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STUDIES OF SURFACE GEOMETRIC AND MAGNETIC STRUCTURE UTILIZING SPIN-POLARIZED LOW-ENERGY ELECTRON DIFFRACTION: Cu(001) AND Ni(111)

by

DAVID MELVIN LIND

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

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STUDIES OF SURFACE GEOMETRICAL AND MAGNETIC STRUCTURE UTILIZING SPIN-POLARIZED LOW-ENERGY ELECTRON DIFFRACTION: Cu(001) AND Ni(111)

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ABSTRACT

Presented here are experimental/theoretical studies of the geometric structure of a Cu(001) surface and the near-surface layer magnetization of a ferromagnetic Ni(111) surface, both using spin-polarized low energy electron diffraction (SLEED). This probe shows great promise both as a high quality structural probe, and also in a variety of magnetic studies.

Significant advances have been made over the past several years in both experimental and calculational LEED techniques. The introduction of r-factor analysis and streamlining of calculational codes now allows the evaluation of increasingly complex structures by LEED I-V analysis. In addition, experimental advances now allow the investigation of not only the intensities, but also the spin-dependence of scattering from many surfaces.

Spin dependence in low-energy electron diffraction is found for scattering from all surfaces, and is due to two effects—the spin-orbit interaction and the exchange interaction. The former is sensitive to the positioning of ions that make up the surface and provides complementary probe of surface geometric structure in addition to LEED intensity analysis. Here we introduce a simple r-factor analysis to evaluate the structure of Cu(001). This surface was chosen because it is well studied, and a highly precise structural determination of the surface based on LEED I-V analysis is available for comparison. Experimental SLEED A-V profiles are compared with calculated profiles to obtain the best near-surface structure. In this study, the comparison between calculated and experimental spin-asymmetry profiles obtained from this surface is unusually good, and further, the best fit is for a structure that agrees well with the previous LEED study.

The present study is the first use of r-factors in a SLEED structural determinations. Several things are readily noted from the present SLEED r-factor analysis. First the precision of structural conclusions obtainable r-factors is much greater than possible using the visual inspection method found elsewhere. Further, because A-V's are self-normalizing, the r-factors are cleaner, requiring no arbitrary scaling factor. Also the spin asymmetries show more sensitivity to structural variations than do the comparable LEED intensities.

The exchange interaction is sensitive to the electron spin-population density in the surface, and thus to surface magnetism. Our preliminary study of the ferromagnetic Ni(111) surface shows very small exchange asymmetry effects. The results are consistent with some enhancement of the sample magnetization at the surface, but a precise layer magnetization determination is beyond the limits of present technique.
ACKNOWLEDGEMENTS:

Many people have contributed to this thesis, and I am indebted to each of them. Dr. G. K. Walters has been the great driving force behind this work, and without his direction, this work would have floundered. But even more, he has been a mentor to whom I could turn in dealing with the trials of the lab, and his encouragement has helped my work greatly.

I am grateful to Dr. F. B. Dunning for his technical skill and assistance. His quick ideas and timely advice have been invaluable in the progress of this work.

I owe a special debt to of thanks to Dr. K. D. Jamison, with whom I spent my early days in the lab, and who built the polarized electron source. Following in his footsteps has made my work much easier.

My special thanks go to Dr. H. L. Davis for a fascinating and rewarding collaboration. I am grateful to be able to call him a colleague and a friend.

And finally, the highest praise must go to my wife, Celeste, for without her unwavering support none of this would be possible. Whether it was the hours of typing she put in, or the cheery smile I got when coming home late, she was always there to keep me going, and I'm grateful for it.
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I. 

INTRODUCTION

The past several years have seen significant advances made in the study of surface crystallography by the analysis of low-energy electron diffraction (LEED) intensity-versus-voltage (I-V) spectra. These advances include significant strides in calculational techniques with the development of more efficient numerical models of the scattering,\textsuperscript{1} streamlining of the computer codes used,\textsuperscript{2} and the introduction of reliability factors \textsuperscript{3} for use in the detailed interpretation of I-V data. This progress has made possible the use and evaluation of increasingly sophisticated surface structural models - models that include such effects as multilayer relaxation,\textsuperscript{4} surface rippling,\textsuperscript{5} and large scale reconstruction.\textsuperscript{6}

Spin-Polarized Low-Energy Electron Diffraction (SPLLEED), a daughter spectroscopy to LEED, was pioneered by work done in this laboratory \textsuperscript{7} and elsewhere over the past decade. O'Neill et al.\textsuperscript{8} performed the first experiment that demonstrated spin-dependent effects in low-energy electron diffraction in a study of W(001) here at Rice University in 1975, and shortly thereafter Müller and Wolf \textsuperscript{9} showed similar results in spin-polarized LEED scattering from Au(110) in 1976.

SPLLEED represents an advance over conventional LEED intensity analysis in that LEED intensities require some method of normalizing the intensities of diffracted beams at different energies and angles, while the beam polarizations are inherently 'self-normalizing' because they depend only on the ratios of scattered spin-up minus spin-down intensities, divided by their sums. Also SPLLEED has the advantage of giving additional and complementary information to that found in standard LEED intensity measurements. Finally, SPLLEED theory represents a more exact formulation of the true electron scattering by the crystal than its spinless LEED analogue.

The recent development of the GaAs polarized electron source by Pierce and coworkers \textsuperscript{10} provides a comparable advance in experimental techniques to the theoretical progress noted earlier, and makes possible the efficient and routine measurement not only of the intensities of LEED diffracted beams but also of their spin dependences. Spin-dependent measurements provide an additional technique with which to probe surface electronic and geometric properties, and provide an
additional test of theoretical predictions based on assumed surface models.

Spin-dependence in LEED may result from either or both the spin-orbit interaction and the exchange interaction. The former occurs in low-energy electron scattering from all surfaces. This spin-dependence, largest for scattering of electrons from surfaces of high atomic number, can effectively be used to study surface geometric structure. Theoretical studies indicate that calculated polarization effects are frequently more sensitive to the choice of interlayer spacing and other surface structural parameters than are calculated intensities. Further, SPLLEED data obtained using polarized electron source techniques can now be obtained in parallel with LEED intensity data with little increase in effort or total data acquisition time. Thus SPLLEED spin-asymmetry data — which becomes readily available through polarized source techniques — can be used as an additional test of surface theoretical models, because these models must correctly predict both intensity and polarization effects when making a structural determination. The availability of a spin-sensitive probe also permits the study of surface magnetism through the exchange interaction.

In the present work we have undertaken two separate and somewhat independent studies of metallic single crystal systems using SPLLEED. The first of these investigations involves the surface structure determination of Cu(001) by a detailed theoretical/experimental comparison of the spin-asymmetry —vs.— energy (ΔV) diffraction spectra for scattering from that surface. The spin-dependences of the various diffracted beams here are due entirely to the spin-orbit interaction and reflect the detailed ionic positions in the surface. The second study, which will be discussed more briefly, is a preliminary investigation of the layer-dependent magnetization of the Ni(111) surface. Here the spin-asymmetries include contributions from both spin-orbit and exchange interactions, the latter of which reflects the spin-populations, and thus magnetization, in the near surface region.

The Cu(001) surface was chosen for this study because this surface is very well characterized, having been studied extensively by a number of investigators using a variety of surface analytic techniques. Cu(001) exhibits multilayer relaxation but no reconstruction of the
clean surface. The amount of repositioning from a so-called 'bulk-termination' structure is quite small, and a rather precise surface structural model has been obtained for it by Davis and Noonan using conventional LEED intensity analysis. The quality of agreement between LEED experimental and calculated intensity profiles for the Davis and Noonan study is unusually good — an agreement reflected by a minimum in the Zanazzi-Jona 4-beam R-factor of slightly below 0.037 for the optimum structure, one of the lowest R-factor results to date. The relative repositioning of the top atomic layers obtained by that comparison were \( \Delta d_{12} = (-1.10\pm0.40)\% \) and \( \Delta d_{23} = (+1.70\pm0.60)\% \), with the error limits reflecting a 95% confidence level for this structure. This represents a precision in structural conclusions to within 0.011 Å for these nearest-surface atomic spacings! The unusually simple and well characterized structure of this surface thus provides an excellent 'proving ground' on which to test the capabilities of SPLEED analytical techniques.

Fully relativistic dynamical SPLEED calculations have been undertaken by Dr. H.L. Davis in collaboration with this study for a range of structural and nonstructural parameters. The calculated polarization effects are quite sensitive to variations in the assumed surface structure, but for the most part show a lower sensitivity to variations in the nonstructural parameters. The relative contributions of these various model parameters are evaluated quantitatively in this study by use of a simple reliability factor analysis analogous to that used in LEED intensity analyses. The use of R-factors in the copper study shown here represents the first implementation of such techniques in SPLEED.

In the present work we show comparisons between the theoretically calculated and experimentally obtained spin-dependences of several diffracted beam intensities from Cu(001). Copper has a reasonably small atomic number (29). Thus spin-dependent effects in scattering from this surface are expected to be small, on the order of a few percent. This is borne out both by experiment and by theoretical analysis. Despite the small effects found, the results obtained show good experimental reproducibility and excellent calculational convergence. Moreover, excellent agreement between theoretical and experimental profiles is
obtained, and the results reflect a structure showing good agreement with the structural model derived from the earlier LEED study. Because of the sensitivity of these small spin dependences in SLEED to variations in surface structure and the highly precise surface structure already obtained for this surface, reproducibility of these profiles from Cu(001) is a strong confirmation of the viability of SLEED analytical techniques. The good agreement between calculated and experimental profiles obtained here, in fact, is not only indicative of high precision in structural conclusions, but also indicative of the applicability of SLEED to high quality structural determinations even for surfaces of low atomic number.

Nickel(111) was chosen as the first magnetic study using SLEED in this laboratory. The sample orientation was chosen so that the (111) face is exposed and the long sample edges are parallel to the [110] crystallographic direction, which is one of the high-symmetry directions in the (111) plane. The purpose for this careful selection of sample orientation was twofold: First it allowed for sample magnetization along an easy <110> magnetization direction, and secondly, it allowed for the separation by symmetry arguments of the spin-dependent asymmetry features due to the exchange coupling (which carries the magnetization information) and the spin-orbit interaction (which is structure-dependent), both of which are present in electron diffraction from ferromagnetic surfaces.

Both because of its intrinsic scientific interest and its technological importance in the magnetic recording industry, surface magnetism is an area of intense current research activity. This is especially important because a number of fundamental questions concerning ferromagnetism remain unanswered, and thus the understanding obtainable through spin-sensitive probes such as SLEED is highly prized. There is considerable debate, for instance, about the effects of surface termination on such collective phenomena as magnetic ordering. A number of different models for surface magnetism have been proposed, with consequences that range from magnetically dead surface layers, to significantly enhanced surface magnetism, and even to 'giant' magnetic moments in monolayer magnetic thin-films.

SLEED analysis might be of use in resolving such controversies
because of its spin-sensitivity to magnetic ordering near surfaces. It is hoped that comparison of experimentally derived exchange-asymmetry profiles with equivalent calculated profiles obtained by Dr. R. Feder of Universität Duisburg for this study will provide a critical test of theoretical models of surface magnetism. The assumed layer-by-layer magnetization can be varied parametrically in the model calculations, and the resultant theoretical SLEED profiles fitted for best match with experimental exchange asymmetries. The results presented here, while being very preliminary, indicate some enhancement of the surface magnetization at the Ni(111) surface over that in bulk nickel.

Nickel, although ferromagnetic, carries a rather small bulk magnetic moment of only \( \sim 0.6 \) Bohr magnetons per atom.\(^{24}\) Thus spin-effects due to the exchange coupling are expected to be small, and this is confirmed experimentally, where the exchange-asymmetries in SLEED from Ni(111) are found to be on the order of 1-2%. This falls very near the reproducibility limit of our techniques. It remains to be seen, therefore, whether the experimental accuracy of SLEED measurements will be sufficient for qualitative surface magnetic moment determinations.
II. THEORETICAL CONSIDERATIONS:

II.A THE ELECTRICAL AND GEOMETRICAL PROPERTIES OF SURFACES

It is known that the electronic and magnetic properties of materials are modified near their surfaces or at interfaces. This modification is due in great part to the termination of the otherwise extended crystalline lattice and the resultant change in coordination of the atoms at the surface. Gradmann notes that this is true for surfaces that exhibit ferromagnetic ordering: "Ferromagnetic order, being a collective phenomenon is modified near the surface of a magnetic system, where part of the participants in the collective process are missing. The features of this modification depend on the mechanism of magnetic coupling in general. Therefore, our understanding of ferromagnetism is connected with our understanding of the magnetic order near surfaces, and one way to study ferromagnetism is by means of its modifications near the surface. In addition to this basic interest, there is technological interest in magnetic surfaces in connection with catalysis. It has been proposed, for example, that the catalytic activity of nickel surfaces might be connected to their magnetic properties." 

Thus the motivating impetus of our surface studies is two-fold. Because processes such as corrosion, abrasion, catalysis, and surface magnetism, which have great technological importance, depend strongly on surface properties and only weakly on the bulk properties of materials, surface studies are the focus of intense current research activity. In addition, studies of the modification of electronic and geometrical properties by the surface termination can give fundamental insights into the physical processes underlying even the overall bulk electronic and geometric properties of solids. Thus these studies are also of great intrinsic scientific interest.

Noonan and Davis, who have focused much of their work on how surface termination affects the geometrical arrangement of the ions in the near surface region, note that the creation of a surface universally and fundamentally alters the atomic arrangement from the structure of the bulk. There are many examples of surfaces of
semiconductor and metal crystals for which a different arrangement of
atoms from the bulk have been demonstrated."

The differences are more easily illustrated for semiconductors, for
which covalent bonds to an atom are broken when a surface is created.
When the uncompleted bonds reform, the energy of reforming is usually
enough to displace an atom from its bulk position. Therefore, the
atomic arrangements of most semiconductor surfaces are dramatically
altered from those of their bulk. A beautiful example of this is the
Si(111) surface which is perhaps the most intensely studied of all
surfaces. When it is cleaned and well-annealed this surface is
reconstructed, i.e., its atoms are displaced laterally from positions
which they would occupy in a truncated bulk crystal, and the unit cell
of the surface layer can be placed on a net of 49 Si atoms which have
the bulk atomic arrangement. The resulting pattern is referred to as
(7×7) because there are seven times more diffraction beams along each
basis vector direction than there would be for the hypothetical
truncated bulk. The complex 'star' array of the Si(111) LEED pattern
provides a beautiful example of a surface being dramatically different
from its bulk."

"The cohesion of metals is significantly different from that of
semiconductors. A metal can be represented, to the first order, as a
lattice of ions in a continuum of electrons. So the termination of a
metal by a surface does not require strong directional bonds to be
broken. However, the truncation of a metal does alter the environment
in which the surface atoms reside...The response of surface atoms to
electrostatic forces induced by the termination generally results in
their being displaced away from truncated bulk positions." Sometimes
this is manifest by reconstruction of the metal surface, but the more
common displacement near the surface of metallic lattices is the
simultaneous shift of entire planes of atoms, usually is in the
direction normal to the surface, which is called relaxation.

Finnis and Heine showed that the termination of a metal causes
the electronic charge at the surface to redistribute in order to reduce
the electronic surface tension. The resultant change in charge density
then induces electrostatic forces on the atomic cores near the surface,
and the surface layer atoms relax away from truncated bulk sites so that
the induced forces are cancelled by the ion-ion interactions with deeper layers. This, in turn, makes necessary the readjustment of ionic and electronic charge within these deeper layers. It was found that the equilibrium electronic charge distribution can not be established by the relaxation of a single atomic layer, but required the progressively smaller relative repositioning of the ions in the top several layers to reestablish an equilibrium charge distribution while accounting for the lattice termination due to the surface. This effect is referred to as surface multilayer relaxation.

Theoretical studies using ab initio calculations based on the density functional formalism have given quite precise theoretical models of the detailed electronic structure of a wide variety of surface systems. This work has led to a number of startling predictions of surface geometrical and magnetic properties. Recent work on ferromagnetic systems predict surface magnetism enhanced over the bulk magnetism of the same crystal, the "possibility of a ferromagnetic surface layer on a bulk paramagnet or antiferromagnet," and further that strongly enhanced magnetization in monolayer ferromagnetic films on noble metal substrates is expected even over the surface magnetization of bulk ferromagnetic systems. This is a considerable shift from early theoretical and experimental studies of ferromagnetic systems, which seemed to suggest the existence of 'dead layers' at the surface, exemplified by strongly reduced or nonexistent ferromagnetic ordering at the surfaces of elemental systems that otherwise would be ferromagnetic. More recent studies indicate that these so-called 'dead layers' reported earlier may have been due to poisoning by contaminants on the surfaces for both experimental studies and theoretical treatments indicate that the ferromagnetism at surfaces is strongly affected by the presence of even submonolayer coverages of contaminants. It is found that for clean surfaces there are indications of early experimental evidence for magnetic enhancement at several surfaces. Because of the surface- and spin-sensitivity of SLEED, this probe shows promise as a method to test predictions of magnetic enhancement at surfaces.

Comparable theoretical treatments of multilayer relaxation predict large surface relaxations in a wide variety of systems. A number of these systems show promise for study by SLEED, including Fe(111),
Pb(001), Mo(001), and Cu(110) where relaxation of the top layer on the order of 10% (and for Pb(001) and Fe(111) of over 25%) are indicated. Detailed experimental studies by LEED and ion backscattering have confirmed this multilayer relaxation in one case, Al(110), where the magnitude of the relaxation has been determined down to and including the fourth interlayer spacing! The surface focused on here, Cu(001), exhibits multilayer relaxation, and while the effect is smaller than for a number of other systems, it is distinctly expressed down to at least the second interlayer spacing, and indications are that it goes deeper.

II.B ELECTRON INTERACTIONS AT SURFACES

Electrons elastically scattered from crystals in the energy range 10 – 300 eV constitute a very powerful probe of surface structural and electronic properties. Much as X-ray diffraction techniques may be used as a probe of bulk crystallographic structure, low energy electrons have characteristics that especially favor them as a probe of surface crystallography.

The strong structural sensitivity of low energy electrons is due to the coherent diffraction of their wavefronts from the regular array of scattering sites presented by a crystalline lattice. The deBroglie wavelength of electrons $\lambda$ is given by:

$$\lambda = \frac{h}{p} - \frac{1}{(150/E)^2} \AA$$

(1)

where $\lambda$ is in Ångströms and the electron energy in vacuum $E$ is in electron volts. Thus, electrons in the energy range 10 – 300eV have wavelengths comparable to the lattice spacing of typical crystals ($\sim 1-4 \AA$). As a consequence, backscattered electrons from ordered surfaces will show constructive interference of their wavefronts and thus will be preferentially scattered in particular directions for any given electron energy. This diffraction effect can be exploited to obtain structural information about the scattering crystal. In fact it was just this attribute (i.e., preferential scattering caused by diffraction) which led Davisson and Germer to perform the first LEED
experiment in 1927 as a demonstration of the wave nature of the electron.44

Figure 1. Mean free path of electrons in metallic solids as a function of their energy. [After Ertl and Küppers, ref. 46, fig.1.2, p.7.]

In addition, when a low-energy electron beam strikes a crystal surface, it interacts strongly with the first few surface layers. Thus any backscattered electrons resulting from these backscattering events will reflect near-surface properties with high surface specificity. This surface specificity arises because both the elastic and inelastic cross-sections for electron scattering from ion cores in this energy range is large, on the order of $10^{-14}$ cm$^2$,45 so that electrons penetrate no more than a few atomic layers into the solid. An indication of this large electron-ion scattering cross-section is given by the mean free path of electrons in solids, as a function of electron kinetic energy, shown in Figure 1. The mean free path, an indication of the distance an electron is expected to travel between scattering events, shows a minimum of only 3–5 Å between 60–80 eV, right in the middle of the LEED energy range.46

Elastic backscattering contributes significantly to this surface specificity, for electrons backscattered from each atomic plane depletes the electron flux penetrating to successively deeper layers. As a result, most backscattered electron flux is that due to scattering from the top layer, then that due to the second layer, and so forth. Because this backscattering is the source of the re-emitted electron flux that makes up the diffracted intensities measured, most of the diffraction
information obtained by LEED is from the top layer, with progressively smaller contributions from deeper layers.

