
**Fig. 3.** Thomas-Fermi-Molière surface potentials $U(x)$ for reflection of 150 keV deuterons at Ni(110) and Co(0001); $x$ = distance from the surface in nm.$^{15}$

<table>
<thead>
<tr>
<th>Reflection plane (hkl)</th>
<th>Beam direction $u^w$</th>
<th>Direction of magnetic field</th>
<th>$P(kkl)$ (%)</th>
<th>(Refs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>experiment</td>
<td>band structures</td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(fcc)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>112</td>
<td>111</td>
<td>$-96 \pm 3$</td>
<td>$-65$ to $-100$</td>
</tr>
<tr>
<td>100</td>
<td>012</td>
<td>021</td>
<td>$-65 \pm 1$</td>
<td>$-75$ to $-100$</td>
</tr>
<tr>
<td>111 (fcc)</td>
<td>001</td>
<td>010</td>
<td>$-64 \pm 1$</td>
<td>$-46$ to $-100$</td>
</tr>
<tr>
<td>120</td>
<td>110</td>
<td>112</td>
<td>$-44 \pm 2$</td>
<td>$+15 \pm 1$</td>
</tr>
<tr>
<td>120</td>
<td>001</td>
<td>210</td>
<td>$+15 \pm 1$</td>
<td>$+17$</td>
</tr>
<tr>
<td>110</td>
<td>210</td>
<td>001</td>
<td>$+16 \pm 1$</td>
<td>$+17$</td>
</tr>
<tr>
<td>Co</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(hcp)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1010</td>
<td>0001</td>
<td>1210</td>
<td>$+33 \pm 3$</td>
<td>$+40$ to $-90$</td>
</tr>
<tr>
<td>1120</td>
<td>0001</td>
<td>1100</td>
<td>$+27 \pm 3$</td>
<td>$+80$ to $-90$</td>
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<tr>
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<td>1010</td>
<td>1100</td>
<td>$-41 \pm 2$</td>
<td>$-50$ to $-100$</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(bco)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>112</td>
<td>110</td>
<td>$+31 \pm 2^a$</td>
<td>$-15$ to $-40$</td>
</tr>
<tr>
<td>100</td>
<td>001</td>
<td>010</td>
<td>$+14 \pm 2^a$</td>
<td>$+50$ to $-50$</td>
</tr>
<tr>
<td>110</td>
<td>110</td>
<td>001</td>
<td>$+13 \pm 2$</td>
<td>$+15$ to $-45$</td>
</tr>
</tbody>
</table>

$^a$ Measured at 250°C.

**Table I-1.** Calculated and measured (via ECS) ESP values.$^{16}$
A.2. Electron Capture Spectroscopy (ECS) using Two Electron Capture (TEC) processes

Two electron capture processes probe local magnetic order of samples in contrast to one electron capture processes which measure long range surface magnetic order. This can be seen by the fact that one electron capture can occur anywhere upon the sample surfaces, but two electron capture happens almost exclusively within one magnetic domain upon a surface. The characteristic length within which an incident hydrogen or deuterium ion can capture two electrons is very small, \( \approx 10-20 \, \text{Å} \).\(^{17}\) Thus the electrons captured must originate from the same "local" surface region. This characteristic length is very small compared to the size of magnetic domains. Magnetic domains are typically of the size from one μm to one mm.\(^{18}\)

A \( \text{H}^+ \) ion striking a ferromagnetic sample could capture two electrons which have their spins aligned parallel to each other. On the other hand, a \( \text{H}^+ \) ion striking a non-magnetic sample like copper could capture two electrons which would have their spin anti-parallel to each other. When two electrons are captured, the result is a \( \text{H}^- \) (or \( \text{D}^- \)) ion. The electrons in a ferromagnetic sample would go to a triplet state like the 1s2s state. The electrons in a non-magnetic sample would go into the singlet ground state 1s\(^2\). It is well known that the \( \text{H}^- \) ion has only one stable bound state, 1s\(^2\).\(^{19}\) (The second electron is loosely bound in the 1s\(^2\) state with an energy of 0.92 eV.\(^{20}\)) As a result, the formation of \( \text{H}^- \) ions is suppressed in
ferromagnetic surfaces as compared to that of a non-magnetic sample surface like that of Cu.

Theoretical calculations for the production of H\(^-\) during a surface reflection are non-existent at this time. As an approximation for simultaneous capture of two electrons, we measure the beam intensity ratio of the H\(^-\) to the H\(^+\), \(R = H^-/H^+\), for a ferromagnetic sample and a non-magnetic sample like Cu. We then directly relate these ratios to the corresponding fractional surface electron numbers \(n_{\text{ferro}}\) and \(n_{\text{Cu}}\) (\(n = n^+/[n^+ + n^-]\)) for a ferromagnetic single crystal and Cu, respectively:

\[
R_{\text{ferro}}/R_{\text{Cu}} = n_{\text{ferro}}/n_{\text{Cu}}.
\] (4)

With \(-1 \leq P \leq 1\) and using \(n^+ + n^- = 1\), we have the relation for the fractional electron number given below,

\[
n = (1 - |P|)/2.
\] (5)

With \(P = 0\) for Cu, we have \(n_{\text{Cu}}^+ = n_{\text{Cu}}^- = n_{\text{Cu}} = 0.5\). We then obtain the polarization as given below,

\[
|P_{\text{sample}}| = 1 - (R_{\text{sample}}/R_{\text{Cu}}).
\] (6)

This provides a measure of the "local" ferromagnetic order existing at a surface on an atomic scale. A comparison of some TEC results is given Table I-2. From the results, the TEC values for the electron
spin polarization (ESP) compare very well to the OEC values for Ni. While TEC doesn't give the sign of the polarization, it gives the magnitude of the polarization. This shows that TEC, besides being sensitive to short-range ferromagnetic order, is extremely useful for looking at unknown surfaces and checking if they are ferromagnetic.

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>ECS</th>
<th>PES</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TEC</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$R_{Ni} \times 10^3$</td>
<td>$R_{Cu} \times 10^3$</td>
</tr>
<tr>
<td>(110)</td>
<td>0.25</td>
<td>5.70</td>
</tr>
<tr>
<td>(100)</td>
<td>1.45</td>
<td>5.25</td>
</tr>
<tr>
<td>(111)</td>
<td>3.05</td>
<td>5.75</td>
</tr>
<tr>
<td>(120)</td>
<td>4.62</td>
<td>-</td>
</tr>
<tr>
<td>polycr.</td>
<td>-</td>
<td>5.37</td>
</tr>
</tbody>
</table>

*Table 1-2.* Experimental data of ESP using ECS on Ni.\textsuperscript{22}

B. Introduction to the novel technique of Spin-Polarized Electron Emission Spectroscopy (SPEES)

Spin polarized electron emission spectroscopy (SPEES) is a novel method of probing a magnetic or non-magnetic surface with an ion beam at glancing angles and examining emitted electrons. At
present, we examine the electrons emitted normal to the surface to obtain data on surface electronic and magnetic structures. The ion beam is used again, as in ECS, at glancing angles to keep the energy component, $E_\perp$, normal to the surface as small as possible, thereby preventing a penetration of the ions through into the bulk.

**B.1. Technique of SPEES**

To examine the electrons emitted after the interaction between the ions and surface, we use an electron detector (see Figure 4) capable of energy and spin analysis of the emitted electrons. We use a so-called low-energy electron spin-polarization detector (see Chapter IV.C). Other Mott-type spin polarimeters use higher electron acceleration energies, typically in the 20 to 30 keV region or at around 100 keV. The electrons emitted normal to the surface are energy-analyzed to obtain more detailed information on the physical processes involved in the ion-surface interactions.

**B.2. Spin Polarimetry**

Electron spin-polarization is difficult to detect. The largest electron spin-dependent effects during the interaction of electrons with matter are the spin-orbit interaction and the exchange interaction. Both are always present and interfere with each other, but for certain conditions, each one can be dominant. The exchange interaction originates from the antisymmetrization of the wave
Detection of Spin-Polarized Electrons using SPEES

\[ H^+ \rightarrow e^- \]

Ion-induced emission of spin-polarized electrons

**Fig. 4.** SPEES detector and experimental set-up.
function as required by the Pauli principle. The exchange interaction is the strongest in the scattering of polarized electrons at spin-polarized single atoms or solids.