It should be noted, however, that along with a significant backscattering probability, there is also a high probability of electrons losing a substantial amount of energy in creating electron-hole pairs or plasmons or in forming a cascade of secondary electrons. All these inelastically scattered electrons now have different energies from the primary beam and thus do not contribute to the coherent diffraction process. In this way much of the incident electron beam intensity is removed from the diffracted electron beam so that the elastically scattered fraction (which contains the diffraction information) that leaves the surface is only 1–5% of the total scattered intensity.

Figure 2. Schematic spectrum of backscattered electrons from a surface generated by a primary beam of electrons at energy $E_p$. The 'quasi-elastic' peak, containing the LEED diffracted electrons, lies at the primary beam energy. The broad maximum at low energies is due to multiply scattered and true secondary electrons. The intermediate energy region contains Auger peaks and characteristic energy loss peaks due to plasmon scattering.

The interaction of a beam of monoenergetic electrons of energy $E_p$ with a solid surface gives rise to scattered and emitted electrons with typical energy spectrum as shown in Figure 2. The spectrum exhibits several distinct regions: First a large broad maximum occurs at low energies and is attributable to 'true secondary' electrons which are emitted as a result of cascade processes in the solid. At $E_p$ the upper energy limit, an 'elastic' peak is observed which actually
comprises the elastically scattered electrons plus the 'quasi-elastic' electrons that have lost a small amount of energy (i.e. a few meV) by phonon scattering. The structural information obtained in LEED and other diffraction studies is inferred from the properties of electrons in this peak. The intermediate region of the emission spectrum is a low flat region and exhibits many smaller maxima which result from characteristic energy loss of the primary beam due to plasmon excitations and interband transitions, and from Auger emitted electrons. These features, especially due to Auger transitions, provide the basis of other spectroscopies that may also be used as diagnostics of surface chemistry and structure.49

Figure 3. Schematic indication of the basic LEED experiment. An electron beam of intensity \( I_0 \) and beam energy \( E \) strikes a crystal surface at polar angle \( \Theta \) and azimuthal angle \( \phi \), and is elastically and coherently scattered into the diffracted beams \( I_{hk} \). [After Marcus and Jona, ref. 2, fig. 1, p. 21]

The basic LEED observation is shown in Figure 3, where experimental details are omitted. Marcus and Jona 50 note that the experiment measures primarily the intensity of the elastic coherent scattering (i.e. diffraction) by a single crystal surface where the intensity, energy, and direction of the incident electron beam are known. "The intensity \( I_{hk} \) of the (hk) diffracted beam (the two integers \( h \) and \( k \) designate the order of diffraction from the two-dimensional crystal grating) is measured as a function of incident energy and directions \( \Theta \) and \( \phi \) (polar and azimuthal angles) with respect to the surface. Actual electron beams have finite cross sections and angular profiles and give rise to a concentrated illuminated spot on the crystal surface and to several on
the detector." Ideally only the elastic part of the backscattered electron current need be included. Most electrons that are inelastically scattered can in principle, be rejected by biasing the grids to reject them. It should be noted however that this ideal breaks down at least partially at any finite temperature for quasi-elastic electrons. These electrons, due to phonon scattering within the crystal are essentially impossible to discriminate against using retarding grids because the energy shift involved in phonon scattering is so small — on the order of a few meV — that it is usually much smaller than the energy spread of the primary electron beam. These electrons (along with those electrons elastically scattered from defects in the crystalline lattice or random irregularities in the surface morphology) contribute a generally uniform, and spatially isotropic background to the measured elastic diffraction peak intensities.51,52 Although these electrons do not participate in the coherent diffraction process, and thus contribute no diffraction information about the extended crystalline lattice, they nonetheless alter the the measured LEED diffraction profiles. It is therefore important that the contribution of these electrons be addressed in the interpretation of LEED experiments. This problem will be the focus of discussion of a later section.

II.C LEED THEORIES — Fundamental Assumptions

In general, all Low Energy Electron Diffraction theories begin with the same fundamental assumptions. They assume a plane wave incident on a crystal which is "...ideally flat and infinitely extended, and that the atomic structure of the surface is perfectly two-dimensionally periodic."53 The models also assume that this two-dimensional surface is backed by a semi-infinite crystal (with thermal motion, but no defects) in which each layer has internal translational symmetry but the spacing between layers can vary from layer to layer (which thus takes into account the possibility of multilayer relaxation), and the top layer may have a different periodicity within the layer than that of lower layers (which can thus account for reconstruction or adsorbates at surfaces).54 The problem consists in modelling the backscattering process completely enough that the calculated intensities of the emergent backscattered
waves compare well with the real backscattered intensities from real crystals.

This places several requirements on any realistic theoretical formalism for describing electron diffraction from surfaces. The realistic inclusion of all the fundamental physics inherent in the electron/surface interaction must address each of the following several requirements: 55

1. The model must fully account for the transmission of the electron waves into and then back out of the surface.

2. Electron waves elastically backscatter strongly enough that they often scatter off more than one ion core before re-emission into vacuum, and thus the model must account for multiple scattering of electron waves from atomic sites within the surface.

3. The electrons interact strongly with the surface not only through elastic processes, but also inelastically through processes that effectively remove electron flux from the elastic channel. Thus the model must account for this attenuation of the waves by such inelastic processes.

4. At any finite temperature, the atoms in the surface are not static, but vibrate about their equilibrium lattice sites. Any realistic model will include such thermal lattice vibrations.

5. In any truly quantum mechanical treatment, electrons are not spinless, but rather exhibit a variety of spin-dependent effects in their scattering from surfaces. 56 While these effects are not in general large, and in conventional LEED formalisms are treated as negligible, they are, in fact, significant in scattering from quite a number of surfaces, and even if found to be reasonably small, can be exploited to give new insights into both the scattering process as a whole and into many of the structural and electronic properties of the surface which causes the diffraction.

Each of these characteristics of the electron scattering from surfaces may be parametrized and carefully included in the LEED diffraction formalism. The first step in this process is the building of a LEED crystal scattering potential.
Figure 4. Ionic scattering potential in the near-surface region.

a) A realistic scattering potential for a high-Z surface, shown to accentuate the interatomic undulation caused by the overlap of adjacent ionic potentials. [After Wimmer et al., ref. 32.]

b) A schematic representation of the muffin-tin potential (solid curve) used to approximate the actual potential (dotted curve). A number of the scattering potential parameters are indicated, and discussed more fully in the text.

II.C.1 LEED Model Parameters:

The standard scattering potential used in LEED theoretical models is shown schematically in Figure 4a and 4b where the potential has a 'muffin tin' form, i.e., spherical around each atom and flat between atoms. In a real crystal, the potential between the atoms is, as for the near-surface potential for W(001) shown in Figure 4b, strongly corrugated due to the superposition of adjacent potentials. In fact, a tungsten potential was chosen here for illustrative purposes because the strong, reasonably large ionic potentials for this high-Z surface
illustrate this overlap of potentials which causes the corrugation, quite well. In practical calculations, however, the interatomic undulation of the potential can be ignored, and this interatomic potential is assumed to be spatially uniform. The level of this flat part of the potential shown Figure 4a (the muffin-tin zero) differs from the vacuum level by an inner crystal potential $V_o$ which is in general complex and energy dependent. The method of muffin-tin potentials is similar to that used in solid state band theory calculations, but its use in LEED theory includes a number of additional factors that should be noted, for they reflect much of the fundamental physics that underlies the electron scattering process at surfaces.

To see this, let us review the parameters that must be included in the 'whole crystal' total scattering potential $V((R_{n}), (V_{at}(n))(F)$, $V_{or}, V_{oi}, \theta_{D})$ that is used to calculate the theoretical relative intensity spectra $I_{hk}^{calc}(E, \theta, \phi)/I_{o}$. The crystal potential is the composite of a number of factors, and depends generally on the ionic lattice positions $(R_{n})$, the form of the atomic scattering potentials $(V_{at}(n))(F)$, the shape and energy dependence of both the real and imaginary parts of the crystal inner potential $V_{or}$ and $V_{oi}$, and on the Debye temperature $\theta_{D}$ of the near surface region. In addition to a dependence on the crystal scattering potential, the theoretical intensity spectra are generally dependent on the incident electron beam's kinetic energy $E$, and its direction with respect to the surface normal $\hat{n}$. (This direction is defined by the polar angles $\theta$ and $\phi$.) The atomic positions in the crystalline lattice $R_{n}$ are the most important factor, for they give the structure of the surface.

The individual atomic scattering potentials $V_{at}$ are usually taken from band structure or free atom calculations but can also be adjusted for best fit. Both full atomic potentials and pseudopotentials (which eliminate the central part of the deep coulombic singularity as well as the inner core wavefunctions) have been used successfully for these atomic scattering potentials in LEED, although the potentials used in SLEED use only the full atomic potentials. This is because the spin-contributions to the scattering are due to deep penetrations into the atomic potential -- the spin-orbit interaction is strongest when the interacting electron penetrates the screening
electron cloud and interacts directly with the bare coulombic nucleus, and the exchange asymmetry for scattering from ferromagnets is due to the incident electron's interaction with electrons in the 3d-orbitals, which are tightly localized about the ionic sites.

The region spatially connecting the vacuum to the periodic lattice is defined as the 'transition region', and is exemplified by a continuous variation of the effective inner potential from the vacuum zero potential to the crystal muffin-tin zero. Feder\textsuperscript{62} notes that this surface potential barrier "...has in the 'near region' also lattice-periodic variations parallel to the surface....How safely these can be ignored, depends on the type of study..." In fact, there is some considerable debate about the relative contribution of the barrier as a whole to the observed features in LEED diffracted spectra. Jennings \textit{et al.}\textsuperscript{63} note that LEED fine-structure at very low energies is strongly affected by the shape of this surface barrier. They state that "...LEED intensity curves at low primary beam energies exhibit surface barrier resonance fine structure. These resonances are due to the interference between electron waves diffracted by the crystal surface and waves internally reflected by the surface barrier." Because of this, it is clear that the form of the surface barrier is most important to the analysis at low energies and at diffracted beam scattering angles that are large, (i.e. for nonspecular beams near emergence energy, or for specular beam scattering at large $\theta$ angles), for these conditions keep the electrons in this surface barrier region for the longest time. On the other hand, for diffracted beams at reasonably high energies (i.e. $\geq 40\text{eV}$) and scattering angle near normal (for example, from nonspecular beams at normal incidence) there is little contribution to the diffracted beams from the exact form of the surface barrier. In fact, in the analysis of the present Cu(001) study, Davis uses an extremely simple 'no-reflective' barrier, that essentially ignores the surface resonance contributions altogether, and the excellent agreement between calculations and experimental results indicates that they are totally unnecessary here.

Within the crystalline lattice the crystal potential between atomic muffin tins $V_0$ has two parts, a real part $V_{0r}$ and an imaginary part $V_{0i}$. The real component is identified with the 'inner potential' of the
crystal. While electron energies are measured outside the surface, in vacuum, the interference effects giving rise to the diffraction are determined by the electron wavelength, and hence the electron energy, inside the crystal surface. This difference in effective energy zeros between vacuum and surface is approximately equal to the sum of the crystal work function $\phi$ and the Fermi energy $E_f$, although Pendry notes that properly it is deduced from the real part of the self-energy of the electron in the solid and shows some dependence on the electron energy itself.

$$V_{or} \approx E_f + \phi.$$  

(2)

The effect of the inner potential on theoretical calculations is that the electron momentum inside the crystal is given by

$$\frac{1}{2}|\mathbf{\kappa}|^2 = E - V_{or}.$$  

(3)

causing the diffraction features in LEED profiles to be shifted down in apparent energy. This shift may be taken into account by performing the entire calculation using the crystal zero potential, and then shifting to account for the inner potential. Alternately, the solution to the crystal scattering may be worked out in full using the method noted by Kambe. "The solution in vacuum is automatically the superposition of the incident wave with the diffracted plane waves including evanescent (damped) waves. With a properly chosen model of the transition region between vacuum and the bulk of the crystal the solution in the vacuum is connected continuously to the solution inside the crystal..." using a 'wave-matching' procedure. As may be guessed from the importance of the exact form of the 'surface barrier' discussed above, there are cases where this wave-matching procedure is rather complicated, while in others, as for example the 'no-reflective barrier' the wave-matching is as simple as shifting the energy within the crystal associated with a given wave-vector by the complex inner potential $V_0$.

$V_{oi}$ accounts for attenuation of the elastically scattered beam resulting from inelastic events. If an electron loses energy in any of its interactions within the crystal, it is effectively eliminated from
any further contribution to the LEED intensities—it will be repelled by the retarding grids at the detector, and will thus not be picked up in the experimental diffracted beam intensity. At least this is the assumption of LEED theory; as noted above, phonon scattering, which is accompanied with very small energy loss doesn’t follow this rule. The point here, however, is that theoretical considerations must include an attenuation of the elastic portion of the electron intensity due to inelastic losses. Electrons are lost from the elastic peaks by energy loss through electronic excitation of target atoms, or by plasmon or phonon creation or scattering of secondary electrons (the last of which is usually much stronger). Often incident electrons rattle around in the crystal until they lose most of their energy or are backscattered out of the crystal with the energy losses large enough that they don’t contribute to the elastic energy peak. These backscattered electrons instead contribute to the secondary electron background spectrum noted above. (See again Figure 2.) Inelastic scattering is included in LEED theoretical calculations as an isotropic loss process removing electrons from the incident and scattered beams either by means of a mean free path, or equivalently by including an imaginary part in the crystal potential $V_0$. The effect in either case is to make an imaginary contribution to the electron wave vector so that $k$ becomes $k_r + ik_i$. For a spherical wave we can then write

$$\psi \sim e^{i(k_r + ik_i)r} = e^{-k_i r} e^{ik_r r}.$$  

$$= e^{-r/\lambda_{ee}} e^{ik_r r}.$$  

(4)

where $\lambda_{ee}$ is the amplitude mean free path and is simply the reciprocal of $|k_i|$. Evidently the intensity decays with a mean free path of $\lambda_{ee}/2$. Alternatively including these losses as an imaginary contribution to the crystal potential, $V_{oi}$, it is easy to show that, providing $V_{oi}$ is much smaller than the total kinetic energy, then

$$\lambda_{ee} \approx \frac{3.90(E)^{1/2}}{V_{oi}}.$$  

(5)

Because the possible loss processes are functions of electron energy,
\( V_{oi} \) (or the equivalent \( \lambda_{\text{ee}} \)) is not constant\(^{68}\) but also is a function of electron energy.

II.C.2 Crystal Momentum Conservation\(^{69}\)

Diffraction studies of crystalline structure rely on the special effects of coherent interference between scattered waves from a periodic structure to produce sharp beams in the elastically scattered signal which can be related to the periodicity of the structure. The effect of the crystal periodicity on the scattering is to modify momentum conservation such that electron momentum is conserved plus or minus any reciprocal lattice vector. In a three-dimensionally periodic system, this momentum conservation may be written as:

\[
\mathbf{\tilde{\mathbf{\Gamma}}} = \mathbf{\tilde{\mathbf{\Gamma}}}_0 + \tilde{\mathbf{g}}_{hkf}
\]

(6)

where \( \mathbf{\tilde{\mathbf{\Gamma}}}_0 \) and \( \mathbf{\tilde{\mathbf{\Gamma}}} \) are incident and emergent electron wave vectors and \( \tilde{\mathbf{g}}_{hkf} \) is a reciprocal lattice vector:

\[
\tilde{\mathbf{g}}_{hkf} = h\mathbf{\tilde{a}}^* + k\mathbf{\tilde{b}}^* + l\mathbf{\tilde{c}}^*
\]

(7)

h, k and l being integers while \( \mathbf{\tilde{a}}^* \), \( \mathbf{\tilde{b}}^* \) and \( \mathbf{\tilde{c}}^* \) are the primitive translation vectors of the reciprocal lattice which is defined relative to the real space lattice primitive translation vectors, a, b and c by:

\[
\mathbf{\tilde{a}}^* = \frac{2\pi b}{V} \mathbf{\hat{a}}, \quad \mathbf{\tilde{b}}^* = \frac{2\pi c}{V} \mathbf{\hat{b}}, \quad \mathbf{\tilde{c}}^* = \frac{2\pi a}{V} \mathbf{\hat{c}}
\]

(8)

\[
V = \mathbf{\tilde{a}}^* \cdot \mathbf{\tilde{b}}^* \times \mathbf{\tilde{c}}^*
\]

(9)

V being the volume of the primitive unit cell in real space. It is easy to derive from equations (6), (7) and (8) momentum conservation conditions necessary for diffraction maxima based on the parameters of the primitive translation vectors in real space. These relations, called the Laue conditions\(^{70}\), are:
\begin{align}
(\vec{k} - \vec{k}_0) \cdot \vec{a} &= 2\pi n \\
(\vec{k} - \vec{k}_0) \cdot \vec{b} &= 2\pi k \\
(\vec{k} - \vec{k}_0) \cdot \vec{c} &= 2\pi \ell 
\end{align}

For a surface, translational symmetry perpendicular to the surface is weakened leaving a system which is two-dimensionally periodic. This means that the special momentum conservation of equation (6) applies only to the component of the wave vectors parallel to the surface. Thus we have:

\begin{align}
\vec{k} \parallel = \vec{k} \parallel^0 + \vec{g}_{hk}
\end{align}

which is equivalent to the first two Laue conditions (i.e. equations (9) and (10)) being valid, where \( \vec{a} \) and \( \vec{b} \) are the lattice net vectors in the surface plane, while the third is eliminated. The \( \vec{k} \parallel \) notation relates to the components of the wave vector lying in the plane of the surface while \( \vec{g}_{hk} \) is a reciprocal net vector of the surface unit mesh:

\begin{align}
\vec{g}_{hk} = h\vec{a}^\ast + k\vec{b}^\ast
\end{align}

\( \vec{a}^\ast \) and \( \vec{b}^\ast \) are the primitive translation vectors of the reciprocal net now being defined relative to the real space net primitive translation vectors \( \vec{a} \) and \( \vec{b} \) and a unit vector normal to the surface, \( \vec{n} \), by:

\begin{align}
\vec{a}^\ast &= \frac{2\pi \vec{b} \times \vec{n}}{A}, & \vec{b}^\ast &= \frac{2\pi \vec{a} \times \vec{n}}{A}, & A &= \vec{a} \cdot (\vec{b} \times \vec{n})
\end{align}

\( A \) being the area of the surface unit net in real space. The momentum conservation, together with an energy conservation equation:

\begin{align}
k^2 = k_0^2
\end{align}

or

\begin{align}k^2\parallel^0 + k^2\perp = k^2\parallel + k^2\perp
\end{align}

totally defines the conditions for the diffracted beams \( k \) and hence forms a three-dimensional statement of Bragg's law. For electrons propagating in the complex inner potential \( V_0 \) of the crystal, this gives possible wave-vectors of the form:
\[ \mathbf{\kappa} = \begin{cases} 0 \frac{\mathbf{\kappa}}{\mathbf{\kappa}} + \mathbf{\hat{e}}_{hk} \mathbf{x} \\ 0 \frac{\mathbf{\kappa}}{\mathbf{\kappa}} + \mathbf{\hat{e}}_{hk} \mathbf{y} \\ \pm [E + V_{or} + iV_{oi} - |\mathbf{\kappa}|_p + \mathbf{\hat{e}}_{hk}^2]^{\frac{1}{2}} \end{cases} \] (16)

where here the surface net is in the xy-plane. It is the imaginary component of this wave-vector normal to the surface that leads to the attenuation of the electron beams as they propagate through the crystal.

The form of the crystal potential \( V_0 = V_{or} + iV_{oi} \), along with its spatial and energy variations, therefore, accounts for much of the fundamental physics underlying two of our five critical SLEED model characteristics. The real part of the inner potential \( V_{or} \), and especially its spatial variation in the transition region right at the surface, accounts for the transmission of electron waves into and out of the crystal, as well as the differences in the effective beam energy inside and outside the sample. In addition, the imaginary contribution to the inner potential \( V_{or} \) (or equivalently, the imaginary contribution to the electron wave-vector \( \mathbf{\kappa} \)) accounts for the attenuation of the elastically diffracted beams due to energy loss mechanisms in the crystal.

We will find shortly that both the spin dependent effects and lattice vibrations are taken into account in the interaction of the electron wave with the individual ionic potentials \( V_{at}^{(n)}(\mathbf{\kappa}) \) (i.e. they are entirely due to interactions within single muffin-tin radii). We will deal with these two factors in succeeding sections. On the other hand, the multiple-scattering problem is not dealt with so easily. The single largest complication found in both the LEED and SLEED formalisms is the inclusion of multiple scattering effects. It is this 'multiple scattering problem' on which the great and complicated structure of LEED theories is based.
II.C.3 Kinematic LEED Theories

Historically, the first attempts at modelling low-energy electron diffraction were formulated in terms of a modified version of classical X-ray diffraction theory.\textsuperscript{71} Much as X-rays incident on a crystal are diffracted in certain directions preferentially by the constructive interference between wavefronts from different scattering centers, electrons are found to be diffracted upon interaction with crystals. The basic differences are that the interaction for electrons is much stronger, both for elastic and inelastic scattering. While the electron-ion core interaction is primarily described by a coulomb potential, the photon-ion core interaction that leads to X-ray diffraction is the relatively weak dipole interaction. This weak scattering allows the X-rays to penetrate deeply into the crystal and carry with them traits which reflected the bulk properties of the crystal. On the other hand, the stronger electron scattering means that fewer and fewer electrons react with each successive atomic layer. Essentially all the elastic electrons are lost to inelastic processes or backscattered out of the crystal within the first 4 - 5 atomic layers.

The assumption basic to such kinematical LEED formalisms is that "scattering by ion cores is weak in the sense that...only a small fraction of the electrons is scattered from the path that would have been taken in the absence of the ion cores."\textsuperscript{72} The assumption is effectively that most of the surface specificity is due to inelastic processes, and not large elastic backscattering. In such a case the inelastic scattering could be included in existing theories by modifying the crystal potential to include an imaginary absorptive term, $V_{oi}$ - a reasonably simple modification. On the other hand, any large elastic backscattering would be dependent on the particular form of the individual atomic scattering potentials, $V^{(n)}(\mathbf{r})$. Strong elastic backscattering is also necessarily followed by strong multiple scattering - requiring a complete reworking of the way the interaction was modeled. The effect of weak scattering would be that only the primary electron wavefronts contribute to the detected scattering intensities while all the scattered wavefronts are sufficiently attenuated by the inelastic scattering processes so that any secondary
or multiple scattering is so small that it may be ignored. The beauty of the assumption was that low-energy electron diffraction could be described reasonably simply by a transcription of the single scattering X-ray diffraction theories, which were available at the time these early kinematic theories were being developed and which describe the weak scattering of X-rays in crystals quite well.

The problem was that elastic backscattering was simply too large and led to measured diffraction features that could not be accounted for by a single-scattering formalism. These multiple-scattering effects cannot be incorporated within the framework of kinematic theories, and thus an entirely new formulation, with multiple scattering integrally included, must be prepared. The dynamical LEED formalism was the result.

II.C.4 Dynamical LEED Theories

The multiple scattering formalism of dynamical LEED theory has been developed and refined by a number of workers to include multiple scattering effects in LEED calculations. The details of the calculation are somewhat different in each version, but for the most part the overall method is generally similar. Our discussion here will start by focusing on the multiple scattering theory developed by Beeby and discussed by Kambe and others, which is typical of the methods used. The formulation starts with the set of equations:

\[ \psi^S_i = t_i(\psi^{(0)} + \sum_{j \neq i} G_{ij}\psi_j^S) \]  (17)

where \( \psi^S_i \) is the scattered wave from the \( i \)-th atom, \( \psi^{(0)} \) the primary wave, \( t_i \) the 't'-matrix of the \( i \)-th scatterer representing its scattering amplitude, and \( G_{ij} \) Green's functions representing the propagation of the wave from scatterer \( j \) to scatterer \( i \).

The method used is described by Kambe for Beeby's theory in a general form using operators. The contribution of single atoms to the diffraction amplitude by the system of atoms is represented by T-matrices, writing in equation (17):
\[ \psi_i^S = T_i \psi_i^{(0)} \] (8)

so that his method is referred to as the 'T-matrix method'....In Beeby's theory there are four kinds of T-matrices \( v, t, \tau \) and \( T \) derived successively by including step by step an additional kind of multiple-scattering processes in calculation." This is shown schematically as follows:

<table>
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<tr>
<th>Approx. 1</th>
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<td>atoms</td>
<td>atoms</td>
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\[ v \longrightarrow t \longrightarrow \tau \longrightarrow T \]

**Step 1**
\[ '\text{multiple scatt.'} \]
\[ \text{inside} \]
\[ \text{atoms} \]

**Step 2**
\[ \text{multiple scatt.} \]
\[ \text{inside} \]
\[ \text{single layers} \]

**Step 3**
\[ \text{multiple scatt.} \]
\[ \text{between} \]
\[ \text{layers} \]

It may be noted that the first two approximations and step 1 are essentially the procedure used in kinematical LEED theory. Jona discusses the procedure involved in these steps thus: "The first step consists in the calculation of the phase shifts \( \delta \) of the atom(s) involved by integrating the radial Schrödinger equation, thereby allowing the calculation of the exact value(s) of the atomic scattering amplitude(s) \( f(\theta) \) by the standard partial-wave method according to the well-known formula with Legendre polynomials \( P_l(\cos \theta) \):

\[ f(\theta) = (2ik)^{-1} \sum_l (2l+1)[\exp(2i\delta) - 1]P_l(\cos \theta) \] (19)

"...In the second step, the scattering amplitude of a single atomic layer is calculated self-consistently, i.e., in such a way that the wave scattered by an atom is proportional to the primary wave plus the sum of all scattered waves from the other atoms in the layer. This calculation is normally done in the so-called angular momentum (or L) representation using spherical-waves. The result of this calculation represents
effectively what is usually called the scattering matrix of the atomic layer considered.

"The third step consists in the calculation of the multiple scattering between atomic layers, a calculation that can be performed either in the L representation or in the linear-momentum (or E) representation using plane waves....For both formalisms, time-saving but less accurate perturbation schemes have been developed."

Pendry 83 notes that "...several schemes have been proposed for handling the multiple scattering problem. These methods are formally exact in the sense that they can be made as accurate as desired by taking sufficient terms in some convergent expansion of the wave function e.g. of a Fourier Series. Several of them have now been used in conjunction with accurate scattering factors for the ion cores, etc.85 The problem is that these methods take a long time, because computational time scales as n^3 where n is the number of beams. Thus perturbative computational methods are often found to speed up the calculations significantly. Here, however, care must be taken that the perturbative series converge sufficiently.

The calculation involved in each of these successive steps is essentially the manipulation of an increasingly complicated matrix equation and is performed numerically on computers. Joyner and Szmoulaj 86 describe the T-matrix formulation of Beeby,87 which was refined and extended by Duke and Tucker 88 thus: T_\lambda is a T-matrix for scattering of an incident electron by the \lambda th layer in the presence of the other layers. The quantity T_\lambda(E_0;E) can be obtained in a convenient algebraic form by means of a partial wave expansion using the conventional spherical harmonics, Y_{jm}(\vec{E}), where \vec{E} is a vector whose spherical components are the angles \theta and \phi:

$$T_\lambda(E, E_0; E) = \sum_{jm} \sum_{j'm'} T_{\lambda}^{jm, j'm'} \ Y_{jm}(\vec{E}) \ Y_{j'm'}(\vec{E_0})$$

(20)

"All directional information for the incident and outgoing beams is contained in the spherical harmonics, and the matrix, T_\lambda^{jm, j'm'}(E), is a function only of energy. Once this matrix is calculated, it is a simple matter to repeat the summation for all beams, h, of interest. It is customary to replace the double index (jm) by a single index (jm) \Rightarrow L.
Using this notation, we may write:

\[ I_{\text{hk}}(E, E_0; E) = \frac{(2\pi)^2}{\hbar^2} \sum_{L, L'} Y_L^*(\vec{E}) Y_{L'}(\vec{E}_0) \sum_{\lambda} e^{i(\vec{E}_0 - \vec{E}) \cdot \vec{d}_{\lambda}} T_{LL'}^{\lambda(\vec{E})} \]  

(21)

"The scattering problem now reduces to calculating the matrix, \( T_{LL'}^{\lambda(\vec{E})} \). The first approximation made is to terminate the summations over \( L \) and \( L' \) yielding a matrix of finite dimensions. ... The matrix \( T_{LL'}^{\lambda} \) can then be obtained from the equation:

\[ T_{LL'}^{\lambda} = T_{LL'}^{\lambda} + \sum_{L''} T_{LL'}^{\lambda} \sum_{\lambda'} \sum_{L'''} G_{\lambda \lambda'}^{L''} T_{L'''}^{\lambda'} L'' L''', \]  

(22)

where:

\[ T_{LL'}^{\lambda} = T_{LL'}^{\lambda} + \sum_{L''} T_{LL'}^{\lambda} \sum_{\lambda'} \sum_{L'''} G_{\lambda \lambda'}^{L''} T_{L'''}^{\lambda'} L'' L''', \]  

(23)

and:

\[ t_{\lambda}^{LL'} = \delta_{\lambda \lambda'} \delta_{\text{mo}} \frac{i \hbar}{4m \hbar} [e^{i2\delta(E)} - 1] \]  

(24)

Equation (24) is a \( t \)-matrix for the elastic scattering of an incident electron of mass \( m \) and wave vector \( \vec{k} \) from a potential characterized by a set of energy dependent phase shifts, \( \delta(E) \). The only conditions on the potential (i.e., ion cores) at this point are that it be spherically symmetrical and that neighbouring potentials do not overlap."  

II.C.5 Lattice Vibrations and LEED

Both an attenuation of the elastic diffracted beam intensities and a rise in quasi-elastic thermal diffuse background are due to the harmonic vibrations of the crystal. Joyner and Somorjai describe the inclusion of temperature into the T-matrix formulation of dynamical LEED theory: Larmmore and Duke have shown that lattice motion can be taken into consideration at this point [i.e., when obtaining the energy dependent phase shifts \( \delta(E) \) in the single muffin-tin potential stage of T-Matrix manipulation] by the renormalization of the site scattering vertices, \( t_{\lambda} \). The renormalized quantity \( b_{\lambda} \) is expressed:
\[ b_\lambda (E, E_0; E) = t_\lambda (E, E_0; E) e^{-W_\lambda (E-E_0)} \]  
\[ (25) \]

where \( W_\lambda (k-k_0) \) is the Debye-Waller factor for the \( \lambda \)th layer. If we use the Debye model for the phonon spectrum, the resulting matrix \( b_\lambda^{LL'} \) is diagonal, as was \( t_\lambda^{LL'} \). The effect of finite temperature is thus to alter the phase shifts, \( \delta (E) \) appearing in equation (24). This is done internally in the computer program by expanding the exponential term in equation (25) in spherical harmonics. Provision is made in equation (25) for a layer-dependent Debye-Waller factor. \(^93\)

Feeder \(^94\) notes that for both LEED and SLEED it is true that "...thermal lattice vibrations... involve, strictly speaking, inelastic processes (electron-phonon scattering)...) and thus supposedly do not need to be included in the formulation of pure elastic scattering. However, there is an effect even on the elastic scattering due to lattice vibrations. The effect on the elastic channel (zero-phonon scattering) amounts to an attenuation of the elastic diffracted beams, and may "...be obtained by means of the Born-Oppenheimer approximation, i.e., by treating elastic scattering from 'frozen' atomic displacement configurations and averaging the T-matrices over the configurations. Assuming a Debye spectrum of lattice modes and neglecting correlations between atomic vibrations, the result amounts to a renormalization of the single-sight \( t_\lambda^{LL'} \) matrix (essentially by a Debye-Waller factor)... If \( t_\lambda^{LL'} \) is diagonal and expressed in terms of scattering phase shifts \( \delta_\lambda^{\pm} \), its renormalization is equivalent to replacing the \( \delta_\lambda^{\pm} \) (which are real for real \( V_n (r) \) and real energy) by effective complex ones \( \delta_\lambda^{\pm} \). The additional imaginary part accounts for the removal of flux out of the elastic channel.\(^95\) Jepsen indicates that the effect of this configuration averaging is to give "...generalized phase shifts for atoms 'blurred' by thermal motion.\(^96\) These are then used in the multiple scattering calculation.

Once the scattering matrices \( T_\lambda^{LL'} \) of equation (22) have been calculated including all multiple scattering and vibrational effects, equation (21) may then be used to calculate the intensities of each of the diffracted beams. These calculations are very long and tedious, requiring the computer-intensive manipulation of a series of very large matrix arrays. Great concern has been expressed that increasingly
precise LEED (and SPLEED) formalisms applied to calculation of increasingly complex structural models would lead to the downfall of the spectroscopy — the calculations would simply become too cumbersome and would collapse under their own weight. In practice, however, the situation has been far from this. The development of a number of streamlined perturbative techniques and the advent of increasingly fast and efficient super-computers have more than compensated for the increasing complexity of the studies. While LEED calculations are far from simple, they are considered readily manageable by state-of-the-art techniques.

II.C.6 APPLICATION OF PERTURBATION THEORY — Renormalized Forward Scattering (RFS)

In the spin-dependent extension of the LEED formalism, two distinct approaches have been taken to account for interlayer scattering. In the approach of Feder and coworkers, the emphasis is on the formally exact approach discussed above, while Davis's work utilizes a spin-dependent extension of Pendry's renormalized forward scattering (RFS), which is one of the more successful perturbative approaches implemented to date. The implications of each of these methods in SPLEED analysis will be discussed shortly. But because of Davis's use of a spin-dependent RFS formalism in his analysis of the present Cu(001) study, we will focus some discussion on this formalism and its assumptions here.

Pendry notes that the basic tenet of RFS perturbation schemes is that "strong elastic scattering is confined to the forward direction, back scattering is weak" and thus the most efficient perturbation expansion is one that "...takes account of forward scattering to all orders leaving only weak backscattering to be treated by perturbation theory." Here 'weak back scattering' implies that the backscattered waves, while far from negligible (which would be equivalent to the requirement for kinematic scattering) are nonetheless small compared to forward scattering.

Van Hove and Tong describe the formulation of RFS perturbation theory thusly, "A convenient way to produce the scattering paths for the lowest order of perturbation is to follow the plane waves generated by
Figure 5. EFS perturbation procedure. The forward-scattered electron wave-fields transmitted through a given layer, indicated by a 't', are calculated exactly. Reflected waves, backscattered by each layer, indicated by an 'r', are taken to be small and are included perturbatively. [After Van Hove and Tong, ref. 1, fig. 9.1, p. 72.]

The incident beams as they forward-scatter from layer to layer into the surface until damping makes them die out; then, starting from the deepest layer reached in penetration, the emerging plane waves, obtained by reflecting the penetrating ones, are forward-scattered outward from layer to layer, picking up reflections from the penetrating waves at each layer; the emerging plane waves constitute the first-order result. The next order of perturbation is obtained by reflecting the emerging plane waves back into the crystal, starting from the top layer, and forward-scattering them inward as in the first order, but now additionally picking up reflections from emerging waves at each layer. Damping again limits the penetration and, as in the first order, the newly reflected emerging plane waves are propagated to the surface, picking up reflections on the way: the second-order result emerges, to be added to the first-order. This procedure is repeated for higher orders until convergence of the reflected amplitudes." The procedure is shown schematically in figure 5.
"The RFS Scheme typically uses 12 to 15 layers and 3 to 4 orders of iteration for convergence. The RFS computation requires relatively small amounts of computation time compared with the generation of the layer diffraction matrices.

"By its very assumptions RFS fails to converge well when the multiple scattering between any pair of successive layers is very strong (due to strong layer reflections). This happens especially at very low energies (E < 10eV) when the electron damping is small (which implies a long mean free path). RFS is also unstable when an interlayer spacing becomes small (less than 1.0 Å), requiring many evanescent plane waves for the description of the wavefield."103

II.D SPIN-POLARIZED LEED THEORY

The next refinement of LEED experimental and theoretical studies is the inclusion of spin dependent scattering into LEED diffraction. Up to this point, the electron has been treated as a spinless particle, having no internal degrees of freedom. In reality, however, electrons are not spinless, and thus their interaction with atoms and solids will manifest spin dependent effects. This spin dependence should be reflected in theoretical calculations as a part of the scattering Hamiltonian, as well as by polarization effects in experimental results. Feder 104 notes that when "...the electron–solid interaction Hamiltonian contains a spin-dependent contribution, the diffracted beams exhibit, in addition to intensity variations, spin polarization effects, which can manifest themselves in two forms: (a) as an asymmetry in the scattered intensities for polarized primary beams of opposite spin alignment; or (b) for an unpolarized primary beam, as spin polarization of the diffracted beams....As for spin-dependent interaction mechanisms, there are two types relevant for LEED: spin–orbit coupling, which is particularly strong for large-Z materials, and — in the case of ordered magnetic structures — the exchange interaction between the LEED electron and the ground state electrons of the solid."50 Each of these spin-dependent interactions may be exploited to give information about near-surface properties.

Kirschner 105 describes the contribution of each to electron/surface interactions: "There are two main physical phenomena
giving rise to spin-dependent effects in the interaction of free
electrons with surfaces: the spin-orbit interaction and the exchange
interaction. Both effects are in general present simultaneously,
interfering with each other, but there are conditions where they may be
isolated to some extent and studied separately. The spin-orbit
interaction is most pronounced in electron scattering... from heavy,
non-magnetic materials. It is essentially due to the interaction of the
spin of an electron with its own angular momentum in the electric field
of a strong scattering potential. The important ingredient therefore is
the presence of a strong attractive ion core. The conduction electrons
and bound electrons do play a role, but they are not essential for the
existence of the effect.

"The exchange interaction, however, is bound to the presence of
other electrons. It is essentially an outcome of the Pauli principle,
requiring the total wavefunction (including spins) of fermions to be
antisymmetric with respect to a permutation of the particles. The
forces arising from the exchange interaction are of Coulombic nature,
and are therefore comparable to those due to the spin-orbit interaction.
When scattering an electron from a surface, exchange interactions are
always involved, even with non-ferromagnetic materials. However, as
spin-up and spin-down electrons are present in exactly equal amounts in
these materials, there is no net effect on the spin polarization or
relative intensities of scattered electrons due to the interaction with
the electrons of the solid. In ferromagnets, this balance is destroyed
and we have polarization effects even if the spin-orbit interaction is
negligible. This allows us to study surface and bulk magnetism and the
electronic structure of ferromagnets via an analysis of the spin state
of the scattered electrons.\textsuperscript{106}

Both experimental and theoretical studies confirm that significant
polarization effects are found in electron scattering with both high-Z
and magnetic surfaces and use of SPEEED in the study of both types of
surfaces is the focus of much recent and current research.\textsuperscript{107} In our
present discussion we will focus first on effects due to the spin-orbit
interaction, and then on those due to the exchange interaction.
II.D.1 Inclusion of Spin-Orbit Effects

Polarization effects due to spin-orbit coupling were first predicted by Mott\textsuperscript{108} in 1929 for large angle elastic scattering of high energy electrons (of about 100keV) by larger-Z coulomb potentials (the so-called 'Mott effect') and were experimentally confirmed by Shull et al.\textsuperscript{109} in 1943. Spin polarization effects in LEED have been qualitatively predicted by a number of investigators,\textsuperscript{110} but quantitative results, which were based on scattering from W(001), were first obtained by Jennings\textsuperscript{111}, Feder\textsuperscript{112}, and Jennings and Sims\textsuperscript{113} using dynamical SPOLEED theories between 1970-74. The first spin-polarized LEED experiment was attempted by Davisson and Germer\textsuperscript{114} in 1929 [by means of a double scattering experiment involving two Ni (111) crystals]. However, a conceptual error on the part of the experimentors led to a null result.\textsuperscript{115} The first successful confirmation of spin polarization effects in LEED was made experimentally in this lab for scattering from W(001) in 1975 by O'Neili et al.\textsuperscript{116} Since then a wide variety of successful SPOLEED studies have been done on systems ranging from ferromagnetic ordering studies to investigations of a wide variety of high-Z/lowZ adlayer/substrate systems.