The spin-orbit interaction term is dominant in processes involving high Z, non-magnetic materials like W, Au, or Hg which have Z = 74, 79 and 80 respectively. The spin-orbit interaction comes from the interaction of the electron spin with its own orbital angular momentum. The spin-orbit interaction $V_{so}$ for electron scattering from an atom is given by

$$V_{so} = \frac{1}{2m^2c^2} \frac{1}{r} \frac{dV(r)}{dr} \mathbf{s} \cdot \mathbf{L}$$  \hspace{1cm} (7)$$

where $r$ is the position of the electron relative to the atom with spin, $\mathbf{s}$, and angular momentum, $\mathbf{L}$. The angular momentum is along the normal to the scattering plane. For a Coulomb potential $V(r) = -Ze^2/r$, we have then

$$V_{so} = \frac{e^2}{2m^2c^2} \frac{Z}{r^3} \mathbf{s} \cdot \mathbf{L}$$  \hspace{1cm} (8)$$

The spin detectors developed today are designed to use the spin-orbit interaction to measure the spin-polarization of electrons. The method of measurement is to focus a beam of electrons on a high Z target like W, Au, Hg, or U. The back-scattered electrons are then detected. The intensities in two directions give a measure of one component of the polarization. The resulting asymmetry $A$ is defined as

$$A = \frac{I_{90} - I_{270}}{I_{90} + I_{270}}$$
\[ A = \frac{N_l - N_r}{N_l + N_r} = PS(\theta) \quad \text{(9)} \]

where \( N_l \) and \( N_r \) are the respective electron intensities, \( P \) is one component of the total polarization \( P \), and \( S(\theta) \) is the so-called Sherman function\(^{25,26}\). The Sherman function is a measure of the analyzing power. It can be obtained by scattering a beam of electrons of known polarization \( P \) and measuring the resulting asymmetry \( A \). The polarization is then given as follows:

\[ P = \frac{1}{S(\theta)} \frac{N_l - N_r}{N_l + N_r} \quad \text{(10)} \]
Chapter III. Sample Preparation

A. Sample Preparation

Surfaces of samples need to be well-prepared and well-maintained (atomically clean, flat etc.) for reliable UHV experiments. Some samples like the amorphous magnet Fe_{80}B_{20} need to be carefully mounted. Fe_{80}B_{20} is available in the form of polished ribbons which need to be mounted around the sample holder in a continuous loop. This allows for a closed magnet shunt. Other sample surfaces like those of Ni(110) picture-frame crystals need to be precisely aligned, polished and annealed before they can be used for the SPEES or ECS experiment.

In the following paragraphs, we describe the steps necessary for preparing our samples for experiments, and in particular we will report in detail on the preparation of Ni(110) picture-frame crystals.

We start with a single crystalline boule of a metal crystal, typically 30 mm long and around 20 mm in diameter. The orientation of the boule is close to a low-index (hkl) crystalline direction. Initially, the boule is mounted on a X-ray Laue machine, and then after a precise surface orientation is obtained, sample holder and sample are moved together to a diamond wire saw to cut the crystal along the desired (hkl) plane. The surface is further aligned using a GE X-ray Laue machine. The principles of X-ray diffraction are well known,27 and therefore, we give only a brief discussion.
In this method a parallel beam of polychromatic X-rays is collimated and directed onto the surface of a crystal. The Bragg condition for X-ray diffraction is

$$n\lambda = 2d\sin\theta$$  \hspace{1cm} (11)

where \(n\) is an integer (order of diffraction), \(d\) is the spacing between the atomic planes, \(\lambda\) is the wavelength of the X-rays, and \(\theta\) is the reflection angle. The angle \(\theta\) and the distance \(d\) are fixed so that each reflection plane of the crystal selects from the polychromatic incident X-ray beam a wavelength which satisfies the Bragg law (see Figure 5).

The diffracted beams, altogether forming a diffraction pattern on a film, reproduce the structural properties of the crystal. The symmetry of the reflection pattern indicates the accuracy of the geometric alignment of the crystal. If the center of the symmetry is in the center of the photo, then a specific crystallographic orientation is parallel to a desired geometric orientation.

Initially, the sample boule is etched to remove any possible surface damage. The boule is then placed on a sample holder and an initial X-ray photo is taken to determine a \((hkl)\) plane parallel to the cylindrical axis of the crystal. The desired symmetry center is then oriented towards the middle of the photo by adjusting the sample holder until the center of the symmetry is within \(p = 1.0\) mm of the center of the film.

The accuracy of the alignment depends on the orientation of the sample manipulator and distance to the film, \(s\). The misorientation of the sample is given by the expression
\[ \theta = 0.5 \arctan \left( \frac{p}{s} \right) = 0.5 \left( \frac{57p}{s} \right) \quad (12) \]

where \( p \) is the distance of "mis-alignment" in mm and \( s \) is the distance between the sample and film in mm. The misorientation angle, \( \theta \), between the crystallographic and geometric surface orientations will then be given in degrees with the above equation. So, for a typical "mis-alignment" distance, \( p = 1 \) mm, and a sample distance, \( s = 57 \) mm, we obtain a misorientation, \( \theta \), of 0.5°.

After the sample has been aligned to within 0.5°, we cut it to the desired size by using a Laser Tech diamond wire saw using a 0.008" diameter and 45 \( \mu \)m grain size diamond wire. A diamond wire saw is used so that the damage done by the cutting procedure is kept to a minimum. The wire saw has the wire perpendicular to the axis of the sample to be cut. The sample holder used on the diamond wire saw is designed to fit on the Laue machine as well, so that we keep the alignment of the sample. After cutting the sample to the desired size, the sample is then chemically etched to remove damaged layers introduced by the cutting. The sample is then mounted on our X-ray diffractometer sample holder with an etched face of the desired surface plane exposed for further alignment.

An X-ray diffractometer is also based on the use of the same Bragg law. The diffractometer uses the Bragg law in a slightly different manner. An X-ray diffractometer fixes an atomic plane spacing, \( d \), of a particular crystal plane orientation and uses a monochromatic beam of X-rays. So, for the strongest Bragg peak, \( n = 1 \),
\[ d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \]  

(13)

and

\[ \theta = \sin^{-1}\left(\frac{\lambda}{2d}\right) \]  

(14)

where \( h, k, \) and \( l \) are Miller indices of a particular plane, \( d = \) spacing between planes and \( a_0 \) is the lattice constant for the material in question. The diffractometer has a source that emits X-rays that are sent through a monochromator. These monochromatic X-rays are scattered off of our sample which is held in a special manipulator that allows us to align samples to within 0.01°.

The sample surface is set at an angle of \( \Theta \) with respect to the incident beam, and the X-ray detector is set at an angle of 2\( \Theta \) with respect to the incident beam (see Figure 5). The sample holder has four screws that define two planes, one in the horizontal direction and one in the vertical direction, which can rotate about a fixed point (see Figure 6). The sample holder and the detector are on two rotatable manipulators which are controlled by a computer and rotatable in steps of 0.01°. Initially, the sample surface is brought parallel to the beam, \( \Theta = 0° \), then both, the holder and the detector, are rotated to their calculated (from equation 14) \( \Theta \) and 2\( \Theta \) angles, respectively. By adjusting screws in one of the planes (vertical or horizontal), we maximize the count rate in the detector. A computer scan of the specific \( \Theta \) angle where the sample holder is located is done in steps of 0.01°. The screws are adjusted until the maximum intensity is seen at the proper angle. The sample is then rotated
180°, and again a Θ-scan is done at this position to check that the maximum intensity is also seen at this proper angle. Next the sample is rotated 90° and the same procedure is repeated again for this plane. This method is repeated until the surface orientation of the sample is exact within 0.01°.

![Diagram of X-ray tube, Monochromator, Sample and holder, and Detector](image)

**Fig. 5.** Schematics for x-ray diffraction.

The next step in the preparation of the sample is the polishing. The sample is lapped on sandpaper while it is still on the same X-ray holder. The sample is then transferred to a commercial Logitech polishing jig and polished on a lead-tin polishing plate with diamond paste from 6 μm to 1 μm grain size lubricated with polishing oil. The result is a highly polished flat surface.

After polishing, the sample is ready to be put into our UHV chamber for more cleaning. Initially, the sample is high temperature
heated in a H$_2$ gas atmosphere to promote flattening of the surface and to clean anneal the sample. This is done in a separate chamber with an electron bombardment heater. The temperature of the anneal varies depending on the melting point of a sample. Typically, it is 200-300 K below the sample's melting point. After the high temperature anneal, the sample then goes into the experimental test chamber.

The main cleaning procedures after the sample is in the main chamber are Ar$^+$ ion sputtering and thermal annealing. Sputtering is the term given to ion bombardment of the sample to clean it from contamination. In this process, part of the kinetic energy of the Ar$^+$ ions is dissipated into the surface atoms.$^{28}$ Some of these surface atoms are removed and are called "sputtered" particles. Most of these particles originate from the topmost surface layers.$^{29}$ This allows us to remove all surface contaminants and adsorbates. The disadvantage of sputtering is to cause surface damage. To restore
the single crystalline state of the surface, we anneal the sample for a period of time. The annealing will also cause dilute impurities to diffuse to the surface from the bulk. This calls for repeated cycles of sputtering and annealing to perfectly clean the surface.

B. Preparing a Ni(110) Picture-frame Crystal

A major part of our sample preparation was preparing a Ni(110) picture-frame crystal. As the name implies, a picture-frame crystal is shaped like a picture-frame (see Figure 7). This is done so that we can magnetize the sample in one domain by wrapping a coil around one leg of the crystal. The magnetic field will then be contained in the sample itself in a closed magnetic loop and stray magnetic fields can be completely avoided.\(^{30}\) Nickel has an easy magnetization axis of the \([111]\) direction.\(^{31}\) So, for this reason, we cut the nickel sample along the \([111]\) directions as we determined from the Laue photo. Our sample is about 9 mm by 9 mm with a 3 mm parallelogram in the middle.

We started with a Ni boule surface-oriented in the \([110]\) direction. Before the Laue photo could be performed, the face of the boule needed to be etched to remove damaged layers caused by cutting. The solution for etching the boule face was HF/HNO\(_3\) in a 1:1 mixture. The Laue photos were then taken to orient the boule axis to within 0.5°. We then cut the sample to the desired width, about 3 mm. After obtaining the Laue photo, we analyzed the photo and determined the \([111]\) and \([111]\) directions. The sample was then cut
Fig. 7. Ni(110) picture-frame single-crystal

along these directions leaving the sample looking like a parallelogram (see Fig. 7).

The sample was etched again to remove the damaged layers. The crystal was then aligned with the X-ray diffractometer setup reported on earlier. The source used was a Cu-target with a $K_{\alpha}$-wavelength of $\lambda = 1.542 \, \text{Å}$. The angles for the settings of the sample holder and the detector are found by using equation 14 and equations 15 and 16.

$$d = \frac{3.52 \, \text{Å}}{\sqrt{1^2 + 1^2 + 0^2}} = 2.49 \, \text{Å} \quad (15)$$
\[ \theta = \sin^{-1}\left(\frac{1.542}{2(2.49)}\right) = 18.04^\circ \] (16)

The sample was aligned to within 0.01° using the procedure mentioned before. The sample was then was lapped with sandpaper. The middle of the crystal was cut out next to form the desired picture-frame shape.

The center parallelogram must be carefully removed to keep the number of dislocations at a minimum. A wire saw is difficult to use. A good tool to use for removing the middle of the sample is a spark cutter. A spark cutter creates a spark discharge between a cutting tool and sample in a dielectric medium. The spark removes material from both the sample and the cutting tool. The sample is grounded and placed in a dielectric bath (we used the dielectric kerosene). The cutting tool, made in the shape of the hole to be cut, is placed at a voltage of 200 Volts. The cutting tool is then slowly lowered until there is a constant preset current between the tool and the sample. This current determines the cutting speed. Material is then removed from both the sample and the tool. Kerosene flows through the tool to float away the cut material. The sample must be carefully aligned before cutting and a slow cutting rate was chosen to keep the number of new dislocations to a minimum. The cutting of the picture-frame crystal took about 4-5 hours. The result is a sample with a hole of about 3 mm by 3 mm with the correct easy-axis orientation along [111] direction.

Using the method described earlier, the sample was then polished in with 1 µm diamond paste until a smooth flat polished
surface was obtained. The polished Ni(110) picture-frame crystal was placed in a small chamber for high temperature annealing. The crystal was annealed to 1000°C for 5 - 6 hours in a hydrogen atmosphere of $10^{-6}$ Torr and then slowly cooled at a rate of 100°C/hr. The sample was then placed in the main experimental chamber. The sample was sputtered and annealed to 350°C repeatedly in the main chamber. After the cleaning was completed, the Ni(110) picture-frame sample was ready for measurements to be performed.
Chapter IV. Experimental Apparatus and Techniques

The ECS experiment is set up in an UHV chamber (see Fig. 8). The apparatus consists of two parts, the ion source and the experimental chamber. The ion source and its operation is discussed in section A, and the experimental chamber is described in section B.

A. Ion Source

We use an IONEX model number 501 ion source (see Figure 8) which operates at 100 W and 80 MHz. It is a radio-frequency (RF) gas discharge ion source. The gas inlet [1] in Fig. 8 allows hydrogen or deuterium gas into the discharge tube where the RF oscillator [3] ionizes the gas thus producing a gas discharge. The solenoid magnet [2] then focuses the gas discharge along the center of the tube and it also increases the pathlength of the excited electrons there, allowing for a very efficient ionization. The ions are then forced out from the discharge tube by a probe tip [4] which is at a positive voltage of 4 kV with respect to the ion source assembly. This pushes the ions out of the discharge tube. The ions leave through the exit canal [5] of diameter 0.053"-0.062". The channel or canal is made of aluminum to insure a high H⁺-ion yield. Aluminum has been found to give the highest yield of monoatomic H⁺. Typically, the H⁺ yield is about 85% of the total H beam current. The beam divergence is also a function of the channel geometry. The channel is designed to keep the beam divergence at a minimum while insuring a high H⁺
ion yield. The channel erodes in time by sputtering processes due to the ion beam and needs to be replaced to keep the source operating at optimum conditions.

The ion source discharge tube is assembled with a vinyl sealing compound (polyvinyl-acetate) which has a low vapor pressure. This method of sealing also enhances the H⁺ output as compared to sealing the ion source with a regular O-ring. The hydrogen is introduced into the discharge tube through a palladium leak valve. A palladium leak valve is used to provide a clean source of hydrogen or deuterium. Palladium, when heated, becomes diffusive to hydrogen (or deuterium) allowing these gases to penetrate through while inhibiting the diffusion of other gases into the system.

After leaving the extraction channel, the ion beam is accelerated to 20 keV by a gap-einzel lens assembly [6]. The source area is placed at a potential of +20 kV while the gap lens is grounded. The gap lens is shaped somewhat like a cone at the end of a cylinder with an aperture in the middle. The entire lens assembly is positioned directly after the ion source. After the beam is extracted and accelerated by the gap lens, it is focussed by the einzel lens. The einzel lens consists of three cylindrical lenses. The lens on each end is grounded and the lens part in the middle is placed at high voltage. It can be operated in the accel.-decel. mode or the decel.- accel. mode depending on the sign of the applied voltages and the charge of the particles to be focussed. After leaving the einzel lens, the ions enter the experimental chamber through a 1" aperture.
Fig. 8. Experimental Apparatus
B. ECS Experimental Apparatus Setup

The experimental apparatus is also seen in Figure 8. The H⁺ ions enter the chamber from the ion source area and are then extracted and focused in the lens area. This method produces a beam of about 5 mm which then goes through two sets of parallel plate beam steerers [7,8] which move the beam in the left/right and up/down directions, respectively. After the initial steering, the beam passes through two apertures [9,10], which are 1.0 and 0.5 mm in diameter. These apertures determine the beam size. The area around the apertures is shielded to prevent secondary electrons produced by the ion beam striking the apertures from entering the experimental area.

The beam is aligned and adjusted for maximum intensity by allowing the beam to pass through two more sets [12,13] of steering plates to allow us more steering of the beam. The beam is directed into a Faraday cup [14] situated in the center of the beam line. The beam current is maximized into the Faraday cup before reflecting onto the sample.

The beam emerging from the apertures is a well-collimated beam of ions with a beam width of 0.5 mm and a divergence of about 0.2°. The beam is then deflected onto the sample by a parallel plate condenser [11]. These plates turn the beam onto the sample [15], which is about 4 mm off axis from the beam axis. The ions strike the sample at a glancing angle and are specularly reflected from the sample. The specularly reflected beam is then directed and analyzed further along the beam line.
We also have two fluorescent screens [16,17] which can be inserted into the beam path to observe the initial beam and the reflected beam. The first screen [16] has two vertical slits to allow only a portion of the reflected beam to be examined by the detector. The slits are about 1.0 mm and 0.5 mm in width. These slits are used to screen the reflected beam which illuminates a large portion of the Faraday cup and detector area [14]. We can also use the screen to block out the part of the initial beam which does not hit the sample. The left/right steering plates [13] behind the sample are used to split the reflected beam into its components (ie. H\(^+\), H\(^0\) and H\(^-\)). The ions can be directed over to the surface barrier detectors [14] for intensity and energy measurements.

As seen in the equation below, the beam always has a portion not covering the sample surface unless the sample is very large,

\[
l_s = \frac{w_b}{\sin \theta},
\]

where \(l_s\) is the length of a sample a beam is capable of illuminating, \(w_b\) is the beam width and \(\theta\) is the scattering angle.

**Fig. 9.** Schematics of an ion beam scattering off of a sample.
Varying the scattering angle for a given incident beam width of 0.5 mm, we can see, from Table IV-1, how long the sample must be for the beam to be entirely scattered off the sample.

<table>
<thead>
<tr>
<th>$\theta$ (°)</th>
<th>$l_s$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>28.6</td>
</tr>
<tr>
<td>1.5</td>
<td>19.1</td>
</tr>
<tr>
<td>2.0</td>
<td>14.3</td>
</tr>
<tr>
<td>2.5</td>
<td>11.4</td>
</tr>
<tr>
<td>3.0</td>
<td>9.55</td>
</tr>
<tr>
<td>3.5</td>
<td>8.18</td>
</tr>
</tbody>
</table>

*Table IV-1.* Examples of the minimum sample length needed for the beam to be entirely on the sample.

Several design calculations were necessary to calculate the voltage ranges needed to steer the ion beam and also to move the beam for reflection and for detecting the charged particles. The main calculation was regarding the parallel plate beam steerers (see Fig. 10). These plates have one side at grounded potential and the other side at a certain voltage. A sketch of a set of the beam steering plates is seen in Figure 10. In Figure 10, $l$ represents the length of the plates, $w$ is the width between the plates, $\theta$ is the angle of deflection and $\Delta y$ is the distance of deflection off the straight beam path at the exit of the beam deflectors.
**Fig. 10.** Beam Steering Plates

Below, a short calculation is given to extract the distance of deflection, $\Delta y$, and the angle of deflection, $\theta$, for a given initial acceleration voltage, $V_1$, a given deflection voltage, $V_2$, the width, $w$, and the length, $l$.