The spin-polarized low-energy electron diffraction formalism is an extension of dynamical LEED methods and include full multiple scattering considerations. The contributions of all the physically relevant elements discussed above under the LEED framework are included here in the same manner. The transmission of waves into and out of the surface as well as inelastic losses are included through the complex crystal potential (or the equivalent complex wave vector \( k \); see eq. 16). The thermal vibrations of the ionic lattice are included through a 'blurred atom' approximation developed by Tamura et al.\textsuperscript{117} which is a spin-dependent extension of the formulation of Laramore and Duke\textsuperscript{118} that gives complex phase shifts for scattering from each ionic core.

The main difference here is that while the unpolarized dynamical LEED calculations start with a spin-less Schrodinger wave equation, the polarized LEED calculations begin with the Dirac equation, which includes spin dependence as a natural result of its formulation.\textsuperscript{119} The effective Dirac Hamiltonian is of the form:
\[ H = c^2 \vec{p}^2 + \beta mc^2 + \mathbf{V}(E, \mathbf{r}) - \beta \boldsymbol{g} \cdot \mathbf{B}(E, \mathbf{r}) \]  

(26)

where \( c \) is the speed of light, \( m \) the rest mass of the electron, with the electron charge \( e = -|e| \). The (4x4) matrices are of the form \( \gamma = (a_1, a_2, a_3, \mathbf{\beta}) \), and \( \mathbf{\gamma} \) are the (4x4) version of Pauli spin matrices.\(^{120}\)

In the nonrelativistic limit, with terms up to the order \( 1/c^2 \), and linear in \( \sigma \) and \( \mathbf{B} \), the Dirac Hamiltonian eq.26 is approximated by the (2x2) form:

\[ H = \frac{\hat{p}^2}{2m} + \mathbf{V}(E, \mathbf{r}) - \frac{\beta^4}{8m^2c^2} + \frac{\hbar}{8m^2c^2} \Delta \mathbf{V}(E, \mathbf{r}) + \frac{\hbar}{4m^2c^2} \frac{d}{dx} \mathbf{V}(E, \mathbf{r}) \hat{\sigma} \cdot \hat{L} - \hat{\sigma} \cdot \mathbf{B}(E, \mathbf{r}) \]  

(27)

where \( \hat{p} \) is the momentum operator, \( \hat{\sigma} \) the Pauli spin operator and \( \hat{L} \) the angular momentum operator. It may be seen that this formula includes four terms in addition to those found in the spinless Schrödinger hamiltonian (which itself comprises only the first two terms in eq.27): two scalar terms, the spin-orbit coupling term, and an interaction term between spin and an external magnetic field. This last term (the last term to the right in both eqs.26 and 27) will be used for including the magnetic exchange interaction shortly, but for the present discussion, which focuses on the contribution of the spin-orbit interaction, it may be neglected. Feder notes that the two scalar corrections (i.e. the third and fourth terms in eq.27) should modify the scattering cross sections (i.e. the intensities), and are small for nonrelativistic energies, while the spin-orbit coupling will introduce spin-polarization effects, and should produce a spin-splitting in the scattering phase shifts \( \delta_j \) (for \( j > 0 \)).\(^{121}\) The effect is that this splits the derivation into two separate scattering problems, one for spin-up electrons, and one for spin-down.

Feder\(^ {122}\) describes the formulation: 'The scattering problem [within each muffin-tin sphere] is solved by a relativistic partial wave analysis, which yields, as a consequence of spin-orbit coupling, for each orbital angular momentum quantum number \( l > 0 \) two scattering phase shifts \( \delta^+_l \) and \( \delta^-_l \), which relate to the total angular momentum quantum numbers \( j = l + \frac{1}{2} \) and \( j = l - \frac{1}{2} \), respectively. A 'direct' scattering amplitude \( f(\theta) \) and a 'spin flip' amplitude \( g(\theta) \) are then obtained as:
\[ f(\theta) = \frac{1}{2ik} \sum_{k} \left[ (\pm 1)e^{2i\delta_{4}^{+}} - 1 \right] + \xi [e^{2i\delta_{4}^{-}} - 1] P_{k} (\cos \theta) \] (28)

\[ g(\theta) = \frac{1}{2ik} \sum_{k} [e^{-2i\delta_{2}^{+}} + e^{2i\delta_{2}^{-}}] P_{k} (\cos \theta) \] (29)

where \( P_{k} \) and \( P_{k}^{\dagger} \) are Legendre polynomials and \( k \) is the length of the momentum vector \( \vec{E} \). The differential cross section (which is proportional to \( I \)) and the spin polarization \( P \) (along \( \hat{n} \), the normal to the scattering plane) for an unpolarized incident beam and the asymmetry \( A \) for incident beams fully polarized parallel and antiparallel to \( \hat{n} \) are:

\[ I(\theta) = |f(\theta)|^2 + |g(\theta)|^2, \quad P(\theta) = A(\theta) = -2 \text{Im}[f(\theta)g^{*}(\theta)]/I(\theta) \] (30)

The actual experimentally measured spin polarization \( P \) (say, of the primary beam incident on the sample) and spin-asymmetry \( A \) (say, of a diffracted beam) may also be written in terms of the spin populations \( I(P_{0}) \) and \( I(-P_{0}) \) in that beam. The spin populations \( I(P_{0}) \) and \( I(-P_{0}) \) are defined as the intensity (or number density) of the electrons with spins aligned parallel and antiparallel, respectively, to a spin quantization direction aligned with \( \hat{n} \). (These populations are equivalently called 'spin-up' and 'spin-down' populations, \( I(\uparrow) \) and \( I(\downarrow) \), respectively; the notation is essentially equivalent.) The beam polarization \( P_{0} \), of the incident beam may be written:

\[ P_{0} = \frac{I_{0}(\uparrow) - I_{0}(\downarrow)}{I_{0}(\uparrow) + I_{0}(\downarrow)} \] (31)

where \( I_{0} \) is used to differentiate incident beam intensities from diffracted beam intensities, which will be given only with \( I \). The spin-asymmetry \( A \), of any one of the diffracted beams, may be written:

\[ A = \frac{1}{P_{0}} \frac{I(P_{0}) - I(-P_{0})}{I(P_{0}) + I(-P_{0})} \] (32)

where, here, the incident beam is not assumed to be fully polarized, but has a polarization \( P_{0} \), defined by eq.31.

The multiple intralayer scattering is accounted for much as is done
in spinless LEED. The SPLLEED theoretical formulation developed by Feder\textsuperscript{123} uses a relativistic analogue of the 'layer-KKR' formulation of Pendry\textsuperscript{124} to calculate intralayer scattering.\textsuperscript{125} The result is a (4N x 4N) scattering matrix $M$ of the form:

$$M_{g'g}^{s's'} = \delta_{g'g} \text{sgn} \frac{8\pi^2}{kK} \sum_{s' \neq s} \frac{1}{2} \left( e^{i2\piK - 1} \right) \sum_{s''} C_{\mu''} \left( \frac{1}{2}, j'' ; \mu'' - s' , s' \right) \chi_{g''}^{-1} \chi_{g'}^{*} C_{\mu'} \left( \frac{1}{2}, j' ; \mu' - s , s \right)$$

(33)

where $\delta_{K}$ are the phase shifts associated with spin-up and spin-down scattering, $\delta_{g'g}^{s's'}$ is a Kronecker delta, and the $C(\frac{1}{2}, j ; \mu - s , s)$'s are Clebsch-Gordon coefficients, and $\chi$ has the elements:

$$\chi_{g'g}^{-1} = \frac{1}{2} \left( e^{i2\piK - 1} \right) \sum_{s''} C_{\mu''} \left( \frac{1}{2}, j ; \mu - s , s \right) C_{\mu'} \left( \frac{1}{2}, j' ; \mu' - s , s' \right)$$

(34)

and here $G_{g'g}^{-1} = \frac{1}{2} \left( e^{i2\piK - 1} \right) \sum_{s''} C_{\mu''} \left( \frac{1}{2}, j ; \mu - s , s \right) C_{\mu'} \left( \frac{1}{2}, j' ; \mu' - s , s' \right) \chi_{g''}^{*}$ is the Green's function describing electron propagation between lattice scattering sites $g''$ and $g'$\textsuperscript{126}. Although the notation is different, the matrix $M_{g'g}^{s's'}$ is equivalent to the intralayer scattering matrix $\tau_{\lambda}^{LL'}$ shown above in equation (23).

The multiple scattering between layers may be approached, as in LEED theory, either by formally exact methods or using a perturbative approach. Feder uses the former, and Davis the latter. Interlayer scattering is included in Feder's formalism by diagonalizing the $M$ matrices and then transforming each into a (4N X 4N) transfer matrix $Q$ which relates the plane waves amplitudes $(u_{gs}^{+}, v_{gs}^{-})$ on one side of the layer to those $(u_{gs}^{-}, v_{gs}^{+})$ on the other.\textsuperscript{127} Then using a generalization of Pendry's Bloch wave method, the contributions of each layer's $Q$ are multiplied until an overall bulk transfer matrix is obtained.\textsuperscript{128} This is essentially a spin dependent version of the $K$-representation formulation discussed above in the spin-less dynamical LEED theory section. The advantage of this method is that it is formally exact, and thus the calculations are assured of convergence even with strong backscattering.

Computationally, this is a very complicated and tedious process. Because both spin components must be included in each calculation, the
dimensions of each matrix solved must be doubled compared to the spinless form. This makes computer memory requirements go up by a factor of four, and computational time, which scales as $n^3$ for matrix operations involving $(n \times n)$ matrices, go up by a factor of almost eight, compared to spinless dynamical LEED theories. There are indications also, both for these formally exact methods, and for perturbative techniques, that a greater number of angular momentum contributions and scattered beams are required in SPLEED calculations than in their spinless counterparts to completely model the scattering. The result is a requirement for even larger matrices and further computer time for use in such calculations.

Davis' SPLEED treatment of interlayer scattering uses a newly developed spin-polarized extension of Pendry's renormalized forward scattering. Here the matrices involved in the perturbative interlayer scattering are, as in Feder's exact formalism, twice the size as in their spinless analogue to account for both spin-up and spin-down scattering amplitudes. This formulation, however, does not require the very time consuming matrix inversion of the formally exact methods, and this allows the computational speed to be much faster, scaling as $n^3$. Even with detailed checks for numerical convergence at several stages in the calculation, which are required of perturbative techniques, this method seems to show the promise of considerable time savings with accuracy comparable to that of exact methods. The weakness here is that RFS perturbation theory will not work for all surfaces, for in cases where backscattering is too strong, or interlayer spacing is too small, the basic assumptions of weak-backscattering RFS perturbation break down.

It is, in any case, found that both approaches show excellent results. The approach of Feder and coworkers has been the basis for experimental/theoretical comparisons of a wide range of SPLEED studies of magnetic and nonmagnetic systems, and shows good agreement with experimental results for a broad range of structural models and diffraction conditions. The SPLEED formulation of Davis, newly developed for the present Cu(001) study, shows excellent agreement with experimental results for its single application to date, although the somewhat 'most difficult' case presented indicates that the method shows
promise for high quality structural determinations on a much wider range of surfaces.

II.D.2 Inclusion of Exchange Effects

The spin-dependence of scattering from ferromagnetic surfaces due to the exchange interaction has been included in the SPLEED formalism of Feder and coworkers \(^{134}\), and is discussed extensively by Feder in a review of current spin-sensitive surface spectroscopic methods. \(^{135}\) Both Kessler \(^{136}\) and Kirschner \(^{137}\) also give excellent reviews of magnetic surface/electron interactions, where the physical origins of exchange asymmetries in electron/surface scattering are discussed in detail.

The exchange interaction, which is a direct result of the antisymmetrisation requirement of the Pauli exclusion principle, \(^{138}\) leads to an intensity difference in the scattering of electrons spin-polarized parallel and anti-parallel to the majority electrons' spins in the target. \(^{139}\) This intensity difference, an asymmetry, makes SPLEED sensitive to the details of the scattering target magnetization in the near surface region.

Generally the spin dependent effects due to the exchange interaction and the spin-orbit interaction are found together, and are of comparable magnitude. This causes them to be difficult to disentangle, both experimentally and theoretically. For an arbitrary scattering geometry, the spin-orbit interaction, with spin and orbital angular momentum not parallel, causes the spin to precess about the total angular momentum vector, thus mixing the spin states. As a result, for each successive scattering event in the multiple scattering chain, the spin-populations of the spin-up and spin-down states are different. In fact, the whole 'spin-orbit only' SPLEED theoretical formalism may be considered in a sense to be merely a bookkeeping system to keep track of these varying spin populations through all of the multiple scattering events. In pure exchange scattering, on the other hand, the spin orientations of the electrons are conserved, \(^{140}\) but the scattering cross-sections of the spin populations are are different.

For general scattering geometries, then, the separation of the two spin-effects is exceedingly difficult because the spin-flipping probability in a scattering event, caused by the spin-orbit interaction
effectively scrambles the information due to any exchange scattering asymmetry that may be present.

Figure 6. Perpendicular scattering geometry. The polarization of the incident electron beam \( \mathbf{P}_0 \) and the sample magnetization \( \mathbf{M} \) are parallel and colinear to the normal \( \mathbf{n} \) to the scattering plane (xz-plane) defined by incident \( \mathbf{K} \) and scattered \( \mathbf{K}' \) wave vectors. \( \mathbf{s} \) is the crystal surface normal. The crystal must be oriented such that the scattering plane is a mirror plane of the crystal. [After Tamura et al., ref. 13.]

For certain high-symmetry diffraction geometries, however, the two effects can be separated. The best geometry for this is called the 'perpendicular scattering geometry' and is shown in Figure 6. If we only consider scattering such that both the incident and diffracted beams lie in a mirror plane of the crystal, and that both the sample magnetization direction and the electron beam quantization direction are perpendicular to that plane, a simple separation can be made. Here the spin and orbital angular momentum are aligned and there is thus no precession of the spins. The exchange asymmetry of a given diffracted beam is the difference in beam intensity when the spin polarization is held constant and the magnetization is reversed. The spin-orbit asymmetry, on the other hand, is obviously independent of sample magnetization, and is the beam intensity difference when the spin polarization of the beam is reversed. Four different beam intensities are observable upon the separate reversal of the beam polarization and magnetization, and may be labelled \( I^\sigma_0 \), where \( \sigma = u(d) \) refers to spin-polarization parallel/antiparallel to a spin quantization direction (in our scattering geometry, this direction is chosen as vertically upward, and labelled 'up'), and \( \mu = \pm(-) \) refers to sample magnetization parallel/antiparallel to that same 'up' direction. The spin-orbit asymmetry for scattering from ferromagnets is:

\[
A_{so} = (I^+ - I^- - I^+_d - I^-_d)/I
\]
and the exchange asymmetry is:

\[ A_{\text{ex}} = (I_u^+ - I_u^- + I_d^+ - I_d^-)/I \]  

(T56)

Tamura et al.\textsuperscript{142} note that in an the experimental determination of \( A_{\text{ex}} \) and \( A_{\text{so}} \), requires absolute intensity measurements for both magnetic field orientations [i.e., both directions of sample magnetization]. Possible inaccuracies, which might thus arise from slight deflections of the beam by stray magnetic fields, are avoided by measuring two basic asymmetries:

\[ A^\mu = \frac{1}{P_0} (I_u^\mu - I_d^\mu)/(I_u^\mu + I_d^\mu) \]  

(T37)

which is effectively the same spin-asymmetry as defined in equation (32), where the label \( \mu = \pm \) denotes that the sample magnetization is 'up' ('down'). The spin-orbit \( A_{\text{so}} \), and exchange \( A_{\text{ex}} \) asymmetries, can be obtained from the measured quantities \( A^\mu \), to first order, by:\textsuperscript{143}

\[ A_{\text{so}} = (A^+ + A^-)/2 \]  

(T38)

and:

\[ A_{\text{ex}} = (A^+ - A^-)/2 \]  

(T39)

There are corrections to each of these asymmetries due to the interference between spin-orbit and exchange effects, but they are considered to be small.\textsuperscript{144}
III. EXPERIMENTAL METHODS

III. A THE EXPERIMENTAL APPARATUS:

The apparatus used in the present experiment is shown schematically in Figure 7 and is similar to that employed in earlier SLEED studies in this laboratory. The apparatus consists of three separately pumped but interconnected ultrahigh vacuum chambers. From left to right in Figure 7 they are the source chamber, the main experimental chamber and the Mott chamber, each name being descriptive of that portion of the experimental setup housed in that chamber.

Figure 7. Experimental Apparatus. The experimental set-up is housed in three separately pumped UHV chambers, for the spin-polarized electron source, the main experimental region, and the Mott polarization analyser.

The source chamber contains the GaAs photocathode facing vertically upward mounted on an xyz manipulator, along with the necessary electron transport optics to carry the emitted electron beam into the main experimental chamber. The laser optics for photoexciting the electrons for emission from the photocathode is mounted on a small portable laser stand attached externally on top of the source chamber and focused through a viewport onto the photocathode crystal.
This chamber is pumped by a 50l/sec D/I Ion pump and is capable after a 200°C bakeout of a base pressure of approximately $3 \times 10^{-11}$ torr and standard operating pressure of less than or equal to $1 \times 10^{-10}$. The chamber pressure and constituent gas partial pressures may be monitored respectively using a nude ionization gauge and a Spectramass quadrupole mass spectrometer, both mounted in this chamber. The beam axis of the polarized electron beam transported into the main chamber is horizontal and colinear with the beam axis of the Mott polarimeter situated across the main experimental chamber opposite it.

The source chamber may be isolated from the main chamber during photoactivation of the electron source by closing an in-line valve half-way along the electron transport optics that carry the polarized electron beam into the main chamber. Also located in the source chamber are an SAES Cesium dispenser and a variable leak source of oxygen for use in the GaAs photoactivation.

The Main experimental chamber contains the final stages of the SPES electron source transport optics as the input electron gun of a 120° 4-grid display LEED system with moveable faraday cup. The faraday cup has two independent ranges of motion equivalent to the polar angles $\Theta$ and $\Phi$ of a spherical coordinate system defined such that the equivalent z-axis is aligned along the incoming electron beam from the polarized electron source. The target crystal is mounted on a multiple motion crystal manipulator designed in-house and described in detail by Dunning and Jamison. The sample holders for the two experiments described here, are mounted on this manipulator and will be described shortly. The main chamber also contains a second 180° LEED optical system (here used exclusively for AES characterization of the sample cleanliness), as well as a second Spectramass quadrupole mass spectrometer head, and a nude ionization guage (the latter two used for background gas pressure measurement and characterization).

The main experimental chamber is pumped simultaneously by a 500l/sec D/I Ion pump, which is supplemented by a titanium sublimation pump with chilled water cooling shroud. The base pressure attainable in this chamber after bakeout at 150°C is approximately $5 \times 10^{-11}$ torr with standard operating pressures in the range $1-2 \times 10^{-10}$ torr.

Both the Main chamber and SPES chamber may be separately connected
to a roughing pump system that contains interconnected a 100l/sec roughing D/I ion pump, two cryogenic sorption pumps and ports for connection to a mechanical roughing pump and an up-to-air value.

The Mott Chamber is connected to the main chamber by a set of electron steering optics and an 100KV accelerating column, and the entire chamber and associated electronics may be floated at this 100KV potential inside its own electrostatic isolation cage. It contains a Mott electron polarization analyzer based on the high energy scattering of electrons off essentially bare gold nuclei. The geometry of the chamber connections is such that the axis of the accelerating column and Mott polarimeter is colinear with the polarized electron source beam axis and allows for the direct polarization measurement of the incident electron beam.

Here the polarization is determined by the left-right Mott scattering asymmetry due to spin-orbit coupling, which in this high energy range is well understood theoretically, and is experimentally confirmed. A number of monographs on the subject may be cited, and the experimental determination of the effective Sherman function describing the asymmetry for the scattering foils used in this apparatus is described in detail by O'Neill and Kalisvaart.

The Mott chamber is separately pumped by a 400l/sec D/I ion pump, which is also used to differentially pump the volume between the rotatable teflon gaskets used in the crystal manipulator in the Main experimental chamber.

III.B DATA ACQUISITION PROCEDURES — An Overview

In this apparatus a beam of spin polarized electrons from the GaAs photocathode electron source is directed at the target surface and the spin dependence of the intensities of the diffracted beams is measured. The spin dependence is specified by a spin-asymmetry parameter \( A(E, \Theta, \phi) \):

\[
A(E, \Theta, \phi) = \frac{1}{P_0^2} \frac{I(P_0) - I(-P_0)}{I(P_0) + I(-P_0)} \tag{40}
\]

where \( P_0 \) is the spin polarization of the incident beam and \( I(P_0) \) and \( I(-P_0) \) are the intensities of the scattered beam with the electron spins in the incident beam parallel and antiparallel respectively to a...
quantization axis defined as being vertically upward in the experimental chamber.\textsuperscript{149}

The polarized electron source used here is similar to that described by Pierce et al.\textsuperscript{150} The physical basis of the photoemission process is described extensively in the literature,\textsuperscript{151} and thus the discussion here will focus on only those aspects of the photoemission process pertinent to obtaining a spin-polarized electron beam. A number of the practical techniques for obtaining reliable, long-lasting photoactivations in our experimental apparatus are discussed in Appendix B, entitled appropriately enough "The Lure and Folklore of GaAs Photoactivation". Because an equivalent technique using photoemission from GaAs,\textsuperscript{62,38} which shows great promise, has been tested in this laboratory, the relative merits of this type of photocathode are discussed in Appendix C.

Photoemission of electrons from a semiconductor is a three step process involving the photoexcitation of electrons from the valence to the conduction band in the solid, transport to the surface, and escape into vacuum. The key to spin polarized photoemission is the spin-orbit splitting of the valence band in GaAs.

It is found that the valence band maximum and conduction band minimum in GaAs have symmetries equivalent to atomic P and S states respectively,\textsuperscript{152} and are found at the Gamma point at the center of the Brillouin zone, making GaAs a direct gap semiconductor. As a consequence of this, if a proper excitation energy is chosen, only transitions of well defined angular momentum P are allowed. At the \( \Gamma \), point, which is the valence band maximum, the otherwise degenerate p band is split into a fourfold degenerate \( p_{3/2} \) level and a twofold degenerate \( p_{1/2} \) level, which is located 0.34eV lower in energy. If we now consider the transitions from the \( m_j \) sublevels shown in Figure 8 we find that a net spin polarization of emitted electrons may be obtained as follows: The optical selection rules controlling photoexcitation require that \( \Delta m_j = \pm 1 \) for \( \sigma^+ \) light (also called right-hand circularly polarized or RHCP light; diagonal arrows in Figure 8), and \( \Delta m_j = -1 \) for \( \sigma^- \) light (or left-hand circularly polarized or LHCP light; which are not shown in Figure 8, but would be for equivalent diagonal arrows, sloped to the left rather than right in that figure). The quantization axis is
Figure 8. The band-structure of GaAs near the band gap. The top of the valence band is spin split into sub-bands of \( P_{1/2} \) and \( P_{3/2} \) character. The electrons in these bands are photo-excited by right-hand-circularly-polarized light into the spin-selected states in the conduction band along the diagonal arrows in the right half of the figure. The relative excitation probabilities are indicated alongside the arrows. Transitions into the conduction band only from the top spin-split valence band give an electron polarization of -50%. Transitions from both valence bands together gives zero polarization.

defined by the light angular momentum direction, and is for our emission geometry parallel to the photoemission direction. The relative transition probabilities may be calculated and are shown labeled by the arrows in Figure 8. For \( \sigma^+ \) light, three times as many electrons go to the \( m_j = -1/2 \) as to the \( m_j = +1/2 \) state because of the relative transition probabilities from the band at \( \Gamma_8 \). We may calculate that for \( \sigma^+ \) light we have \( P = -50\% \), and for \( \sigma^- \) light we have \( P = +50\% \). When electrons are also excited from the lower band at \( \Gamma_7 \), the polarization goes to zero. It is found that the maximum polarization is obtained if transitions from \( \Gamma_7 \) are not allowed, but rather have photon energies less than 0.1eV greater than the band gap energy.

Circularly polarized light from a GaAlAs diode laser emitting at 807nm is directed at normal incidence onto a GaAs(001) surface that has been prepared by cesiation and oxygenation to provide negative electron affinity. Photoelectrons ejected from the GaAs surface by the incident
radiation are longitudinally polarized. These electrons are accelerated and passed through a 90° electrostatic deflector. The emergent electrons, now transversely polarized, are focussed by a series of electron lenses onto the target surface being studied. The incident current at the target is approx. 0.2 microamps, and the polarization \( P_0 \) of the incident beam, which is measured directly using Mott polarimetry, is \( 28 \pm 2\% \). The polarization of the incident beam may be simply reversed \( P_0 \rightarrow -P_0 \), without influencing the beam current or trajectory, simply by changing the sense of circular polarization of the laser light incident on the GaAs photocathode. In practice the sense of circular polarization is modulated sinusoidally at 500Hz using a Pockels cell. This makes possible the simultaneous measurement of the spin-asymmetry parameter and spin-averaged intensity of each of the various diffracted beams. The intensity of each beam is collected and measured using a moveable faraday cup. The AC component of the collected current, which is measured directly using phase sensitive detection techniques, gives the spin-dependence of the scattered intensities (i.e. \( I(P_0) - I(-P_0) \)). The DC current into the faraday cup, which is measured using an electrometer, gives the spin-averaged intensity \( (I(P_0) + I(-P_0))/2 \). These two quantities, measured together, are then divided and scaled by the incident beam polarization to obtain the normalized spin-asymmetry parameter \( A(E) \). Some aspects of the data acquisition path are discussed further in appendix A.

III.C SAMPLE PREPARATION — Cu(001)

The copper crystal used in this study was cut from the same boule as those used in earlier LEED intensity studies by Davis and Noonan\(^ {153} \) and by Noonan and Davis.\(^ {154} \) The sample was aligned using Lane techniques and cut to expose the (001) face, electro- and mechanically polished, and then attached to the end of a thin molybdenum can that contains an electrically isolated tungsten filament. This assembly was mounted in the main experimental UHV chamber to our multiple motion sample manipulator.

Initial Auger analysis of the 'dirty' sample showed large peaks in the AES spectrum due to carbon, oxygen, and sulfur. The sample was cleaned in situ by sputtering for 30 minutes with 750eV Ar\(^+ \) ions at a
time-averaged current density of 30μA·cm⁻², followed by annealing at 500°-550°C for 30 minutes. Subsequent Auger analysis indicated no detectable contaminants remained on the surface following this treatment. Because copper is relatively inert to background gases (e.g. CO₂, H₂, CO₂, etc.), data could be collected for several days before any appreciable increase in contaminants was found by Auger. However, to insure the best possible cleanliness conditions, the sample was routinely cleaned and annealed prior to each data acquisition run. The observed sharp LEED pattern and good agreement with measured I-V profiles reported in earlier studies¹⁵⁶ indicate that the surface is well ordered.

III.D SAMPLE PREPARATION - Ni(111)

The nickel crystal used in this study was obtained from the Materials Science Center at Cornell University and required no preliminary surface preparation before introduction into the vacuum system, for the sample was properly oriented and highly polished as received. The sample had been cut to expose the (111) face with the long edge of the sample oriented along the [110] crystallographic axis. The short edges (along the [221] direction) were aligned to be parallel and polished flat. (The purpose for this careful selection of sample orientation was twofold: 1) First it allowed for magnetization of the sample along an easy ⟨110⟩ magnetization direction, and 2) It allowed for the separation by symmetry arguments, of the spin-dependent asymmetry features due to the exchange coupling (which carries magnetization information) and the spin-orbit interaction (which carries only structural information) of several of the diffracted beams.) The sample was mounted length-wise between the pole faces of an Armco soft-iron 'keeper' C-magnet. This keeper magnet was wound with a 20-turn magnetizing coil that allowed easy magnetization to saturation of the Ni(111) sample both parallel and antiparallel to the ⟨110⟩ direction. Studies of the sample magnetization, using the magneto-optic Kerr effect (MOKE) showed that the sample retained a remnant magnetization at very close to saturation in this mounting configuration for both magnetization directions. Sample magnetization, the MOKE studies, and the reduction of small stray magnetic fields around the
sample are discussed further in Appendix D. This assembly along with a tungsten filament/molybdenum can and sample heating block, was then mounted in the UHV main experimental chamber on the multiple motion sample manipulator.

Nickel is considerably more difficult to clean than is copper, and a variety of techniques were employed in reducing the contaminants to a level that shouldn't affect the experimental exchange asymmetry data. Immediately after pump-down and bakeout, the sample showed a 'dirty' surface characterized by very large Auger features for carbon, sulfur, and oxygen. Three or four preliminary sputtering runs with 1000eV Ar$^+$ ions at room temperature, each followed by a 400–500°C heating cycle completely eliminated all sulfur from the surface, and it was not subsequently observed. This procedure also reduced the oxygen concentration observed by Auger, but carbon levels were not significantly affected. The problem is that the carbon/nickel surface system has two somewhat difficult traits: 1) the triple peak Auger lineshape for carbon on this surface indicates the carbon to be rather tightly bonded to the surface at room temperature, and 2) the mobility of carbon is such that it tends to dissolve into the bulk at elevated temperatures and segregate to the surface as it cools. Systematic experimental constraints did not allow rapid sample cooling rates, and thus we were not able to 'freeze' the carbon into the bulk. The carbon concentration was, however, significantly reduced (by about a factor of 5–6) by heating the sample to approximately 350°C while flowing oxygen into the chamber at a partial pressure of approximately 1 x 10$^{-8}$ torr while monitoring both the carbon and oxygen AES signals. The heating increased the mobility of the carbon in the surface region and allowed for formation of CO and CO$_2$, which was more easily thermally desorbed than the more tightly bound free carbon on the surface. The problem with this was that a more careful titration of oxygen and carbon was required than was possible in our system to keep the oxygen concentration on the surface from increasing significantly. Subsequent long term (approximately 15 to 20 hours cumulative time) sputtering with 500eV Ar$^+$ with concurrent short heating cycles to 400°C was able to bring contaminant levels down to approximately 4–5% of a monolayer of carbon and approximately 1% of oxygen.
Because of the more reactive nature of the nickel surface,160 data runs of only three to four hours could be attempted between cleaning cycles. The initial 'dirty' nickel surface showed a poorly ordered surface net characterized by a very weak and diffuse LEED diffraction pattern and very large diffuse background. The final surface state obtained with only low contaminant levels showed the sharp, well ordered three-fold LEED pattern signifying a clean (1x1) (111) surface of the proper orientation. The corresponding LEED I-V profiles obtained in this study agree well with those obtained earlier from conventional LEED studies.161

![Figure 9](image_url)

**Figure 9.** The spin-asymmetry of the a) (10) and b) (10) beams for scattering from Cu(001) at normal incidence as a function of beam energy. Notice the mirror symmetry between the two profiles which is a good indication of accurate alignment to normal incidence.
III.E REDUCTION OF SYSTEMATIC EFFECTS IN DATA ACQUISITION

In Figures 9a and 9b are shown the spin-asymmetry versus energy (A-V) profiles for the symmetric (10) and (1̅0) diffracted beams from Cu(001) obtained at normal incidence. The experimental data is shown here as a series of vertical bars. The vertical extent of each data point represents the standard deviation about the mean of the asymmetry values recorded at each energy on several separate occasions, and therefore reflects both the run-to-run reproducibility of the data and the statistical uncertainties involved in each individual measurement. The electron energies shown are corrected for the work function difference between the GaAs photocathode (with a work function, due to NEA, of -0.18eV) and the Cu(001) surface (with a work function of 4.59eV)\(^\text{162}\) and therefore give the mean kinetic energy of the incident electrons in vacuum.

Great care has been taken to minimize or take into account any sources of systematic errors in the data acquisition that could affect the analysis, especially those due to crystal alignment and diffuse background. Several other systematic checks and compensations are discussed at some length in Appendix A. One source of error normally associated with LEED intensity analysis, however, is notably absent here. The asymmetry parameter is defined as a ratio and, in consequence, systematic errors associated with measurement of absolute beam intensities are cancelled. Thus no scaling of the data is required in comparisons with theory.

The copper sample was aligned for normal incidence by comparing the intensities as well as the A-V profile structure of the complimentary (10) and (1̅0) beams (See Figure 9a and 9b). Comparisons between the (10) and (1̅0) data indicated that \textit{normal incidence} is achieved to within \(\pm 0.25\text{deg.}\), with \textit{positioning reproducibility} on the same order (i.e. \(\pm 0.25\text{deg.}\)). For specular beam data taken off normal incidence, the rotation axis is parallel to the [01] direction in the face of the sample. However, in the case of the specular beams, complementary positions were not investigated, and thus the angle of incidence (\(\theta\)) of these beams is less precise than for normal incidence, on the order of \(\pm 0.5\text{deg.}\).
The scattering geometry in our experiment is such that the spin quantization axis (vertically upward in our experimental chamber in Figure 7) is aligned with the [01] crystallographic axis in the face of the Cu(001) sample. Symmetry considerations therefore require that for this laboratory-fixed quantization axis, the (10) and (1̅0) beams should have spin-asymmetry parameters equal in magnitude but opposite in sign for scattering at normal incidence. Experimental A-V profiles obtained with the sample positioned at small angles off normal incidence indicate that the realization of this mirror symmetry in the A-V's is a very sensitive test of sample alignment. The data of Figures 9a and 9b clearly satisfy the mirror symmetry, and demonstrate that normal incidence was achieved. It is not mandatory, however, to obtain full A-V profiles for a pair of complementary diffracted beams whenever setting up for a data run to find normal incidence, and a simple visual inspection technique, described in Appendix A, was used for all subsequent data taken after the initial alignment to normal incidence was established, both for the Cu(001) study and for Ni(111).

III.E.1 Cu(001) Data:

In Figures 10a, 10b, and 10c are shown the A-V profiles for the (10), (1̅1), and (20) diffracted beams respectively, measured at normal incidence. The data shown for the (10) beam in Figure 10a is the statistical average of the symmetrically equivalent (10) and (1̅0) asymmetry profiles, where the asymmetry of the (10) data is flipped before averaging. The average magnitude of the asymmetry parameter for diffraction from copper is, as noted before, generally small and the magnitude of even the asymmetry maxima seen here are only on the order of 6-8%. Although the asymmetry features are small, they are nonetheless quite reproducible. A good indication of the run-to-run reproducibility is found in the well-defined profile structures and the generally small vertical extent of the error bars on the data, as again we note that each of the profiles shown is the statistical average of of several data runs.

In the accompanying Figure 11a, 11b, and 11c are shown the intensity spectra for the (10), (1̅1), and (20) diffracted beams for scattering from Cu(001), again at normal incidence. These profiles were
Figure 10. Spin-asymmetry profiles of the a) (10), b) (11), and (20) diffracted beams for scattering from Cu(001) at normal incidence. Shown are both the experimental (vertical bars) and calculated profiles (plusses).
Figure 11. Experimental intensity vs. voltage I-V profiles for a) (10), b) (11), and c) (20) diffracted beams at normal incidence for scattering from Cu(001). Also shown for comparison are I-Vs obtained for the same scattering geometry by Noonan and Davis, ref. 15.

obtained simultaneously with the respective asymmetry profiles shown in Figure 10. As has been noted above for the asymmetry data, our experimental profiles are shown as a series of vertical hashes which represent the statistical analysis of a number data runs for equivalent diffraction conditions. The data is normalized with respect to the primary beam current incident onto the sample times an arbitrary, energy independent scaling factor. The experimental I-V profiles obtained by Noonan and Davis are also shown for comparison. Peak positions and rough relative peak heights are reproduced reasonably well except at low
energies where some beam broadening causes a loss of diffracted current collected into our Faraday cup.

The apparent loss of beam intensity from the diffracted beams is highly dependent on the exact diffracted beam collection method used, including Faraday cup bias, entrance aperture size, and geometrical and field constraints in the experimental region. The resultant lack of highly precise lab-to-lab I-V reproducibility may be considered a shortcoming of the present work, because no significant efforts to minimize or eliminate it were undertaken. But because the primary focus of this work was the reproducible and exact production of asymmetry profiles, it was considered only a secondary issue here.

It is important to note that this systematic defect in the acquisition of intensity data (i.e., the apparent diffracted beam intensity loss at low energies) does not, however, affect the asymmetry profiles obtained. This is because the spin-asymmetry parameter is a self-normalizing quantity. Both measured quantities from which it is derived, the spin-difference current \[ I(P_0) - I(-P_0) \], and the spin-averaged intensity \[ I(P_0) + I(-P_0) \]/2 are simultaneously collected through the same aperture and any systematic errors associated with the current measurement process are thus cancelled. This is not true, on the other hand, of conventional LEED intensity data, which must be normalized to the incident current onto the sample, itself a quantity which must be separately measured.

Corrections must also be made for incoherent diffuse background contributions to the measured A-V and I-V profiles. There is a small, usually quite uniform contribution to the current collected in the Faraday cup that is not due to the coherent diffraction from the atomic planes in the surface. This diffuse background is due to the incoherent scattering from defects in the crystal or quasielastic electron-phonon scattering, and is found empirically to be spin-independent. This background, which contributes no useful structural information, nonetheless is reflected by changes in both the A-V and I-V profiles, and must therefore be accounted for carefully in the analysis. The effect of this diffuse background is simply to add an intensity offset in the I-V profiles. However, it folds into the spin-asymmetry profiles differently, here as a preferential washing out of the A-V profiles in
regions of lowered intensity, one of the areas where asymmetry data is normally most pronounced.

Corrections for this background in the measured I–V and A–V profiles are easily accomplished by exploiting the spatial uniformity and spin-independence of the diffuse background. This is done by positioning the Faraday cup adjacent to the diffracted beam of interest such that only electrons resulting from the diffuse scattering could enter. This contribution is then subtracted from the spin-averaged intensities obtained for the beam of interest, and the resultant 'pure diffraction' intensity is then folded in to obtain the true spin asymmetry of the collected diffracted beam current. This background subtraction is further described in Appendix A. All the data shown here, both for Cu(001) and for Ni(111), reflect this background subtraction.

III.E.2 Ni(111) Data

Shown in Figures 12a, 12b, and 12c are shown preliminary experimental profiles for the exchange asymmetry $A_{ex}$, spin-orbit asymmetry $A_{so}$, and normalized intensity $I/I_0$, for the ($\bar{1}0$) diffracted beam from Ni(111) taken at normal incidence. The experimental I–V profile for the ($\bar{1}0$) beam of Demuth et al.165 is also taken at normal incidence, is also shown in Figure 11c for comparison. Peak heights, positions, and even some of the subtleties of peak shapes are reproduced quite well.

The data acquisition for the $A_{ex}$ and $A_{so}$ profiles shown involves the measurement of two separate asymmetry profiles $A^\uparrow$ (See equation (37)), one for magnetization 'up', and the other for magnetization 'down' (i.e. parallel an antiparallel, respectively, to the quantization direction we have defined earlier). From these, the spin-orbit and exchange asymmetries are obtained using equations (38) and (39).

An inspection of the asymmetry profiles of Figures 12a and 12b indicates that the spin dependence of electron diffraction from Ni(111) is not large. The spin-orbit asymmetry $A_{so}$ is on the same order of magnitude as the asymmetries (also due to the spin-orbit interaction) for scattering from copper, with maxima on the order of 6–8%. On the other hand, the exchange asymmetry $A_{ex}$ is somewhat smaller, with maxima on the
Figure 12. Intensity and spin-asymmetry profiles for scattering from ferromagnetic Ni(111) for the (10) beam at normal incidence. a) The exchange asymmetry $A_{\text{ex}}$ experimentally obtained along with profiles calculated by Feder for two different surface magnetism models. b) The spin-orbit asymmetry $A_{\text{so}}$ obtained experimentally and using calculations. c) The intensity of the (10) beam. It may be noted that both the intensity and spin-orbit asymmetry obtained experimentally agree well with theory and with other experimental work.
order of 1–2%, for this diffracted beam. Multi-run data averaging, described above for the Cu(001) data, is also employed here.