Energy of $H^+ = m(v_y)^2/2 = eV_1$

E-field between plates = $E = V_2/w$

$\Rightarrow$ so: $a_y = eV_2/mw$

the time between the plates, $t \equiv l/v_x$

$v_y = v_{oy} + a_yt = v_{oy} + la_y/v_x$

now initially $v_{oy} = 0$; so $\Delta y = \frac{(v_y)^2}{2a_y}$,

thus $\Delta y(l) = l^2V_2/4wV_1$ \hspace{1cm} (18)

also $\theta = \tan^{-1}(v_y/v_x) = \tan^{-1}(lV_2/2wV_1)$. \hspace{1cm} (19)

Again $\Delta y$ represents the off-axis beam deflection at the exit of the beam steerer and $\theta$ is the angle of deflection of the beam off of the initial horizontal axis.
The sample sits on a sample holder [15] which allows two degrees of freedom in the sample orientation. We can rotate the sample through an arc of about 40° which is more than enough needed to reflect the ion beam for a glancing-angle reflection. We also have the ability to move the sample up or down with respect to the beam a distance of about 30 mm. This gives us a chance to scan the beam across the sample in one dimension.

The UHV chamber is also equipped with other items necessary to make UHV measurements. We have a variable energy ion sputter gun [18] (see Fig. 8) with an energy range of 900 eV to 7000 eV to clean (or sputter) the sample. This ion sputter gun operates by using a cold cathode discharge. An annular anode sits at a high potential (900 V to 7000 V) in the middle of a cylindrically grounded gun. Fast electrons are trapped in an electric saddle-field produced by the geometry of the gun.\textsuperscript{32} These fast electrons are then oscillating through the anode back and forth sustaining an ion plasma (normally Ar\textsuperscript{+}). The positive ions are then accelerated out along the axis of the gun. In the process, the ions collide with the fast electrons which can create a neutral beam of Ar\textsuperscript{0} used to clean the sample. The sputter beam typically consists of about 30-70 % neutral Ar atoms. The chamber also has other normal vacuum chamber devices such as, a quadrupole mass spectrometer used primarily for leak detection, and a UHV ion gauge for pressure measurements.

After the ion beam has been specularly reflected off the sample, several components of the specularly reflected beam can be analyzed for the TEC measurement. A silicon surface barrier detector is used
to measure the intensity of the ions. Our surface barrier detector has an active surface area of 7 mm². To protect the detector from receiving too many particles, we placed a 50μ aperture in front of the detector. Surface barrier detectors³³ operate by creating an electric field in the Si wafer resulting from an externally applied bias voltage between the front and rear of the detector. Free charge carriers created by the ionizing radiation or particles striking the silicon are separated by the electric field. The integration of this current produced by the particles yields a charge proportional to the energy of the incoming particle.

The detector outputs a signal to a ORTEC 120-3F preamplifier. The signal then goes to an ORTEC 572 amplifier which sends the signal to an ORTEC ACE MCA interface board, which sums the number of counts, in an IBM-XT computer. This can be seen in Figure 11. The preamplifier is designed to be used with a cooled detector. We cooled the surface barrier detector via a liquid nitrogen cooling reservoir. Cooling the detector extremely lowers the background noise level. This allows us to detect the TEC signal above the background noise level. Typical count rates obtained for H⁻ and H⁺ are 100 - 300 cts./sec. and 10000-30000 cts./sec., respectively.

C. SPEES Experimental Setup

SPEES uses the same experimental chamber and system as the ECS system described previously in section B. The difference between the ECS measurement and the SPEES measurement is the
Fig. 11. TEC detection electronics.
particles that are detected after the ion beam scatters off the sample.

In ECS using TEC, we measure only the ion beam components of the specularly reflected beams, and in SPEES we use a "low-energy diffuse scattering" spin polarimeter with energy analysis to measure the electrons emitted normal to the sample surface. The SPEES measurement only needs a spin polarimeter with energy analysis installed into the ECS system.

The low energy electron spin detector was developed to allow us an alternative method of measuring the spin polarization of a ferromagnetic sample. The detector used for our measurements is shown in Figure 12. The SPEES detector is placed normal to the sample surface directly below the Ar sputter gun shown in Figure 8. The detector is placed about 20 mm in front of the sample surface. The detector consists of three basic parts, the extraction lens and beam focusing area, the electrostatic energy analyzer, and the electron spin analysis region. In the following paragraphs, we'll discuss these parts.

The first part is the extraction lens and the beam focusing system. The first lens [1] in Fig. 12 in the detector is the extraction lens and it is also the first lens in the first einzel-lens set [2] to initially focus the beam. This lens is placed at a positive voltage, normally 0 to +90 volts, with respect to ground. The sample is grounded. An aperture [3] of .125" is placed in front of this lens which gives an acceptance cone of about 11°. This lens serves to accept the electrons into the SPEES detector. The first three lenses
Detection of Spin-Polarized Electrons using SPEES

Electrostatic Energy Analyzer [4]

[2]

[5]

[3]

[1]

Ni

H⁺ H⁻ H⁰
Ion-induced emission of spin-polarized electrons

Detector for electron spin [8]

Channeltron A

Channeltron B

Au-Al target

Au evap. source

e⁻
e⁻

Fig. 12. SPEES detector and experimental set-up.
make up the initial einzel-lens which focusses the beam into the energy analyzer. As stated earlier, the first and third lens are at the same voltage and the middle part is adjusted to focus the electron beam at the entrance to the energy analyzer.

The next section of the detector is the electrostatic energy analyzer [4] (see Fig. 13). The energy analyzer is a radial cylindrical analyzer and passes only particles of a certain energy range. The radial cylindrical design produces a radial electric field which bends the path of the charged particles (in this case electrons) without rotating the spin. The radial electric field is given by the following equation,

\[ E_r = \Delta V/r(\ln(c/a)), \]

(21)

Fig. 13. Electrostatic energy analyzer [4].

where a, b, and c are the inner, mid, and outer radii of the energy analyzer, respectively. The entrance and exit apertures are w and w'. \( \Delta V \) is the voltage difference between the inner and outer
surfaces, which typically is varied between 25-60 Volts. The energy of a particle entering the initial aperture, $w$, and exiting the final aperture, $w'$, of the analyzer is given by the following expression,

$$E_0 = qΔV/2\ln(c/a) - V_{ref} + Δ\phi$$  \hspace{1cm} (22)

where $V_{ref}$ is the reference voltage of the lens [5] before and after the energy analyzer, typically we have this voltage at 0 to +30 V, and $Δ\phi$ is the difference in work function between the sample and analyzer. The value of our analyzer constant, which is the quantity $2\ln(c/a)$, is 1.022. The energy resolution is given by the following term to first order,

$$ΔE/E = w'/b + 4/3 \, α^2.$$  \hspace{1cm} (23)

where $w'$ is the width of the exit aperture and $α$ is the angular divergence of the electron beam at the entrance aperture.

After the electrons pass through the energy analyzer, they proceed through a second set of focusing lenses [7] and a beam steering lens [6]. This allows for a well-focussed beam of electrons entering the spin analysis section. The spin analysis section [8] is a "low energy diffuse scattering" spin detector based on the original version developed by Pierce, Unguris and Celotta.\textsuperscript{34} We accelerate the electrons to 150-eV and scatter them off of a high-Z target such as Au. By detecting the backscattered electron intensities in two
channeltrons positioned at an angle of 135° relative to the initial beam direction, we get a measure of one component of the spin polarization, P.

The Au target is kept at a voltage slightly higher than surrounding surfaces so as to focus the electrons onto our 2 mm Au target. To provide a clean Au target, we evaporate Au onto a 2mm Al pin. We can evaporate Au on the target by simply rotating the target 180° to face the Au evaporator. The Au evaporator is a 40-mg drop of Au melted at the tip of a 0.25 mm tungsten wire. On the other side of the Au target is an Al target which is used to calibrate the polarimeter for zero polarization (see [8] in Fig. 12).

There are two grids located in front of the channeltrons. The first grid serves to set up a field-free region when the electrons enter the spin detector. The second grid is used to screen out the low-energy inelastically scattered electrons and is placed at a potential of 50 Volts. Pierce et al. found that relevant polarization information is found from inelastically scattered electrons of energies above 40 eV. For this reason, we placed the second grid at lower voltage with respect to the field-free region to accept electrons scattered with energies above 100 eV into the channeltrons. The polarization is then found from the following equation,

$$ P = \frac{1}{S(\theta)} \frac{X - 1}{X + 1} \quad (24) $$

where X is the ratio of the count rates in channeltron A to the count
rates in channeltron B and \( S(\theta) \) is the Sherman function. In our case \( S(\theta) = -0.11 \pm 0.02 \). In case of U, \( S(\theta) = -0.25 \). \(^{36}\)

Equation (24) is for scattering from a perfectly aligned beam with no instrumental asymmetries. The problem is that for each instrument there is some instrumental asymmetries. \(^{37}\) To correct for instrumental asymmetries, we can change the polarization of the incident beam of electrons. We can change the electron beam polarization by changing the magnetization of the sample. This flipping of the polarization allows us to eliminate any instrumental asymmetries. To explain this, we observe the counts in each detector. These are given by \( N_i \) and \( N_r \). As seen in equation (25) below, the ratio of the counts is given by the polarization of the incident electrons, \( P \), the Sherman function, \( S(\theta) \), the term describing the instrumental asymmetry, \( \delta \).

\[
\frac{N_i}{N_r} = \frac{1 + PS(\theta)}{1 - PS(\theta)} \delta \tag{25}
\]

Now, after flipping the polarization, the ratio will be given by equation (26).

\[
\frac{N_i}{N_r} = \frac{1 - PS(\theta)}{1 + PS(\theta)} \delta \tag{26}
\]

Now, we can eliminate \( \delta \) and get,
\[ P = \frac{1}{S(\theta)} \frac{X - 1}{X + 1} \]  

with \( X = \sqrt{\frac{N_r N_i}{N_r' N_i'}} \).