Because of the subtraction process necessary to obtain the exchange asymmetries, and the inherent statistical errors associated with run-to-run reproducibility, it is found that asymmetry features below about 1% are only poorly reproduced. This is especially true for regions in the energy spectra that have low diffracted intensity, and even more so for nonspecular beams, where the optimum diffracted beam position must be tracked manually with the movable Faraday cup as the beam moves with energy. (See Appendix A.) The indication, therefore, is that effects due to sample magnetization that give rise to changes in the profiles below about a percent are indistinguishable using present techniques.
IV. THEORETICAL/EXPERIMENTAL COMPARISON:

IV.A R-FACTOR ANALYSIS IN LEED AND SPEEED:

Early LEED structural analyses relied on the visual inspection of experimental and calculated profiles to obtain the best structure. There, the parameters of the structural model were varied and calculated I-V profiles obtained for each assumed structure. The set of structural parameters that gave the calculated I-V profiles that best matched the experimental profiles then was called the true structure.

![Diagram of a vacuum and crystal structure with annotations showing contraction and expansion of interlayer spacings.](attachment:diagram.png)

**Figure 13. Multilayer Relaxation.** The relative motions of the atomic layers are parametrized by the percent change in the actual near-surface interlayer spacings away from bulk spacings. An expansion of the lattice is denoted by a positive percent change (as in that for the second interlayer spacing \( \Delta d_{12} \)), and negative for a contraction of the lattice (as that for the top interlayer spacing \( \Delta d_{13} \)).

Typically, a number of the crystal model parameters would be varied, both those that parametrized the structure, as well as non-structural parameters. Those of greatest interest, of course, were those that localized the ionic positions, and thus defined the structure. For unreconstructed surfaces (i.e., those that did not show additional fractional order diffracton spots in LEED), all the ions
within any given plane parallel to the surface were not repositioned, but the spacings between planes could be. Thus the structural parameters used in the analyses of such surfaces were these interplanar spacings, usually denoted by the percent change from an unperturbed bulk interplanar spacing, where a positive (negative) percentage denoted a relative repositioning outward (inward). (See Figure 13.)

However, it was found that the procedure for matching of profiles by eye was simply too subjective; while it was not difficult to compare a few features of a single pair of calculated and experimental profiles, the comparison of the large number of profiles necessary to obtain a precise structure was much too cumbersome to do 'by eye'. It is far too difficult to evaluate the overall match between an ensemble of profiles, especially when the features of some of the profiles seemed to improve their match as the structure is varied, while the features of other profiles worsened. Without some form of accounting system to keep track of the changes in each feature and evaluate the relative importance of each of them, the procedure would be hopeless. A more quantitative technique was needed to evaluate the correlation between profiles.

Thus over the past several years a wide and powerful array of so-called 'reliability-factors' or ρ-factors have been developed for LEED to help in the detailed analysis of I-V profiles. These ρ-factors - each sensitive in varying degrees to a number of different features of the profiles, such as peak positions, relative heights, and peak shapes - provide a numerical measure of the overall quality of experimental/theoretical fits, taking into account all the experimental and calculated profiles. ρ-factors are designed so that a good correlation between curves is represented by a low value, and poor correlation, which implies a poor structural determination for that surface, is indicated by a high value. Often ρ-factors are quasi-normalized, so that good agreement is denoted by values approaching zero, and poor agreement by values approaching one. An excellent review of ρ-factor analysis in LEED is given by Van Hove and Koestner, who discuss the relative merits of many of the ρ-factors now in use, as well as techniques for using them. These workers, and others outline the procedures for implementing structural searches
using profile comparisons, which are applicable for both LEED and SLEED analyses.

Structural analysis by SLEED now can take advantage of all the same tools available to its parent spectroscopy. The same techniques, and in many cases even the same $r$-factors that are used in LEED I-V analysis can be used here. The only difference lies in the A-V profiles themselves that are used for the analysis. While the asymmetry parameter is sensitive to structure, that structural information is manifested differently in A-V profiles than it is in I-V profiles. The A-V profiles emphasis different regions of the energy and angular spectrum than are emphasized in intensity analysis, and reflect a sensitivity to a different part of the scattering potential of the surface as well. Because of this, SLEED A-V analysis may be thought of as a second, complementary probe of surface structure, providing a confirming check on the structural analyses using LEED I-V analysis.

Calculated spin-asymmetry profiles have been obtained for a variety of assumed Cu(001) surface structural models. In Figures 14a–f, are shown calculated A-V profiles for the (10) beam at normal incidence, for nonstructural parameters identical to those used in the conventional LEED I-V analysis of Davis and Nooman, and also for a structure with the second atomic interlayer spacing $d_{12}$, and all deeper interlayer spacings fixed to be equal to the bulk interlayer spacings. Here the top interlayer spacing $d_{12}$ is varied in steps of 2.0% of the bulk interlayer spacing between $\Delta d_{12} = +4.0\%$ (denoting an expansion), and $\Delta d_{12} = -6.0\%$ (for a contraction), with respect to bulk spacings. In Figures 15a–e, the (10) beam A-V profile is shown for the same conditions as above, except that the top interlayer spacing is held fixed at $\Delta d_{12} = -1.0\%$, and the second interlayer spacing is varied (again in 2.0% steps) between $\Delta d_{23} = -3.0\%$ to $\Delta d_{23} = +5.0\%$. Shown superimposed on each of the calculated profiles are the experimentally obtained (10) beam A-V profile for these same normal incidence diffraction conditions.

An indication of why $r$-factor analysis is needed in SLEED may be seen by inspecting the profiles shown in Figures 14 and 15. As can be seen by comparing the theoretical (10) diffracted beam A-V profiles in Figure 14 with the accompanying equivalent experimental A-V profile,
Figure 14. a-f) Variation of the calculated (10) beam asymmetries with variation of the top interlayer spacing. The calculated (solid) curves are superimposed on the experimental profile for the same diffraction geometry (i.e. the vertical hashes). An inspection of the curves, especially in the energy range between about 85-140 eV, shows strong correlation of both shape and magnitude of many of the features for experimental and calculated profiles for $\Delta d_{23} = 0\%$, but the agreement worsens as the structure is adjusted away from that.
Figure 15. a-e) Variation of the calculated (10) beam asymmetries with variation of the second interlayer spacing. Here the changes are more subtle than in fig.14 for top interlayer spacing variations, but the trend is toward best fit at $\Delta d_{22} = -1\%$, and $\Delta d_{33} = +1\%$.

Variations in the surface model parameters in the calculations leads to
significant changes in the profile contours. Some profile features grow and change shape as the assumed structure is varied, while others wash out and disappear. Thus some calculated profiles more closely reflect the contours of the experimental profiles than others. Visual inspection indicates that the peak positions and relative peak heights of the profiles for $\Delta d_{12} = -2.0\%$ and $\Delta d_{12} = 0.0\%$ show evidence of better agreement with experiment than those for $\Delta d_{12} = +4.0\%$ or $-6.0\%$. This is seen especially clearly for the energy range between 90eV and 120eV, where the contours of the experimental profile are rather faithfully reproduced near $\Delta d_{12} = -2.0\%$, but only poorly so for structures further away. The profiles for the $\Delta d_{12} = +4.0\%$ and $\Delta d_{12} = -6.0\%$ structures clearly have a number of features shifted significantly in energy, peak height, or overall shape, from the comparable features of the experimental profile, indicating that these structural models only poorly reflect the true scattering and interference conditions at the surface which lead to the contours of the A-V profiles.

But as the optimum structure is approached, the variations in profile shape become less pronounced. Deciding between $\Delta d_{12} = -2.0\%$ or $\Delta d_{12} = 0.0\%$ as the closest match to the experimental results by visual inspection becomes a very subtle comparison between individual profile features, and if there is no quantitative measure of the relative importance of the different features, then there will obviously be no clear best choice. The analysis is complicated by the fact that, even for the structure we have called the 'best' in this set, there are several energies where the asymmetry values and even gross profile structure don't match the experimental curves, and that even the 'worst' structures have energies that do. For a good structure, these discrepancies should make up only a small part of the total energy range.

The more subtle variations of the profiles when the second interlayer spacing $d_{21}$ is varied in Figure 15 indicates that changes in the positioning of deeper-lying atomic layers (e.g., through variation of the interlayer spacing $\Delta d_{21}$) has less influence on the measured A-V profiles than are caused by variations in the top layer positioning. This lower sensitivity to variations in structure deeper within the crystal is found in I-V analysis, and is caused by the attenuation of
the electron flux which accompanies electron propagation into the crystal. This seems to be the case for A-V analysis as well, for the variations in profile shape with variation in structure are more subtle here (i.e. for changes in $d_{12}$ in Figure 15) than for profiles in Figure 14 (which are the result of comparable changes in $d_{13}$).

In addition, it is highly desirable to formulate a structure based on the widest possible data set. Thus our analysis was extended to the diffracted (11) and (20) spin-asymmetry profiles as well. Comparison between calculated and experimental (11) and (20) beam profiles show comparable changes in features with structural variations as those seen above, although the best fits for different regions and different profiles seemed to be for slightly different structural model conditions. Some improvement over simple visual inspection is therefore mandatory if we are to have any hope of obtaining a precise and unambiguous surface structure. Here the techniques developed for structural determination by LEED I-V analysis can be used as a guide.

Following the precedent set in LEED, we may define reliability factors for use in comparing SMLEED calculated and experimental asymmetry profiles. A number of different possible r-factors are equally valid. The choice made here was to select the simplest one based on the mean square differences between the two curves. A SMLEED equivalent of the single beam r-factor for comparing two profiles may be defined as:

$$R_i = \frac{N_i}{\sum_{j=1}^{N_i})} \frac{(A_{\text{calc.}})_j - (A_{\text{expt.}})_j}{(A_{\text{expt.}})_j} \left( \frac{2}{\sum_{j=1}^{N_i}(A_{\text{expt.}})_j} \right)^2$$

which is simply the square of the difference between the asymmetry values of the calculated and experimental profiles taken point by point over the energy range of the two spectra, normalized to the average magnitude of the experimental asymmetry. This r-factor is analogous to the R2 reliability factor defined by van Hove et al.\textsuperscript{171} for use in LEED I-V analysis. There is, however, one notable difference between the r-factor defined in equation (41) and those used universally in I-V analysis - there is no arbitrary scaling factor between calculated and experimental profiles here. This is possible because the
spin-asymmetries are truly self-normalizing quantities.

In equation (41), the experimental and calculated asymmetries used for each \( j \) in the summation are taken at the same energy, and the parameter \( j \) is varied over all the energies measured for the diffracted beam of interest with the following two provisions. First, if the calculated diffracted intensity of the beam of interest at a given energy goes below .001% of the incident beam intensity, then that data point is eliminated from the analysis. Second, if the standard deviation of the experimental asymmetry at a given energy exceeds 2% of the diffracted beam intensity, then that data point is also eliminated. These provisions only eliminate about 6% of the data collected, but are effective in suppressing contributions from those regions where confidence in the data is reduced due to difficulties in the experimental measurement (usually where the diffracted beam intensities are very small), or due to difficulties in achieving numerical convergence in the theoretical calculations. The parameter \( N_i \) in equation (41) indicates the total number of data points in each profile used in the analysis.

A second reliability factor which utilizes a number of diffracted beams to obtain an overall numerical estimate of the quality of the structural model may also be defined:

\[
R = \frac{\sum_{i=1}^{n} N_i R_i}{\sum_{i=1}^{n} N_i}
\]

(42)

where \( i \) ranges over all the \( n \) different beams used in the analysis. This Total \( R \)-factor weights the contributions of each of the various beams by the energy range over which that beam is measured and thus supposedly by the amount of structural information that that profile contains.

IV. B RESULTS OF THE Cu(001) COMPARISON:

In the present Cu(001) study the first and second interlayer spacings between atomic planes in the surface were varied parametrically over a range of \( \Delta d_{12} \) and \( \Delta d_{13} \), and spin-asymmetry profiles were calculated for each assumed structure. These A-V profiles were compared with the experimentally obtained A-V profiles using the simple SPLEED
r-factors defined above. The total 3-beam R-factor obtained for these various structural models are listed in Table 1. As may be seen from the table, the minimum overall R-factor shown is that for the structure near $\Delta d_{12} = -1.0\%$ and $\Delta d_{23} = +1.0\%$. This structure, although close, is not the best determination possible, however, because the R-factor is a smoothly varying function of the two interlayer spacing parameters. Because the values of assumed structures, that have been tested, for which we have obtained actual r-factors, form such a loose grid in the 2-dimensional space defined as a function of interlayer spacings $\Delta d_{12}$ and $\Delta d_{23}$, a clearly more precise structural determination can be made by interpolating between these points. It is found that the optimum structure, obtained in this manner, to within $\pm 1.0\%$, is $\Delta d_{12} = -1.20\%$ and $\Delta d_{23} = +0.90\%$.

This structure is in excellent agreement with that obtained earlier by the LEED analysis of Davis and Nooman. The calculated A-V and I-V profiles for this optimum structure for the (10), (11), and (20) diffracted beams are shown superimposed on their equivalent experimental profiles in Figures 16 and 17.

While there are some small variations between the curves, overall the match between experimental and calculated profiles is excellent, and is reflective of one of the the best SLEED theory/experiment comparisons to date.

Some intriguing aspects of r-factors and their use in SLEED merit comment here. First, the present work is the first SLEED investigation where an attempt has been made to use r-factors in structural determination. To date a much simpler 'trial and error' technique based on visual inspection has been used Feder and coworkers, although the indications are that r-factor analysis is in the offing. While no claim is made that the present r-factors are the optimum ones to use when analysing SLEED asymmetry data, it is clear from the high quality of the agreement between calculated and experimental profiles, that the implementation of even simple r-factors allows for the determination of quite a precise structural model.

It should be clear that such a good agreement could not have been possible without the use of some type of r-factor to guide the optimization. The potential of SLEED A-V analysis as a dynamic and
Figure 16. Comparison between the experimental spin-asymmetry profiles for the various diffracted beams with the calculated asymmetry profiles from the model optimized for best match, with $\Delta d_{44} = -1.20\%$ and $\Delta d_{33} = +0.90\%$. 
useful tool for structural determination is therefore aptly demonstrated. The further refinement of r-factors to utilize in SLEED
analysis will do nothing but make the technique applicable to even a wider range of such determinations.

IV.C PRELIMINARY RESULTS OF THE Ni(111) COMPARISON:

Because of the preliminary nature of the nickel study, and because the primary goal of the study is to evaluate the ability of the spectroscopy to reproducibly measure and compare small exchange asymmetry features, only a simple visual comparison of the experimental and calculated profiles was accomplished here. Feder\textsuperscript{174} describes the comparison method used for this study: 'Numerical calculations are performed using the full multiple scattering theory for physical model assumptions, which are varied within physically reasonable limits. One then looks for beams and regions in \((E, \Theta, \phi)\) space, for which the calculated quantities are selectively sensitive to changes in the model assumptions, i.e. respond strongly to one model characteristic... and not (or weakly) to the others.... Comparison with the corresponding features in experimental data then determines the actual value of this particular model characteristic.' The effect is to select one small region or feature in a single profile that seems to be especially sensitive to variations in the parameter one is interested in. (Here that parameter is the ratio between the average magnetic moment in the top layer compared to the magnetic moment in the bulk, which we will call \(M_1/M_{\text{bulk}}\).)

Numerical calculations were performed to simultaneously obtain the intensity \(I_{hk}/I_0\), the spin-orbit asymmetry \(A_{\text{so}}\), and the exchange asymmetry \(A_{\text{ex}}\) for a number of different diffracted beams and diffraction conditions. The \(A_{\text{ex}}\) calculated beam profile that seemed to show the most sensitivity to top layer magnetization was a particular low-energy region of the \((\bar{1}0)\) beam (around 50 ev) for scattering at normal incidence. The exchange asymmetry \(A_{\text{ex}}\), calculated for that beam for a top layer magnetization equal to that of bulk nickel (i.e. \(M_1/M_{\text{bulk}} = 1.0\)) and for a 10\% enhancement over the bulk (i.e. \(M_1/M_{\text{bulk}} = 1.1\)) are shown plotted as Figures 18a, and 18b, and may be compared with the experimental exchange asymmetry shown as Figure 18c.

A visual inspection of the curves in the energy range 45ev to 60ev shows a distinct double hump which switches relative peak height for
Figure 18. Experimental/theoretical spin-asymmetry comparison for the exchange asymmetry parameter $A_x$ measured for the (10) diffracted beam from Ni(111), with comparable asymmetries calculated for magnetization models having the magnetic moment of the top atomic layer a) equal to that in the bulk, and b) 10% enhanced over that in the bulk.

Profiles obtained from the two calculated models. This is probably the single most sensitive profile feature to variation in the assumed layer magnetization found in the calculational survey performed by Dr. Feder for the ferromagnetic Ni(111) surface, and that survey covered a number of beams and diffraction geometries. A comparison of the experimental profile with those obtained from calculations indicates that the closer match seems to be with the calculated profile for a 10% magnetization enhancement at the surface.

Several notes of caution are in order, however. First, although the agreement seems better for the enhanced magnetization case, this indication could be misleading for, even in the range of interest, the contours of the two curves only grossly follow each other in shape or magnitude. Clearly, some refinement of either the structural model or the experimental profiles, or both, is needed. Further, and this is the much more serious concern, the variation in the asymmetry due to this enhancement is very small, on the order of perhaps a quarter of a
percent, while the experimental run-to-run reproducibility is at best at least twice that (and the quoted best run-to-run reproducibility, at \(\pm 0.5\%\), is for a non-moving specular beam. See Appendix A.) This is further complicated by the fact that the beam of interest is a nonspecular beam at very low diffracted beam intensity. Thus, while some enhancement seems to be indicated, either an improvement in our effective 'signal-to-noise' or confirmation by other techniques is needed for a more definitive statement. While the quality of the data is good enough to indicate the general trend of effects due to variations in this type of surface properties, significant advances are called for before quantitative surface layer magnetization can be obtained using present techniques.
The present investigation deals with two distinct, but interdependent studies, one on the layer magnetization of ferromagnetic Ni(111), and the other dealing with multilayer relaxation in Cu(001). These two studies, taken together, provide an excellent 'benchmark' test of the ability of SPEEED spectroscopic techniques to probe small spin-dependent effects in electron scattering from surfaces. Because both nickel and copper are reasonably low atomic-number elements, and because the magnetic moment of the one ferromagnet, nickel, is small both theoretical and experimental techniques may be evaluated.

The study of the (001) face of copper indicates the strengths of SPEEED techniques in performing high precision structural studies. The present study is the first implementation of r-factor analysis in SPEEED to date, and indicates that even when a very simple reliability-factor is chosen that quite a precise structural model is obtainable. An optimum structure of $A_{12} = -1.20\%$, and $A_{23} = +0.90\%$, is obtained for the top two interatomic spacings, which agrees well with the results of earlier conventional LEED I-V analysis by Davis and Noonan. The match between experimental and theoretical spin-asymmetry profiles is among the best obtained to date. It should be clear that the excellent reproducibility of experimental and theoretical profiles is indicative not only of experimental techniques that are able to suppress contributions due extraneous systematic effects, but also that the theoretical formalism used adequately includes all of the physics important to the electron diffraction process. The good agreement between theory and experiment is not only indicative of highly precise structural conclusions, but also of the applicability of SPEEED to high quality structural determinations of a wide range of surfaces, including those of low atomic number.

In addition, the nickel study showed that both spin-orbit asymmetry $A_{SO}$, and exchange asymmetry $A_{EX}$ measurements can be taken concurrently for scattering from ferromagnetic surfaces. Further, we have established the rough magnitude of the limits on the distinguishability
of small effects in exchange scattering. Using present techniques, magnetic effects that lead to profile changes below about 1% are not clearly distinguishable by SPLS. Because of this, it is apparent that, while some enhancement of the surface magnetic moment seems to be indicated for the Ni(111) surface, that quantitative enumeration of these effects are beyond the limits of present techniques.

It can be concluded that, while SPLS is still a young spectroscopy, it has shown promise in a number of very divergent areas, not the least of which are the areas of high resolution structural determinations and surface magnetization studies.
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APPENDIX A: Systematic Error Reduction

The analysis of experimental intensity and asymmetry profiles is used in LEED and SLEED to determine the optimum surface structure for the crystal under study, and the structure obtained is strongly dependent on the contours of the experimental profiles. It is therefore important that experimental profiles used in structural determinations include only those effects due to the actual diffraction of electrons from the crystalline lattice, and be as free from systematic instrumental effects as possible. It is, as a result, important that all of those factors in the data acquisition that could influence the experimental contours, but that are not actually due to the coherent diffraction process, be accounted for and eliminated from the analysis. A number of such factors that potentially could lead to systematic errors are listed here, and our discussion which follows will focus on how each has been accounted for:

1. sample alignment to normal incidence
2. reproducibility of that alignment
3. diffuse background subtraction
4. details of the data acquisition path
5. instrumental zero offsets
6. instrumental pickup noise
7. absolute energies of the electron beam in vacuum
8. normalization of diffracted intensities to the true incident current
9. motion of the faraday cup and optimization on the diffracted beam position
10. beam steering by stray fields
11. beam blossoming at low energies

In the discussion which follows, we will focus on the data acquisition techniques and experimental apparatus actually used in this
lab, but the discussion has implications that also go further. Our discussion may be considered on two separate levels: On one level, this is simply a set of 'lab notes' for using the Rice SLEED experimental apparatus. But it is hoped that it may also be considered in another light. The discussion describes a number of the problems (and some of the possible solutions) inherent in all LEED and SLEED experimental technique, and at this level, may have wider applicability than in simply working through the nuts and bolts of our experimental problems.

SAMPLE ALIGNMENT TO NORMAL INCIDENCE:

Because normal incidence provides the highest symmetry conditions for electron scattering, and because the calculations of theoretical profiles with which our experimental results are compared is greatly simplified by this high symmetry, it is highly desirable to reproducibly align the actual experimental scattering geometry to these conditions. Obtaining reproducible, high-symmetry alignment requires the development of two procedures — first, to obtain normal incidence diffraction conditions, and second, to reproducibly align the sample to those conditions. Techniques for each have been developed and are discussed in this section one following.

The symmetry of the crystal being studied (i.e. Cu(001)) can be exploited to obtain the normal-incidence alignment. For scattering at normal incidence, and an assumed 'spinless' electron beam, the (10), (01), (10), and (01) diffracted beams are degenerate, and would have identical I-V spectra. When spin is included, with the electrons’ spins polarized parallel to the [01] surface net vector, the 4-fold symmetry is reduced, but 2-fold symmetry remains — to first order, the (01) and (01) beams are 'spinless', because the spin-orbit term in the Hamiltonian, \( \mathbf{\sigma} \cdot \mathbf{\mathcal{L}} \), goes to zero when spin and orbital angular momentum are perpendicular. On the other hand, the (10) and (10) beams have, for this lab-fixed quantization axis, spin-orbit asymmetry profiles that are generally nonzero and symmetric, and identical but opposite in sign.

Further, as the angle of incidence moves off normal, these two beams (i.e. (10) and (10)) move off equivalent symmetry. As the angle of incidence (\( \Theta \), which has a rotation axis parallel to the [01] surface
Figure A1. Schematic of the sample alignment to normal incidence. The sample is initially positioned a) at an angle \( \gamma \) with respect to normal, then the sample is rocked through an angle \( \varepsilon \) to the configuration in b). The incidence and emission angles \( \gamma \) for specular reflection are equal, and thus if the diffraction geometry before and after are to be mirror images of one another (which is what causes the profiles to be mirror images, in their turn, of each other) then their internal half-angle \( \gamma \), must also be half of the rocking angle \( \varepsilon \).

As the rocking angle (or net direction) increases, the angle of emission of the (10) beam increases, while the angle of emission of the (10) beam decreases. The following procedure is used to obtain conditions for normal incidence:

1. The \( A-V \) profile for the (10) beam is measured at an initially unknown, but near normal angle of incidence \( \gamma \) (found later to be at \( \theta = -0.25^\circ \)), and the external \( \theta \)-motion vernier reading is noted.

2. Then this profile is compared for best match with a family of (10) beam \( A-V \)'s, each taken at slightly different angles of incidence, where the vernier readings of each have been noted.

3. The angle of incidence \( \gamma \) is then directly obtainable, for it is the negative of half the angle between the external \( \theta \)-rotary vernier readings for the angle at which the original (10) beam \( A-V \) profile was taken and the angle at which the (10) beam profile with which it best matches was taken. (The reason for this simple half angle relation, \( \theta(\gamma) = -\frac{1}{2} \Delta \theta \), is easily derived, and is shown in Figure A1.)

With this procedure, we can position the sample incidence angle to within \( 0.25^\circ \) of normal, and further we know the external manipulator positions associated with that alignment.
REPRODUCIBILITY OF SAMPLE ALIGNMENT:

The reproducibility of experimental A-V profiles is dependent on several factors, the most important of which are probably the reproducible positioning of the crystal to give the proper diffraction geometry (usually to normal incidence), the reproducible tracking of diffracted beams with the Faraday cup as they move with energy, the proper subtraction of incoherent diffuse background, and the elimination of noise and drift in the data acquisition electronics. The first of these factors is dealt with in this section.

The angular positioning of the sample is adjusted by two external rotaries, one aligned vertically in the plane of the crystal face (which is the θ adjust, and is called 'TR'), and the other parallel to it, but offset 1.75 inches behind the crystal face (called 'BR'), which moves the sample between stations for Ar⁺ sputtering, SPES/SPLLED data acquisition, and AES sample characterization.

BR is set to 0°00' for data acquisition when using the SPES, and is adjusted by approaching the bottom rotary position from below using a fine adjustment thumbscrew, while viewing to bottom rotary vernier through a magnifying telescope. The angular positioning is accurate to within ~ ±0°05'.

TR has two adjustments, one for coarse motion, and the other, a micrometer, which allows for very fine adjustment (to within ~ ±0°01'). This rotary adjustment would give very precise angular positioning, except that there is considerable backlash in the control elements between the vernier and the actual sample position (on the order of 1°-2°).

To eliminate angular inaccuracies due to relative motions of these elements, the following alignment procedure, based on the visual inspection of the LEED pattern from the sample, has been developed:

1. The BR rotary is set to 0°00'.

2. The SPES/LEED system is set up to view the LEED pattern for the sample, and the beam energy is adjusted to a reasonably high beam energy (i.e. >100eV) to give diffraction conditions near a specular beam maximum. (The high energy is to reduce beam steering, and the (00) beam maximum is so that this particular beam is easily seen during the following procedure. An energy
of ~135eV was used for the Ni(111) alignment, and ~150eV for the Cu(001) alignment.

3. The fine adjustment micrometer on TR is turned 'all the way out' (i.e. all the way counterclockwise to lowest angular adjustment).

4. The bellows that connects the sample manipulator head to the chamber is twisted from side to side and then released, to eliminate any torsional stresses that may exist there. Because they float free and are easily twisted, these bellows, along with the tilt ball that sits directly above them, are a significant source of angular 'slop', and thus must be set to a fixed position, and not rotated after the 0-alignment is set.

5. The TR coarse adjustment is turned to the lowest possible angle, and then slowly turned upward in angle until the 0-vernier reads about 4-5° below the approximate normal incidence reading (Normal incidence, in the current setup, is expected at ~350°20' ± 40'). and then the coarse adjust is pinned with a thumbscrew.

6. The LEED pattern should be sharp and show the bright (00) beam spot about 8-10° to the left (i.e. 'lower' in angular position) of the electron gun aperture. While watching the (00) beam LEED spot, slowly turn the TR fine adjustment micrometer in (upward in angle) until the LEED spot completely disappears into the hole surrounding the LEED gun. This angular position is called the 'disappearance point' and has been found empirically (see above) to be 2°15' lower in 0-position than normal incidence.

7. Turning the TR fine adjust 2°15' farther will give the normal incidence crystal geometry. A similar approach can be used to obtain any positive-0 angular positioning, by simply adding the incidence angle sought to the 2°15' moved off the disappearance point. This procedure will not work for negative 0-positions, for it does not remove the manipulator backlash.

This procedure incorporates three elements critical to any angular adjustment on this system: 1) approach all angles from the same direction to eliminate effects due to backlash, 2) relate any angular position sought to a known angular condition that can be visually verified, and 3) don't rely on the external vernier for any absolute positions, only for the differences between positions.

DIFFUSE BACKGROUND SUBTRACTION:

There is a small diffuse background collected by the faraday cup
that is not due to the coherent diffraction process, but rather to scattering from randomly positioned defects in the crystal, irregularities in surface morphology (i.e. random surface steps), or from phonon scattering. The need for background subtraction as well as the general method of approach, are introduced in the body of the text, but a few notes on implementation of the procedure are provided here:

The subtraction of background is done by measuring and recording a 'background' data file identical in format to the standard SPLEED data files and subtracting the measured background intensity stored in this file from the diffracted intensity of the beam of interest. The data file may be collected using the standard SPES/SPLEED data acquisition routine PLEED3.SAV on the LSI 11/02 computer.

![Faraday Cup Positioning](image)

**Figure A2.** Faraday cup positioning to collect the diffuse background that is subtracted from the diffracted beams.

The background file is obtained by positioning the faraday cup approximately 10° in ϕ off the position of the diffracted beam of interest. (See Figure A2.) This position is far enough off the diffracted beam position that the faraday cup will collect only diffuse background and not the fringes of the gaussian-profiled diffracted peak. The entire background energy spectrum may be taken at one faraday cup position, and is a function that generally rises in intensity with increasing energy with a few small fluctuations.

The actual subtraction is performed using the MASSG2.SAV program. The subtraction routine in MASSG2.SAV goes point by point in energy, subtracting the stored background intensity from the stored diffracted
beam intensity and replacing the stored diffracted beam data file with
the new 'pure diffracted beam' intensities. This routine allows for an
energy offset between the data points of the two files, and sets the
'pure diffraction beam' energies at the values that were contained in
the old diffracted beam data file. The program assumes as an initial
condition that both the diffracted beam and background data files have
been normalized to 'total' incident current, but that neither have been
shifted in energy to correct for the computer energy shift or for the
sample work function.

DETAILS OF DATA ACQUISITION PATH:

Three quantities are measured for each energy value during data
acquisition:

1. The difference between the spin-up and spin-down currents (i.e.
   $I(P_0) - I(-P_0)$), called the 'difference current'.

2. The spin-average diffracted intensity, $[I(P_0) + I(-P_0)] / 2$.

3. the absorbed incident current to the target.

The data acquisition path of each of these sampled quantities is
shown schematically in Figure A3 and is described in some detail below.

1. the 'difference current':

   >> The 500Hz AC component of the current is collected into the
      movable Faraday cup, and is fed into a PAR preamp.

   > The preamplifier output is a voltage that is linearly
      proportional to the measured current, and scales as
      $1 \times 10^{-8}$ A/V. This signal is fed into a PAR lock-in amplifier.

   > The lockin amplifier is tuned to 500Hz. This lock-in
      internal source frequency then drives the Pockels cell, which
      modulates the helicity of the light, and hence the sense of
      electron beam polarization. The output of the lock-in
      amplifier is a DC signal between -10V and +10V which is equal
      to the rms voltage amplitude of the input signal at the
      frequency and the phase angle selected [ref.].

\[ V_{out} = \langle V_{signal} \rangle_{rms, \phi} \cdot PARG \]

where $\langle V_{signal} \rangle$ is the input voltage signal time averaged over
Figure A3. The SPES/SPLLEED data acquisition path showing the physical vacuum configuration of the source, transport optics, and target, and indicating schematically the data and control paths of the various measured quantities. The data path is described in detail in the text.

one lock-in amplifier time constant, and PARG denotes the PAR lock-in gain, which is:

\[
PARG = 10V / \text{(lock-in sensitivity)}
\]

NOTE: The phase angle used in the lock-in must be selected carefully, because an improper phase angle will cause 1) the asymmetry data to scale improperly, 2) an improper sign reversal of the asymmetry, or 3) both errors. The proper phase angle between the reference signal and the 500Hz Faraday cup AC signal (chosen here for a linear polarizer in the laser optics aligned parallel to the electron transport optics axis; for a linear polarizer rotated 90 degrees from this, the sign of the polarization is reversed) is found to be 270° + 43°00′, and gives a proper positive asymmetry for positive lock-in output voltage or meter deflection. The main factors leading to this phase shift are 1) the RL phase difference across the step-up transformer which gives an effective phase shift near -90° (or
+270°), and 2) the time delays in the PA amplifier and electron transport optics which lead to a positive phase shift.

The lockin output signal is fed into an analog-to-digital-converter (ADC) connected to the LSI 11/02 computer, and a value proportional to the signal (here, simply a real number between -2047 and +2047) is recorded in an array YDAT(1,j) where the index j scans all the energy points.

2. the 'diffracted beam current':

The DC component of the current into the Faraday cup is fed into the preamp and scaled identically to the 'difference current'. The output voltage of the preamp is then fed into a Keithley electrometer.

This electrometer may be used as a monitor while optimizing manually for maximum diffracted current into the Faraday cup, as well as a manually adjustable gain element in the data path. The output of the electrometer ranges from 0–10V and is the signal voltage times the gain across the electrometer:

\[ V_{\text{out}} = V_{\text{signal in}} \cdot \text{KG} \]

where KG denotes Keithley gain and is:

\[ \text{KG} = \frac{\text{full scale deflection voltage}}{3V} \]

The electrometer output is fed into a second channel of the multiplexed ADC and recorded in the data array as YDAT(2,j).

3. the 'absorbed incident current':

The target crystal is grounded through a second Keithley electrometer set on DC Amperes mode (usually 3μA full scale) and the current that drains to ground through the sample (i.e. the incident electron beam current minus all electron flux both elastic and inelastic backscattered out of the sample) is measured.

The incident current Keithley electrometer output is read by a third channel of the ADC into YDAT(3,j).

**INSTRUMENTAL ZERO OFFSETS:**

In the data acquisition paths of each of the three data channels there are several sources of instrumental DC voltage offsets. Standard zeroing procedures (e.g. for the Keithley electrometers, PAR lock-in amplifier and ADC) may be used to minimize offsets in many of the electronic components. But any residual offsets due to leakage current...
into the Faraday cup or other effects, unaccounted for by these methods, may be easily subtracted by the following procedure.

Before a data run commences, the laser light is blocked, thus shutting off the photoelectron flux incident on the sample. Then each of the three data channels are sampled by the computer. The values obtained are used as zero offsets, and are subtracted from each subsequent data point taken on that channel. It is assumed that these zeroes do not drift with time, although provision is made to allow for the sampling and updating of the zero-offset values while the data run is under way, if the need arises.

INSTRUMENTAL PICKUP NOISE:

There are a number of sources of noise, reflected by random fluctuations of the measured data values, that are due to instrumental pick-up. The reduction of these sources of noise is especially important in our Faraday-cup/LEED system because the actual signal detected in the Faraday cup is often very small, on the order of $10^{-11}$ to $10^{-10}$ amperes. There are a number of sources for this noise. Any externally connected lead wires tend to pick up radio frequency and 60-cycle noise. In addition, shot noise, and even movement in the room (which induces small current changes in the lead wires by vibrating them in the static magnetic field of the Earth), cause random AC currents on the data lines. Effects due to this noise, which show up as random statistical variations of our measured signal, are minimized by the following standard techniques:

1. The careful shielding of all exposed leads using coaxial cables and BNC or MHV connectors throughout the data acquisition paths eliminates most of the rf-noise.

2. Noise on the 'difference current' channel, upstream of the lock-in amplifier, that does not fall at 500 Hz, is effectively eliminated from that channel by the phase sensitive detection process.

3. In addition, each data point is digitally filtered in the following manner:
   Each ADC channel is sampled 50 times, and the 50 samplings are then averaged to obtain an 'averaged sample' data point. This sampling process is supposed to be long enough that it
averages out any residual rf or 60-cycle noise that may remain in the data.

That 'averaged sample' is then repeated IADC times and the mean and standard deviation of this sampling are recorded in YDAT(i,j) - the format is such that the standard deviation for the data recorded in YDAT(i,j) is recorded in YDAT(i+3,j). The standard deviation recorded here is supposedly due only to the actual variations in the data itself.

These methods eliminate random noise in the data, and the resulting data can be treated by standard statistical methods. Usually the standard deviation is a small fraction of the total signal. Only at points having very low intensity or near 'zero-crossings' of the asymmetry (i.e. where the value of the asymmetry changes sign as the energy is scanned) are the error bars unusually large. The error bars on low intensity features are a true measure of the uncertainty of the measurement, for these are, by far, the most difficult data points to reproducibly measure. On the other hand, large zero-crossing error bars are usually an artifact of the way standard deviations are defined, for although the actual quantities can be measured rather precisely, the form of the standard deviation includes the measured quantity in the denominator, which causes the standard deviation to 'blow up' in regions of near-zero asymmetry.

ABSOLUTE ENERGIES OF THE ELECTRON BEAM IN VACUUM:

The electron beam energy must be known in vacuum. The beam energy is a function of both the bias of the photocathode with respect to ground (and thus also with respect to the target crystal, which is grounded), as well as the work functions of the photocathode and target crystal.

The photocathode bias is controlled by the LSI 11/02 computer through an external DAC, and as each data point is taken, the computer records the voltage equivalent of the digital signal it sends to the DAC and places it in an array that accompanies YDAT(i,j). Two energy adjustments must be taken into account in the analysis of the data:

1. In the digital-to-analog control path that governs the photocathode bias, there are small offsets and imperfections in scaling that must be accounted for. (i.e. The voltage that the computer 'thinks' it is setting and thus records in the
data file, and the actual external bias voltage on the photocathode (which may be measured directly) are slightly different.) The difference between the real bias voltage and the bias voltage recorded in the computer may be easily obtained, and is a linear function that scales directly with energy. It has been found empirically to be:

$$V_{\text{bias, real}} = 0.993636 \cdot V_{\text{computer}} - 0.545455$$

where both voltages are given in eV. A routine is `MASSG2.SAV` may be used to shift all energies in the data file to account for this scaling.

2. The work function of the photocathode is essentially zero (actually slightly negative as that is the defining condition for NEA, but for our purposes zero is close enough, for the photocathode work function is within ~ 0.1-0.2eV of zero in any case). In addition, the work function of the target crystal is obtainable from the literature. The work function difference between the photocathode and the target crystal is the contact potential between the two crystals, and is added to the bias voltage to give the true electron beam energy in vacuum:

$$E_{\text{beam, vacuum}} = V_{\text{bias}} - \Phi_{\text{target}}$$

A second `MASSG2.SAV` routine shifts the electron beam energies to account for the target work function (which is taken as an input parameter), and gives the true electron beam energies in vacuum.

NORMALIZATION OF DIFFRACTED INTENSITIES TO THE 'TOTAL' INCIDENT CURRENT:

LEED I-V profiles must be normalized by dividing the measured diffracted intensity by the total incident current to the sample. To first order of approximation, this normalization is not necessary to obtain normalized A-V profiles which are simply the ratio of two purely back-diffracted beam measurements. But because the background subtraction requires the subtraction of two data sets with different incident currents, this normalization of the I-V's is at least secondarily important in the generation of good A-V's. The problem is that this total incident current is not precisely known.

The absorbed current to the sample is measured as one if the three data points taken at each energy during data acquisition, but this quantity is not the total current to the sample. As noted above, a fraction of the incident current to the sample is lost back out into
vacuum by backscattering. In one sense, this is an obvious point, for otherwise we would have no elastic LEED diffraction intensities to measure. There is also a significant flux of inelastic electrons that are backscattered out of the sample and lost from the incident flux measurement.