This corrects for the instrumental asymmetry. For a more detailed examination of ways to correct for errors in the polarization measurement, we refer to an article by Kessler. For further details, we refer to Zhang's master thesis which gives a summary that is easier to understand.
Chapter V. Experimental Measurements

A. General Experimental Methods

In this chapter, I will discuss the method we used to make our experimental measurements. The first section will be concerned with the general use of the ion beam, and the next sections will deal with the specifics of the measurements performed. These specifics consist of the particular ECS and SPEES measurements performed in this thesis.

In any of our measurements using the chamber, discussed previously in Chapter IV, we use a hydrogen ion beam to perform the measurements. First we warm up the palladium valve for about 20-30 minutes. This is a sufficient time for enough hydrogen to enter the source bottle to offer a good discharge. The discharge occurs after the RF oscillator is turned on and it is purple in color for an H+ discharge. If the source is new or there is some contamination in the source tube, the discharge appears more light blue in color. This comes from residual nitrogen in the source area or from residual polyvinyl-acetate glue used leaving some acetone residue on the bottle when gluing the bottle to the source probe and the base plate.

Once a good discharge is obtained, the beam is then accelerated and steered into the main beamline Faraday cup (see Fig. 8) to measure the current. The normal operating current is between 15-80 nano-Amps. The beam is left on for 30 minutes to an hour to
allow it to stablize. At this time a liquid N₂ cooling line is filled to cool the surface barrier detector and to assist pumping. After this initial preparation, the ion beam is ready for the experiments to begin.

B. ECS Measurements

Once the beam has warmed up and the sample has been cleaned, the system is ready for an ECS measurement. For the ECS measurement, we use the surface barrier detector discussed earlier (see Fig. 8). After the beam has been stablized and the detector has cooled down to about -25° C, the ion beam can be reflected off of the sample. The specularly reflected beam consists now of H⁺, H⁻ and H₀. The H⁺ and H⁻ component parts are directed over to the detector and measured. The ratio of H⁻ to H⁺, when compared to a non-magnetic sample, is a measure of the spin polarization of the electrons captured (see Chapter II.A.2). A measurement of the background counts must be taken before the TEC measurement.

In TEC experiments we use a "non-magnetic" H⁻/H⁺ ratio from Cu for zero calibration. The ratio of the H⁻ to H⁺ is typically about 1%. The copper H⁻/H⁺ ratio in our case is about 1.58%. The ferromagnetic samples will be demagnetized when measuring the H⁻/H⁺ ratio, except when measuring to see how magnetic field could affect the TEC measurement (see Chapter II.A.2).

The first ECS measurement done on the system was on amorphous (met-glass) Fe₈₀B₂₀ which doesn't possess any
significant crystalline structure. Magnetic and non-magnetic ions are packed randomly.\textsuperscript{40} The met-glass was provided by Dr. H. Hopster of the University of California-Irvine. Other met-glass samples are easily obtainable from Allied Metglas Products. They will normally provide a small strip more than long enough to make an inexpensive sample.

An excellent review of the properties of amorphous ferromagnetic alloys (met-glass) is given in an article by Luborsky.\textsuperscript{41} The met-glass samples have to be carefully installed in a special holder designed for ferromagnetic ribbons. The holder is designed with a coil wrapped around each of the ends so a magnetic field can be applied. The met-glass is then cleaned. The met-glass Fe\textsubscript{80}B\textsubscript{20} took only about 15 minutes to sputter at 2.2 kV and 10 μA. We annealed it for only about 1 hour at 70° C. A measurement of the met-glass was then taken with the sample demagnetized at room temperature (25° C). A 20 keV H\textsuperscript{+} ion beam at an angle of 3° was used for the met-glass measurements. The results will be discussed in Chapter VII. The next measurement performed with the met-glass was to check if the ESP measured via TEC (Two Electron Capture) varied as a function of the applied magnetic field. For a TEC measurement, there should be no change in the polarization, if the electrons are captured from the same magnetic domain. The local spin orientation in each domain doesn't depend on an overall magnetization direction. The results of this measurement are discussed in Chapter VII.
C. SPEES Measurements

SPEES measurements use the same ion beam arrangement discussed earlier (see Chapter IV). We investigate the effects of changing different experimental parameters on the polarization and energy distribution of the emitted electrons. The parameters we can change in our experimental system are the ion beam energy, the ion beam angle, the applied magnetic field, and the sample temperature. The first SPEES measurement we performed on the met-glass mentioned before in Chapter V.B.

The ion beam is reflected off the surface and the electrons emitted normal to the surface are examined. These electrons are energy analyzed and spin analyzed. In this initial SPEES measurement, only one specific energy of the analyzer was used, the peak energy of the electron energy distribution. The spin polarization of these electrons was then measured. These measurements served as a test for the detector and the operating procedure for using the spin detector.

The next set of experiments was performed on the Ni(110) picture-frame crystal discussed earlier. This study was a more refined examination of the capabilities of the detector. We wanted to see how the ion beam energy affected the energy distribution of electrons emitted from the sample surface. This measurement was done by varying the incident ion beam energy from 15 kV to 30 kV at an angle of 2°. At each of these ion beam energies, we measured the energy distribution of the electrons emitted (n(E) vs E) (Fig. 20-23).
Next we examined the effect of the incident ion beam angle on the energy distribution. Measurements were taken at angles from $1/2^\circ$ to $4^\circ$. We also checked this measurement at two different ion beam energies. This will show us if the angle of the ion beam has any effect on the energy distribution of the electrons emitted from the sample. The angular effect should be similar to any effect changing the ion beam energy would cause because both changes affect the energy $E_\perp$ normal to the sample surface (see Chapter II.A).

We also changed the energy resolution of the detector to see how it affected the energy distribution. The resolution is dependent on the width of the exit aperture, $w'$, and the central radius, $b$, of the detector as seen in the equation (23),

$$\Delta E/E = w'/b + 4/3 \alpha^2. \quad (23)$$

The next experiment was to improve the resolution. We inserted an aperture with a 0.007 inch slot after the energy analyzer to increase the resolution. This increased the resolution to $\Delta E/E \approx 0.0093$ from $\approx 0.0417$. We then measured the energy distribution, $n(E)$, with an ion beam energy of 25 keV at an angle of $1^\circ$. The electron spin polarization was then measured at several electron energies. These measurements allow us to examine various processes by which electrons are being emitted from the sample's surface. These interesting results will be discussed in Chapter VII.

The temperature of the sample was varied next to see if it influences the energy distribution or the polarization. The
temperature was raised above the curie temperature for Ni, $T_c = 354^\circ C$. The energy distribution was measured at different temperatures above $T_c$. The polarization was measured above $T_c$. Above $T_c$, the sample is not ferromagnetic and the polarization should be zero. This gives us another method of calibrating our detector for zero polarization.

Another idea to vary the system parameters was to change the sample and look at a non-magnetic sample like copper for instance. The copper sample was inserted into the chamber and the energy distribution and the polarization were measured. The polarization of the copper sample should give $P = 0$ because the copper sample is non-magnetic. This measurement will give us one more test of the electron detector and enable us to see what information we can get from these different studies.
Chapter VI. Theoretical Background

A. Low Energy Secondary Electrons

Low energy secondary electrons can provide a measure of the magnetization at the surface of a sample.\textsuperscript{42} Most of the work to date has been done by examining secondary electron cascades produced by bombardment with primary electrons. There are some studies of secondary electrons produced by ion beam bombardment.

A.1. Electron-induced Secondary Electrons

The first works dealing with the spin polarization of secondary electrons were published by Chrobok and Hofman in 1976\textsuperscript{43} and by Unguris, Pierce, Galejs, and Celotta in 1982.\textsuperscript{44} These studies showed that a large secondary electron spin polarization can be observed when primary electrons are scattered off the surface of a sample. The secondary electrons emitted at low energies, less than 20 eV, have an intensity characterized by a large peak at low kinetic energies around 1 to 2 eV. This can be seen in Figure 14.\textsuperscript{45} We see in this figure how the polarization spectrum depends greatly on the electron energy. This figure also shows a decrease in polarization with increasing electron kinetic energy. As the kinetic energy increases, we get into a region of rediffused primary electrons and cascade electrons. The reduction in polarization is caused by the fact that rediffused primaries possess nearly no polarization.
Fig. 14. Spin polarization and intensity as a function of kinetic energy for primary electron energy of 400 eV on Ni(110).\textsuperscript{45}

Fig. 15. Schematic of secondary electron emission spectrum.\textsuperscript{46}
A characteristic energy distribution of secondary electrons produced by a primary electron beam can be seen in Figure 15. A typical spectrum has the normal low-energy peak and then as the kinetic energy of the electrons increases, there are Auger peaks and plasmon loss peaks on top of the background of cascading secondaries and also the elastic peak of scattered incident electrons.

Experiments show that the secondaries have a pronounced polarization spectrum depending on the kinetic energy. From 0 eV to 10 eV there is a rapid fall off of the polarization until a plateau of about the bulk band polarization of Ni is reached, as can be seen in Figure 14.

The use of spin polarized secondary electrons has led to the development of many new fields of study. One such development, which we mention here, is in magnetic domain microscopy. When a secondary electron spin analyzer is used conjunction with an electron microscope, a researcher has the ability to scan over and map out the magnetic domains by looking at the secondaries produced by the bombardment of the sample with electrons from the electron microscope.

Another area of interest is in magnetic depth profiling. The depth dependence of the magnetization at the solid-vacuum interface at a temperature near the Curie temperature, $T_c$, is of particular interest here. Since the magnetization at the surface can differ strongly from that of the bulk, one would then expect strong effects near $T_c$ which could extend into the bulk quite deeply.
Experimental research in both of these subjects is benefitting greatly from this development of the use of secondary electrons.

A.2. Ion-induced Secondary Electrons

It has been shown in many papers that ion bombardment of solid surfaces produces secondary electrons.\textsuperscript{50} Generally, the studies have just investigated the electron energy distribution when a target was struck by high energy ions at normal incidence. An example of such a distribution is given in Figure 16. This figure shows the energy distribution for a variety of metal targets bombarded by ions at high energies normal to the surface. To date, there exists only one study where the average (angle- and energy-integrated) spin polarization of ion-induced secondary electrons is examined.\textsuperscript{51}

In this study,\textsuperscript{51} the authors examine the spin polarization of the secondary electrons produced by sputtering a surface with heavy ions. The ion energies ranged from 0.5 keV to 4 keV. The ion beams were incident upon the sample surface at an angle of approximately 45°. The polarization results showed a non-zero spin polarization of the secondary electrons from a Fe(110) surface for all ion energies and all ion species used so far. The authors claimed that even though there is surface damage caused by sputtering, the magnetic order is preserved.
Fig. 16. Energy spectra of secondary electrons emitted from nine metal targets during proton bombardment at 500 keV.\textsuperscript{52}

B. Electron Emission due to Ion Bombardment

In the literature, the emission of electrons from a metal by the impact of ions is described by two basic mechanisms: "potential" emission and/or "kinetic" emission. The electrons can be emitted by using either the potential energy and/or the kinetic energy of the ion-solid system. For a very good review of the interactions of atomic particles colliding with a solid surface, we refer to the review by Arifov.\textsuperscript{53}
B.1. "Potential" Emission of Electrons

In "potential" emission, the release of potential energy involved in the ion-solid interaction can provide the energy required to free electrons from the solid into the vacuum. The kinetic energy of the ion can often be neglected in this process. Potential emission is closely associated with such processes as surface ionization, neutralization, charge exchange, and further Auger-type processes.

A positive ion which approaches the surface of a metal can be neutralized thus releasing enough energy to allow an electron to be emitted into the vacuum. This was first mentioned by Holst and Oosterhuis in 1922,\textsuperscript{54} and observed by Penning\textsuperscript{55} in 1928 and Oliphant in 1930.\textsuperscript{56} Oliphant and Moon\textsuperscript{57} promoted a theoretical model for "potential" electron emission. Shekhter\textsuperscript{58} further advanced this model on "potential" emission of electrons by ion-solid interactions. In his model, Shekhter's idea was that the ion-metal system is always an excited system. By de-exciting the system, the ions could release energy in neutralizing. This idea is similar to the Auger\textsuperscript{59} effect. The potential energy released by the neutralization of the ion by one electron from the solid is transferred to another electron in the metal which can be emitted into the vacuum.

Shekhter's treatment of this emission process is the basis for the "modern" theory of the potential emission of electrons from a metal. Hagstrum\textsuperscript{60,61,62} did a series of careful experimental and theoretical studies of potential emission processes and advanced
Shekhter's model. Hagstrum\textsuperscript{63} even assumes that different Auger processes are involved when noble gas ions approach the surface of a metal at very low velocities: Auger neutralization and Auger de-excitation. This is illustrated in Figure 17a and 17b.

The "potential" emission of electrons by an ion-solid interaction, where the sample surface is bombarded with an ion having a low normal energy, was thought to have a high number of secondary electrons associated with the emitted spectrum.\textsuperscript{64} Hagstrum and Takeishi\textsuperscript{65} examined the observed electron emission spectrum and showed that the secondary electrons constituted no more than 10\% of the total emission. In general, "potential" emission is just ejection of electrons due to the ion-solid interaction using the potential energy of the ion as the source of the energy for the process.
He\(^{+}(1s)\) incident.
Electron (1) neutralizes the He\(^{+}\) ion.
He\(^{+}(1s) + e^{-} \rightarrow He^{0}(1s^{2})
Electron (2) is emitted into the vacuum with energy, \(E_{el} = E'_{i} - \alpha - \beta\).

Metastable He\(^{*}(2s)\) incident.
Electron emitted with energy, \(E_{el} = E'_{x} - \beta\) via two methods.

\[\begin{align*}
E_{el}(e^{+}) &= E'_{i} - \alpha - \beta \\
E_{el}(e^{-}) &= E'_{x} - \beta
\end{align*}\]

\(\phi = \text{work function}\)

1. Electron (1) de-excites to the ground state, electron (2) is emitted.
2. Electron (2) de-excites, electron (1) is emitted.

**Fig. 17.** Diagrams illustrating a) Auger neutralization, b) Auger de-excitation (2 possible mechanisms, 1 and 2, are shown).\(^{65}\)
B.2. "Kinetic" Emission of Electrons

Another source of energy for the emission of electrons is the kinetic energy of the ion, thus the term "kinetic" emission applies to the emission of electrons where the kinetic energy of the ion is involved in the electron emission. Kinetic emission occurs under various conditions where different solids are bombarded by ions of different properties. Kinetic emission occurs above a definite threshold energy and the electron intensity increases rapidly with increasing ion energy above this threshold.\textsuperscript{67}

The first attempt to try to describe "kinetic" emission theoretically was by Kapitza.\textsuperscript{68} He considered that, upon striking the solid, the ion would give up some of its energy to a small volume of the metal thereby, producing local heating. This theory became known as the "thermal" theory of kinetic electron emission. This theory was advanced by several authors and then abandoned. It was found that the exchange of energy between the electron and phonon was negligible.\textsuperscript{69}

Many other theories for "kinetic" electron emission were discussed in the literature but the electron yields obtained in experiments were never correctly predicted. In these theories, a three-step mechanism is used to describe this phenomenon: (1) the electrons in the solid are excited by the incoming projectile ion; (2) movement of the electrons to the surface with or without "secondary" effects (cascading of the electrons); (3) penetration of the surface barrier potential.\textsuperscript{70,71,72} The transfer of kinetic energy
to the electrons can be done by using inelastic scattering processes including the "excitations" of electrons to describe the electronic part of the energy loss of the ions.\textsuperscript{73} The effects of the electron emission from recoil atoms must also be considered. For an improved understanding of kinetic emission of electrons, we need better theoretical models which include the mechanisms mentioned above and also further solid state effects such as plasmon excitation and decay.\textsuperscript{74,75}

The observed electron energy distributions from experimental works with energetic ion beams, exhibit high secondary electron yields. Some authors expect that the secondary electrons emitted by "kinetic" emission make up more than 90% of the total intensity of the emitted electrons.\textsuperscript{76} An example of an electron energy distribution obtained by using highly energetic ion beams is given in Figure18. It shows an intense peak at around 2 eV followed by a monotone decrease of the intensity. The figure is very similar to that given in Figure 14 for electron-induced emitted electrons.

To summarize, we conclude that more theoretical and experimental work is needed to advance this important field, however this is hard to formulate.
**Fig. 18.** Energy distribution of secondary electrons emitted from a molybdenum target bombarded by Ar\(^+\) ions of 2 keV (triangles), 5 keV (full circles) and 15 keV (open circles).\(^{77}\)
Chapter VII. Experimental Results and Discussion

The experimental results are presented in two parts, the ECS results and then the more detailed SPEES results. The ECS results will be discussed in part A, the SPEES results in part B.

A. ECS Experimental Results

The first ECS measurements were performed using copper (Cu) poly-crystalline samples. Two electron capture (TEC) measurements are performed. The measurement was made using a 20 keV H⁺ ion beam at a reflection angle of 2°. This gives us a "non-magnetic" ratio, $R_{\text{non-mag}}$, which together with a magnetic ratio, $R_{\text{mag}}$, allows us to calculate the polarization, $P$ (see equation (6)). We find

$$R_{\text{non-mag}} = R_{\text{Cu}} = \frac{H^-}{H^+} = 1.58\%.$$

In next measurements, we used on the amorphous ferromagnet, Fe₈₀B₂₀. Again, we used a 20 keV H⁺ ion beam at a reflection angle of 2°, at room temperature. With $R_{\text{mag}} = 0.71$, we find an electron spin polarization, $P$, of about 55%. In Figure 19, the ratio, $R$, is on the left-hand axis, the corresponding polarization, $P$, is on the right-hand axis. These values are then plotted against the applied magnetic field, $H$. 
**Fig. 19.** TEC measurement of R and P vs. mag. field, H, the curves 1, 2, and 3 are successive measurements.
This figure shows two very interesting results: (1) a magnetic field has no effect on the electron spin polarization; (2) the ion beam, even at glancing angles, cleans the sample surface by sputtering off non-magnetic surface contaminations. This causes an increase in the electron spin polarization (ESP) from around 47% to around 55% between the subsequent measuring runs.

The result that the magnetic field has little or no effect on the polarization is expected if two electron capture (TEC) processes measure the "local" or short-ranged electron spin polarization (ESP), as discussed in Chapter II. For the measurement of short-ranged ESP, a sample does not need to be magnetized as is required in experiments on the existence of long-ranged magnetic order. We note that the size of the existing microscopic magnetic domains (μm-mm), which are always spontaneously magnetized, is larger than the overall distance (10-20 Å) within which two individual electrons are captured. Thus, one would expect no magnetic field effect as we could prove for the first time.

The average value of P of around 55% for the short-ranged ESP is in good agreement with the value of the spin polarization of electrons emitted near the photo-threshold in photo-emission experiments at the surface of the amorphous ferromagnet, Fe$_{83}$B$_{17}$.79

B. SPEES Experimental Results

The initial studies using the novel SPEES technique were performed on the Fe$_{80}$B$_{20}$ amorphous ferromagnet. The initial ion
beam operating conditions were for an ion beam energy of 20 keV and an angle of incidence of 3°. The polarization data, taken on the amorphous ferromagnet, were measured repeatedly at only one selected electron energy where the electron beam intensity was at a maximum. These measurements were done using a low resolution mode with an energy resolution, ΔE/E, of about 0.083. The value of the energy, E, is about 30 eV, so ΔE is then about 1.25 eV.

The polarization, P, measured in these initial tests of the spin detector were around +(15-20)%. This clearly established that this surface was ferromagnetic. The electron spin polarization (ESP) value obtained compares favorably with the value of the total average magnetization (+21%)\textsuperscript{80} and with the ESP of electron-induced secondary electrons emitted from surfaces of amorphous Fe\textsubscript{83}B\textsubscript{17} amounting to around +10%\textsuperscript{81}. The work on the amorphous ferromagnetic indicates that SPEES can be used as a novel and unique tool to study surface magnetism.

Next studies were performed on a Ni(110) picture-frame crystal (see Chapter III). The picture-frame crystal allows us to reliably control the magnetic properties of the sample.

The first investigations on the Ni(110) picture-frame crystal were done to see the effects of the ion beam energy and the angle of incidence on the electron energy distribution. Figure 20 shows the effect of the ion beam energy on the energy distribution for an angle of incidence of 2°. The ion beam energy was varied from 15 keV to 30 keV in 5 keV steps for an incident angle of 2°. Data taken at other ion beam energies in this range resulted in the same data.
The ion beam energy has no significant effect on the electron energy distribution. As seen in these figures, there is a peak in the electron energy distribution around 3-4.5 eV. This is completely different from electron energy distributions due to secondary electron emission, which are characterized by a steep rise to a peak around 1-2 eV. The rise in our spectrum begins at higher energies as compared to spectra for secondary electrons. These electron energy distributions have a rapid rise followed by a slow decline. The non-dependence of the electron energy distribution on the ion beam energy possibly could imply that "kinetic" emission of electrons has no significant effect on the energy distribution of the emitted electrons. This statement does not exclude "kinetic" emission of electrons as a possible mechanism. In these experiments, the energy of the ions normal to the surface of the sample is small (between 18-36 eV). A higher normal energy, $E_\perp$, may be necessary to cause substantial kinetic emission. One way to increase the normal energy, $E_\perp$, is to change the angle of incidence (see also equation (3)). Therefore, in the next studies we varied the angle keeping a fixed ion beam energy.

The next energy distributions were made using an ion beam energy of 25 keV and varying the angle between 1/2° to 4°. One related experiment for 25 keV and 2° is already given in Figure 20 c). The results of using other angles are plotted in Figure 21. All of these distributions show a sharp peak in the electron energy distribution around 4-5 eV. The basic shape of these plots is similar. They exhibit a steep rise in the distribution to a peak
Fig. 20. Electron energy distribution for an angle of incidence of $2^\circ$ at Ni(110) and ion beam energies of a) 15 keV b) 20 keV c) 25 keV d) 30 keV ($\Delta E = 1.25$ eV) (note change in scales).
**Fig. 21.** Electron energy distribution for an incident ion beam energy of 25 keV at Ni(110) and angles of incidence of a) 1/2° b) 1° c) 2° d) 4° (ΔE = 1.25 eV) (note change in scales).
around 4 eV then a decline to zero at around 15 eV. The normal energy, \( E_\perp \), ranged from 2 eV to 120 eV. The distributions again did not change significantly from one angle to another.

The energy resolution of the detector was then increased by installing a smaller aperture in the energy analyzer in the detector. The new resolution, \( \Delta E/E \), was about 0.0093. Again using an electron energy of around 30 eV, this gives a \( \Delta E \) of about 0.30 eV. With this new energy resolution, we are able to distinguish many characteristic features in the energy distribution, that could not be resolved before. The first spectrum measured was for an ion beam energy of 25 keV and an incident angle of 1° at room temperature (25°C). This energy distribution is given in Figure 22.

As seen in this electron energy distribution, there are many interesting features. It has the same characteristic high intensity peak around 4 eV. Another smaller peak becomes apparent in the low energy region at around 2-3 eV. The major peak rises steeply and then gradually decreases, almost showing another peak in the shoulder of the spectrum. Trying further to understand the various processes causing the shape of the electron energy distribution, we measured the electron spin polarization, ESP, as a function of the electron energy. This could help us to unravel which physical processes are involved in ion-surface interactions at grazing incidence. For the electron spin polarization \( P(E) \) versus electron energy, see Figure 23.

The spin polarization spectrum, \( P(E) \), has many interesting features which can help us to understand the underlying physical
**Fig. 22.** Electron energy distribution for an angle of incidence of 1° and an ion beam energy of 25 keV, T= 25°C, with good resolution ($\Delta E/E = 0.0093$) at Ni(110) ($\Delta E = 300$ meV).
**Fig. 23.** Electron spin polarization, $P$, versus electron energy for 25 keV $H^+$ ions with an angle of incidence of $1^\circ$, at $T = 25^\circ$C at remanently magnetized Ni(110).
processes causing the electron energy distribution, \( n(E) \) given in Figure 22. \( P(E) \) is characterized by a slight rise in the polarization at \( E = 1-2 \) eV and then a sharp decline to around \(-13\%\) at \( E = 2.5 \) eV and then a sharp rise to \(+18\%\) at \( E = 3.5 \) eV and again a rapid decrease to a plateau region of approximately \( 5-6\% \). This plateau region has several additional features in it.

The electron energy distribution along with a polarization distribution gives us a method to help describe possible SPEES processes. In the following paragraphs, we discuss several mechanisms which could occur at or near the Ni(110) surface and possibly contribute to the emission of spin-polarized electrons in SPEES.

We examine the neutralization of an incoming ion and the ejection of an Auger electron from the Ni(110) surface. The maximum energy via a two-electron Auger effect depends on the energy levels of the ion and the work function of the sample surface.\(^{82}\) For the work function of Ni(110), we use \( \phi = 5.04 \) eV,\(^{83}\) and for the 1s ground state of hydrogen, we use a value of \( E_{1s} = -13.58 \) eV. This gives for the maximum of the kinetic energy \( E_{\text{max}} \) of the ejected electrons:

\[
E_{\text{kin}}^{\text{max}} = E_{1s} - 2\phi
\]

\[
E_{\text{max}} = 13.58 \text{ eV} - [2 \times 5.04 \text{ eV}]
\]

\[
E_{\text{max}} = 3.5 \text{ eV}
\]

In general, we get for \( E_{\text{kin}} = E_{1s} - E_1 - E_2 \) with \( E_{\text{kin}} > 0 \).
Fig. 24. Diagram illustrating Auger neutralization of H+.
where $E_{\text{max}}$ is the maximum kinetic energy that an ejected electron can obtain by Auger neutralization of the incoming H$^+$-ion. We note that $E_{1s}$ can be lowered slightly due to the screening of the 1s hole of the incoming proton by the electrons at the Ni(110) surface. This effect can reduce the maximum kinetic energy of the ejected Auger electrons.

From earlier ECS experiments\textsuperscript{85} and other spin-sensitive experiments done on Ni(110), it is well known that electrons originating from energy levels near ($< 0.5$ eV) the Fermi energy level possess a predominant minority spin orientation (negative electron spin polarization) of about $-96\%$, whereas electrons from energy levels below this range possess a majority spin polarization (positive electron spin polarization). We can use this information to help explain the observed SPEES polarization and energy spectrums. We would anticipate that the spin polarization of the electrons from the Auger neutralization of the incident H$^+$-ion would have a negative value for energies around 3 eV and change towards a positive polarization with decreasing electron energy from 3 eV to zero. This is indeed what we observe (see Figure 23). This implies that the small feature at around 2-3 eV in the electron energy distribution (Fig. 22) could originate from these electrons emitted during Auger neutralization of the incoming H$^+$-ion.

Next, we discuss transfer of electrons into resonant or autoionizing states of (negative hydrogen) H$^-$ ($^1S$, $^3S$, $^1P$, $^3P$) located near the $n = 2$ threshold with an electron affinity of around $-3.4$ eV.\textsuperscript{86} Again, taking screening effects into account, which would
increase the electron affinity and broaden the energy levels, the energy range of the ejected electron is restricted to the values between 3.5 eV and 6.78 eV with $E_{\text{max}}$ given as follows,

$$E_{\text{kin}}^{\text{max}} = 13.58 \text{ eV} - [2 \times 3.4 \text{ eV}]$$

$$E_{\text{kin}} = 6.78 \text{ eV} \tag{29}$$

We would expect to see negative polarization values around 3.5 eV followed by positive polarization values with increasing kinetic energy of the electrons. This is again due to the band structure of Ni(110). This is indeed observed.

We discuss the transfer of electrons to the stable bound state, $1s^2$, or the unstable bound state, $2p^2$, of H- and subsequent electron loss to the continuum states. The corresponding electron affinities of these states is -0.92 eV$^{88}$ and -0.009 eV$^{89}$, respectively. The upper limits on the energy ranges for these processes are given by

$$E_{\text{kin}}^{\text{max}} = 13.58 \text{ eV} - [2 \times 0.92 \text{ eV}]$$

$$E_{\text{kin}} = 11.74 \text{ eV} \tag{30}$$

and

$$E_{\text{kin}}^{\text{max}} = 13.58 \text{ eV} - [2 \times 0.009 \text{ eV}]$$

$$E_{\text{kin}} = 13.56 \text{ eV} \tag{31}$$

The screening process should be significant again in increasing the electron affinities and in broadening the energy levels. The range for each one of the processes will be from 3.5 eV to 11.74 eV for the
1s² state and from 3.5 eV to 13.56 eV for the 2p² state. The P(E) curve should again be characterized by negative values around 3.5 eV, followed by a change to positive values of P with increasing electron energies, which is observed.

The processes discussed above were concerned with using potential electron emission. The kinetic energy is another possible source of energy for electrons emission. Part of the kinetic energy of the incident ions could be transferred by inelastic collisions during interactions of the ions with steps and other structural inhomogeneities located at the surface of the sample.

The average polarization of around 5.5% observed for electron energies between 9 and 12 eV might be correlated to these "kinetic" processes. The observed value of about 5.5% measured in this range is close to the well known value of 5.6% found for the total average magnetization of electrons in Ni.⁹⁰

In the next studies on the Ni(110) sample we investigated the effect of temperature on the electron energy and spin distribution. The first energy distribution at higher temperatures was measured at 377°C and is given in Figure 25. It possesses the same sharp peak in the energy spectrum around 4 eV, however the shoulder features at higher energies becomes more prevalent. The next distribution was taken at even higher temperatures (407°C) (see Figure 26). It again has the 4 eV feature with a stronger shoulder feature which is taking the shape of a peak around E = 5.5 eV.

The polarization curve for a temperature of 405°C is given in Figure 27. It shows that the polarization, P(E), is roughly equal to
zero at all energies. This is to be expected because the temperature is above the Curie temperature, $T_c$, for Ni of 354°C. We note that, contrary to TEC experiments, we expect $P = 0$ for $T > T_c$ in SPEES experiments although the two electrons involved in a specific process originate from one magnetic domain. TEC is sensitive to a short-ranged spin-spin correlation between two electrons whereas in SPEES, we detect single, non-correlated electrons.

The last study was to measure the electron energy distribution and the polarization distribution for a non-magnetic sample like Cu. The curves are given in figures 28 and 29. The electron energy distribution curve has a similar peak at around 4 eV, but this curve is more symmetrical about 4 eV than the Ni(110) curves. It also drops off more quickly to zero intensity at about 6 eV. The polarization curve shows the expected polarization value of around 0% that one would expect to observe from a non-magnetic sample. A non-magnetic sample should show no long-range ferromagnetic order at any temperature.

The last two polarization measurements on the Ni(110) at high temperature and the Cu sample were done more as a test to check out the spin detector. These measurements were performed to see if we could measure a true zero polarization. We expected the polarization to be 0% within error in both cases.

Finally, we note that, for observation angles not normal to the beam direction, electrons originating from moving ions should exhibit a Doppler shift. These shifts in the electron energy spectrum do not occur for electrons emitted from the solid, a fact
**Fig. 25.** Electron energy distribution for an angle of incidence of 1° and ion beam energy of 25 keV, $T = 377^\circ$C, with a good resolution ($\Delta E/E = 0.0093$) at Ni(110).
**Fig. 26** Electron energy distribution for an incident angle of 1° and ion beam energy of 25 keV, T = 407°C, with a good resolution (ΔE/E = 0.0093) at Ni(110).
**Fig. 27.** Electron spin polarization, $P$, versus electron energy for 25 keV $\text{H}^+$ ions with an angle of incidence of $1^\circ$, $T = 405^\circ\text{C}$ at Ni(110).
**Fig. 28.** Electron energy distribution for an angle of incidence of 1° and ion beam energy of 25 keV for a Cu sample at T = 25°C.
**Fig. 29.** Electron spin polarization, $P$, versus electron energy for 25 keV $H^+$ ions with angle of incidence of $1^\circ$, on Cu at $T = 25^\circ$C.
which should further help to identify the specific emission processes.
Chapter VIII. Conclusions

For the first time, we have successfully performed two electron capture (TEC) measurements at low ion beam energies (15 keV to 30 keV). A non-zero electron spin polarization of 55% was found for the amorphous ferromagnet Fe$_{80}$B$_{20}$, which agrees well with other experimental findings. We have also shown that applied magnetic fields have no effect on the local magnetic order.

We have also developed the novel and unique surface technique: spin polarized electron emission spectroscopy (SPEES). Using this method, we have measured the long-range surface magnetic order of Fe$_{80}$B$_{20}$ surfaces which amounts to +15-20%. This result compares very well with other experimental and theoretical results.

We have studied a Ni(110) picture-frame crystal using SPEES. We have found several interesting features in the energy distribution of the emitted electrons and also in the polarization distribution. The electron energy spectrum obtained using SPEES is different from that of "secondary" electron spectra induced either by electron or ion bombardment of a sample surface. The results show that using SPEES electron energy distributions together with a polarization distribution, helps to unravel the processes and mechanisms of an ion-surface interaction at a grazing angle. These results have demonstrated the capability of SPEES and open the way for refined studies of surface electronic and magnetic properties.

In the future, we plan further SPEES studies in connection with secondary electron emission to magnetically video-map a surface by
using a micro-focused ion beam. Work is also in progress to investigate the spin polarization of characteristic MVV or LMM Ni Auger electrons located near 61 eV and 848 eV. The use of SPEES to analyze and measure the spin polarization of these emitted Auger electrons should be very interesting. We also plan to use this SPEES technique at higher ion energies (150 keV) to continue with investigations of other sample systems. We also propose to use different ion species to probe the surface. We intend to do the same types of experiments with other ions (for instance He+ or Ar+). We will also be able to use a micro-focused (500 Å beam diameter) liquid metal gallium ion beam as a probe.

The further advancement and improvement of the SPEES technique, to be able to measure at different angles relative to the incident ion beam direction would enable us to measure the Doppler shift of the emitted electrons. This would help us to further identify the processes as to where the emitted electrons are originating from: the moving ion or the solid surface. The development of these ideas, thereby improving the SPEES method, will prove to be very interesting.
References


6. C. Rau, see ref. 1.


8. C. Rau, see ref. 1, 147.

9. C. Rau, see ref. 1, 143.

10. C. Rau, see ref. 1.


14. C. Rau, see ref. 1, 155.

15. C. Rau, see ref. 1, 151.

16. C. Rau, see ref. 1, 155.


22. C. Rau, see ref. 1, 165.
24. J. Kessler, see ref. 23, 56.
33. Silicon Surface Barrier Radiation Detectors Instruction Manual, ORTEC.
35. J. Unguris, D. T. Pierce and R. J. Celotta, see ref. 34, 1319.
36. H. Hopster, personal communication.
37. J. Kessler, see ref. 23, 233.
38. J. Kessler, see ref. 23.


46. X. Zhang, see ref. 39, 58.

47. M. Landolt, see ref. 42.


49. M. Landolt, see ref. 42.


52. D. Hasselkamp, S. Hippler and A. Scharmann, see ref. 50.


55. F. M. Penning, Physika 8, 12 (1928).


60. H. D. Hagstrum, Phys. Rev. 89, 244 (1953); 91, 543 (1953).


66. H. D. Hagstrum, see ref. 63, 339.


68. P. L. Kapitza, Phil. Mag. 45, 989 (1923).


73. N. Benazeth, see ref. 67.

76. N. Benazeth, see ref. 67.
77. N. Benazeth, see ref. 67, 407.
80. F. E. Luborsky, see ref. 41.
82. M. L. Oliphant and P. B. Moon, see ref. 57.
84. H. D. Hagstrum, see ref. 63, 339.
85. C. Rau, see ref. 1.
87. R. N. Hill, see ref. 19.
88. H. B. Shore, J. H. Rose and E. Zaremba, see ref. 20.
90. C. Rau, see ref. 1.