The ratio of backscattered electrons to total incident electrons (which we will call $X(E)$), or equivalently its complement, the ratio of absorbed current to total incident current (which is $1-X(E)$), is a function of energy, and if this ratio (a simple energy dependent fraction) is known, then the absorbed current data measured with each data file can be normalized to compensate for backscattered losses. Thus a new 'total incident current' data set can be generated and this, in turn, used to normalize the diffracted current of each LEED I-V profile measured.

A data set which may be subsequently used to normalize absorbed incident current to give total incident current, may be generated empirically by the following procedure:

1. The incident current from the polarized electron source to the sample of a clean surface is measured with the sample grounded through an electrometer for beam energies ranging from 10eV to 250eV.

2. Immediately after, the incident currents are measured over the same energy range with the sample biased at +300eV.

3. The first data set gives the absorbed current typical of a LEED data set, while the second gives the total current to the sample for the same beam conditions. This is because any electrons that could potentially be backscattered out of the sample are not energetic enough to do so, for the energy required to overcome the +300V bias voltage is at least 50eV higher than the maximum primary beam energy.

4. A normalization data file is then generated by dividing these two incident current data sets, the second by the first, energy point by energy point, which gives the ratio of the total current to the absorbed current as a function of beam energy (i.e. $1-X(E)$ discussed above).

The normalization file thus generated (for scattering from Cu(001)), and used for all data presented here (both for copper and nickel data), is titled INCUR2.DT2, and the MASSG2.SAV program contains
a routine to which uses this (or any equivalent normalization file) to provide a total incident current normalization for the data sets associated with both actual diffraction data and background data.

MOTION OF THE FARADAY CUP AND OPTIMIZATION ON THE DIFFRACTED BEAM POSITION:

Because nonspecular beams change their angular positions as the beam energy is scanned, measurements of the diffracted beam intensities or asymmetries requires the movement of the detector used to measure those quantities (here a Faraday cup). In addition, small stray fields in the experimental chamber cause even the specular beam to move a little with energy, although this effect is only about 1°-1.5° at the very lowest energies measured ≤ 25eV, becoming negligible above ~ 60-70eV. This requires the Faraday cup position to be optimized between every pair of successive data points (each taken ~ .95eV apart) for nonspecular beam data or for low energy (< 50eV) specular beam data, and once for every 3 - 5 data points for higher energy specular beam data.

The Faraday cup used in the present experimental apparatus is adjustable in two independent orthogonal ranges of motion, θ and φ. The optimization of the Faraday cup position on the diffracted beam position is done manually using two rotary feedthrough dials. While monitoring the diffracted current Keithley electrometer meter deflection, the θ-motion feedthrough in spun in and out, rocking the Faraday cup back and forth past the optimum beam position in smaller and smaller sweeps until the maximum deflection (and thus the maximum diffracted beam current into the Faraday cup) is arrived at. Then the φ-motion is optimized. (Usually this φ-adjustment is very small, except at low energies, and is only required every 10 points or so.)

At this point, the data for each of the three data channels at that beam energy may be recorded into the computer. (The data acquisition routine PLEED3.SAV is provided with a 'wait state' routine that refreshes the terminal graphic display with real-time diffracted current and 'difference current' information while this optimization is going on. The data is not stored, however, until the <cr> character on the
terminal is depressed. There is also provision in the routine to retrace back in energy, and retake data points if the beam gets 'lost', which can easily happen while scanning through diffracted intensity minima.)

The Faraday cup optimization is a very slow and tedious process and accounts for about 90% of the time required for a typical data run. In addition, it is one of the largest sources of error associated with run-to-run reproducibility. Because of inaccuracies in the positioning optimization process, and because of beam steering problems due to motion of the LEED system/Faraday cup assembly when the Faraday cup is moved, the accurate reproducibility of measured I-V and A-V profiles is somewhat limited. The probable limits of run-to-run A-V profile reproducibility in our system, especially for nonspecular beams such as those shown in the present studies, due to Faraday cup positioning inaccuracies and other effects, are on the order of ±0.50–0.75%. This may be seen in the standard deviation in the recorded data for the Cu(001) A-V profiles of Figures 9 and 10 in the text, where the typical error bars, which reflect the variation in recorded profiles of a number of data runs, are in this range.

This may also be seen by inspection of Figure A4, which shows A-V profiles for (00) specular diffraction from Ni(111) at Θ = 30°. Here the sample is demagnetized using AC current through the magnetizing coils, and then, without repositioning the sample alignment in any way, two data runs are taken in rapid succession. The diffracted beam shown is the specular beam and thus there is only very little Faraday cup repositioning required, but still the two curves do not exactly reproduce one another. The variation between the profiles, shown in the upper part of the figure, is found to be up to almost one percent, and this gives a reasonable lower limit to our run-to-run reproducibility. For exchange asymmetry data, which requires two data runs under identical scattering conditions (with the exception of magnetization reversal) to obtain a single A_{ex}-V experimental profile, the run-to-run reproducibility error is effectively doubled, and the best reproducibility one could expect is on the order of ±1.0%.

For many studies performed to date, on high-Z or strongly ferromagnetic systems, the spin-asymmetry profiles measured have
Figure A4. Run-to-run reproducibility study described in the text. The upper part of the figure contains the difference between the two profiles shown below. The horizontal dotted lines denote plus and minus one percent deviation.

features on the order of 30-40% or higher, and reproducibility on the order of a percent or so is not a major concern. But for many of the more interesting upcoming studies, including magnetic thin film work, where the ferromagnetic exchange asymmetry is expected to be small, some method of reducing these error limits will have to be found before highly quantitative results are obtainable.

BEAM STEERING BY STRAY FIELDS:

Small residual magnetic fields exist in the experimental chamber, and are of serious concern in spin-polarized LEED work for two reasons. Even small magnetic fields will deflect the electron beams from their undeflected paths, which changes the primary beam incidence angle, and
causes otherwise unnecessary Faraday cup tracking of the diffracted beams. In addition, because the electron beam is polarized, the magnetic moment of these electrons will interact with an external magnetic field, and effectively change the beam polarization. Any stray magnetic fields in the experimental region will rotate the electron spin-polarization direction of electron beam that passes through the region, through an angle equal to the beam deflection angle.

Generally these two effects are very small for the small magnetic fields (≤10–20 milligauss), present in the experimental chamber, giving deflections and rotations on the order of ~1–2° for beams at the low end of our measured energy range, and negligibly small effects above ~50eV. The following steps were taken to minimize stray magnetic fields in the experimental chambers:

1. The entire experimental region is encased in μ-metal shielding. Even with the large number of holes required for viewports, feedthroughs, and segments of the experimental apparatus, this reduces the Earth’s magnetic field and fields due to other external magnets by a factor of 2-100.

2. The φ-rotary used in the Cu(001) sample holder contained a stainless steel bearing which was magnetic. This bearing was carefully shielded with μ-metal.

3. The keeper c-magnet used to hold remanent magnetization in the Ni(111) sample would itself become magnetized along with the sample, and unreasonably large stray magnetic fields would remain right in the region around the sample face when the magnetizing current was turned off. It was found, by tests performed out on the bench-top using the crystal as it was mounted in the chamber, that these stray fields could be eliminated by a careful 'back-driving' of the current through the magnetizing windings.

BEAM BLOSSOMING AT LOW ENERGIES:

The electron optical characteristics of very low energy electron beams are very poor, and the beams tend to blossom, or spread out spatially. Because the Faraday cup used to measure the diffracted intensities has an acceptance angle of about 2.8°, any beam spread that is wider than this will cause part of the diffracted beam to be lost. This beam-spreading is an energy-dependent effect, and the lower the energy of the diffracted beam, the larger the fraction of the beam that
will not be collected in the Faraday cup. As has been noted in the text, and may be seen from the experimental I-V profiles compared in Figure 11, there is some diminution of the the diffracted beam intensities taken in this study even up to \( \sim 100 \text{eV} \), when compared with the experimental intensities reported by Noonan and Davis. In their study, great care was taken, by using very large Faraday cup apertures, to collect all of the diffracted beam flux.

As has been noted, this loss of the outer beam fringes, does not affect the measured asymmetry profiles, and thus no great care was taken to compensate for losses due to beam blossoming, but this does affect the lab-to-lab reproducibility of our intensity data. A more careful study of I-V normalization, including possible empirical tests using a variety of different Faraday cup aperture sizes, would be required to improve the results shown here.

**RUN-TO-RUN REPRODUCIBILITY — A REVIEW:**

As has been noted throughout the past several sections, there are a number of factors that must be folded into the problem of obtaining good run-to-run reproducibility. Among these factors are the reproducibility of sample alignment between runs, the optimization of Faraday cup positioning, and a number of other effects. But the limiting test in obtaining run-to-run reproducibility is how well does the data itself reproduce when all the angular alignments and adjustments are held constant. This condition may best be seen in Figure A4. In this figure are shown A-V and I-V profiles for the (00) specular beam at \( \Theta = 30^\circ \), for diffraction from an unmagnetized Ni(111) crystal.

The data shown here is for the simplest reproducibility conditions possible because: 1) the beam studied is a specular beam and thus (except for the low energy end) requires no Faraday cup motion, 2) the runs were taken back to back with no crystal repositioning done between them (thus eliminating both crystal alignment reproducibility problems and any effects due to differences in crystal cleanliness or aging), 3) the sample was carefully demagnetized so that there is no difference between runs due to exchange asymmetry changes, and 4) the diffraction conditions are such that the LEED spot and Faraday cup position are
easily viewed through viewports in the chamber (which allows for the easiest possible positioning of the Faraday cup on the diffracted beam position). We note that first, the deviation between curves is larger at lower diffracted intensities, and second, that even under the most reproducible conditions, small A-V profile features are not reproducible, using present techniques, much below ± 0.5%.
APPENDIX B: The Lure and Folklore of GaAs Photoactivation

The procedure used to prepare a GaAs crystal so that it gives a large photoelectron flux per unit laser power is called photoactivation or simply activation of the photocathode. It involves the cleaning of the surface of contaminants and then codeposition of cesium and oxygen on the surface. A good activation will reduce the effective GaAs work function to zero, (in fact slightly below zero, to a condition called negative electron affinity or NEA\textsuperscript{178}) and the electrons photoexcited into the conduction band will practically tumble out into vacuum.

Because the relative quality (i.e. average photocathode lifetime, quantum yield, and decay rate) are strongly dependent on the physical environment of the cathode, presence of contaminants, and other factors, the activation process has developed into somewhat of a 'black art'. The activation process requires quite a bit of 'tweaking'—continually optimizing of the relative flow rates during the codeposition process—and thus requires each worker to develop a 'feel' for how the activation is progressing on his own apparatus.

In effect, each experimenter needs to develop his own set of recipes for obtaining a good activation. It is thus important to note that there are a number of checks possible to evaluate the relative quality of a particular activation, both while the activation is in progress, and afterwards. While none of the guidelines listed here are 'hard and fast' rules, these procedures have been found to work well on our machine at Rice, and thus can be of use in setting up procedures on other machines as well.

The format of this discussion will be as follows: First we will deal with the general procedures for preparing and cleaning the photocathode, both before insertion into the chamber, and then at vacuum during the activation process. A number of 'tricks of the trade' will then be discussed. Finally we will focus on the procedures used in activation of GaAs photocathodes, and on the properties of good photoemission both during and after activation. An accompanying appendix (Appendix C) will deal with the relative merits of the GaAs and GaAsP electron guns.
PREINSERTION PROCESSING — Cleaning and Etching: The general procedure for preparing GaAs samples before insertion into the vacuum system follows very closely that recommended in the Appendix of Pierce et al. Several notes however are in order:

a) Every effort was made to use the highest grade solvents and chemicals available for this cleaning procedure because any residual contaminants degrade the cathode, shorten its life, and reduce the photoyield. Electronic grade acetone, methanol, and trichloroethylene are used, as is distilled (not deionized) water, each to reduce trace elements.

b) The cleaning of the GaAs crystal should usually be the last item on the agenda before bringing the system to vacuum, because delays with the newly cleaned and etched GaAs crystal at atmosphere allow contaminants free in the air to degrade the cathode quality. It is possible to leave the GaAs crystal in a methanol bath for several hours after all cleaning steps are completed, until the chamber is ready for pump-down; but this is not advised, for it is found that the contaminants adhering to the surface, even from the bath itself (supposedly carbon), require additional attempted activation cycles in vacuum before a good activation is obtained.

c) The cleaning procedure generally takes about 1.5 to 2 hours. Thus it is often helpful to have two workers, one concentrating on the GaAs preparation and the other on preparations for the pump-down itself.

d) It is often good to insert a new Cesium source when a new photocathode is inserted. The contaminants given off by old, almost depleted Cs dispensers (which must be driven to 6.5–7.0 Amps to obtain enough Cs) generally tend to keep the activations poor, with rapid decay times. In addition, the cesium dispenser, which emits the alkali vapor when ohmically heated, must be kept in a dry atmosphere when not at vacuum. Cycling to atmosphere for any length of time to change cathodes will cause the dispenser to pick up excess water vapor. Replacement of the Cs dispenser with the insertion of each new
cathode would eliminate any potential cathode contamination from the Cs source. The Cs dispensors used are obtained from SAES Getters USA\textsuperscript{180} and require approximately 4.7 to 5.0 Amps early in their life and up to about 6.0 to 6.3 Amps late in life for emission of Cs. The Cs source is outgassed both before and during bake-out by running 4.0 Amps through it for approximately two minutes. The sources have a lifetime of from 6 to 10 full activations in addition to a number of repeakings, depending on how hard they are driven.

e) The oxygen used in photoactivation is leaked into the source chamber through a Varian leak valve which allows very fine continuous adjustment of the oxygen flow rate. The source is a one liter flask of ultra-high purity oxygen which is separately valved to allow small slugs of gas to be introduced behind the Varian Leak Valve while keeping the bottle itself valved off. The oxygen source is baked, up to the seal-off valve, with the Varian leak valve open. The lifetime of this source is for our purposes, essentially infinite, and limited only by back-contamination of the oxygen bottle through its valves.

**PHOTOACTIVATION - Overview:** The activation procedure follows the technique that Pierce et al.\textsuperscript{181} describe as their primary heat-cleaning and activation procedure, and all their comments apply equally well to our system. In our procedure, we heat the photocathode to 640°C for between 5 and 10 minutes and then to 650°C for 30 to 90 seconds. (Because this temperature is very close to (within 7-8°C of) the melting point of GaAs, great care must be taken to use highly regulated power supplies to float the cathode heating filament, to monitor the crystal temperature continuously while hot, and to make sure that the GaAs crystal is in very good thermal contact with its supporting molybdenum can before insertion.) This step is followed by cooling rapidly to 20° to 30°C and deposition of Cs and then coadsorption of Cs and oxygen while illuminating the photocathode through a viewport in the top of the chamber with a 40 watt white light bulb and biasing the first aperture above the photocathode at approximately +140V. This is done with the photocathode-crystal-manipulator in retracted position, in direct line
of sight of the Cs dispenser. The photocathode is grounded through a Keithley electrometer and strip-chart recorder to monitor the photocurrent. A number of 'tricks of the trade' to be used for the activation, are relevant to the discussion here:

Background Gas Contamination: Almost anything that is found in the background gas of our UHV system is considered a potential contaminant to the photocathode, and may poison it so that the photoyield and/or lifetime of the cathode is significantly reduced. This is true especially for hydrocarbons,\textsuperscript{182} and there are indications of cathode decay due to other adsorbed gases as well. Thus we go to great lengths to reduce the base operating pressure of the source chamber and clean out contaminants.

a) Leave the ionization gauge and PPA in the source chamber off after base pressure is reached, and especially do not turn them on after photoactivation. Ionized gases tend to stick to the surface more readily than comparable pressures of un-ionized gas.

b) Leave the interlock between chambers closed when not in use. This is to keep the photocathode as clean from contaminant background gas as possible, and is necessary because the main experimental chamber has a higher base pressure that the source chamber, and especially has a higher partial pressure of hydrocarbons such as CH\textsubscript{4} and its cracking fractions, which outgas from the discharged ion pump during sputtering.

c) It is generally not good to have MACOR\textsuperscript{183} insulators too near the cesium sources used for the activation because MACOR decomposes and gives off boron and HF above 600°C\textsuperscript{184} which is right at the dispenser emission temperature.

d) It is seen from partial pressure scans that the tail end of a Cs source charge seems to contain a high fraction of CO and H\textsubscript{2}O. These contaminants are kept to a minimum if the Cs sources are replaced reasonably often.

As a general rule, carbon cracked from hydrocarbons seems to be the worst contaminant for poisoning photocathodes, but heavy over-oxygenation or exposure to other background gases seem to be detrimental
as well.

Low First Activation: The first activation of a new photocathode always seems to be poor. Successive activations are progressively better. There are several possible explanations for this:

a) There are indications that there are still contaminants on the surface of the photocathode at this point, due to contamination at atmosphere, which one heating cycle will not remove, and repeated heating cycles effectively 'scrub' it cleaner and cleaner.

b) On the other hand, the initial activation may be weaker due to imbalances in the Cs and $O_2$ levels in the newly baked chamber. Pierce et al. 185 note that "...the behavior of the photocathode after activation depends in large part on the Cs-$O_2$ balance in the chamber. In commercial phototubes there is an excess of Cs to maintain a partial pressure of Cs in the tube. We find that in a freshly baked ultrahigh vacuum chamber our photocathodes become Cs deficient quite rapidly. Fortunately, this can be corrected by opening the Cs valve and 'peaking up' with Cs. This may be done with the crystal in operating position; line of sight is not required as some Cs moves around the chamber at room temperature....A fresh vacuum chamber becomes 'seasoned' after a few activations or peaking up with Cs."

Both cathode contamination and poor Cs-$O_2$ balance are probably contributing factors in low cathode activation, and therefore considerable effort is made in our procedure to compensate for each.

First Activation Tricks: We have found that a couple of simple techniques used prior to the first activation in the freshly baked UHV chamber help improve subsequent activations, the philosophy here being that the depletion of the Cs-$O_2$-Cs overlayer is one of the key factors in the decay of photocathode life and quantum yield. 84

a) Oxygen is very reactive and seems to stick to the walls of the vacuum chamber preferentially over most other UHV residual gases. Thus when oxygen is first introduced into a chamber under vacuum, it causes the desorption of large amounts off
'junk' from the walls, even before bake-out. Thus, oxygen can be used to desorb the contaminants off the chamber walls out into the chamber, where they are pumped away into the roughing system; and the system seems cleaner and less readily poisoned later when an activation is underway.

b) Carbon, a major photocathode poisoning agent, can be pulled off the cathode surface by the introduction of oxygen (a langmuir or so) into the chamber shortly before the preactivation heating cycle. The carbon then comes off the surface by the thermal desorption of CO — a process apparently a much more energetically favorable than the desorption of the free carbon from the surface.

c) Cesium is readily depleted in the newly baked system; repeated activations improve the background pressure of Cs and thus the longevity of the activations. This improved Cs background pressure can also be obtained by simply turning on the Cs source at low current overnight before the first activation. In addition, if one finishes an activation by cutting the Cs source current back (to say 2.0 Amps) but not off, the additional evaporated Cs 'refreshes' the Cs pressure in the chamber, and the activation stays higher longer.

**Activation Procedures:** While actually performing the photoactivation, the following checks are strong indications of a good activation:

a) Most good activations show a detectable photocurrent on the Keithley electrometer with a sensitivity of \(1 \times 10^{-9} \text{ A} \) (full scale) within 15-20 minutes of the start of Cs deposition (although there have been some excellent activations that didn't 'start up' for over an hour). The photocurrent should rise exponentially through several orders of magnitude in about 10-20 minutes with cesium deposition only.

b) Usually a good activation peaks with Cs deposition only at about \(0.3 \mu\text{A} \). If it peaks more than a factor of 2 higher, there is too large of a partial pressure of oxygen already, indicating a poor bakeout or that the leak valve is not
sealing. If much lower, then other contaminants are severely poisoning the cathode, and another cleaning cycle is needed.

c) Most of the recent 'good' activations, (i.e. those that maintain a steady, reasonably constant photocurrent for several hours, and are amenable to long lasting peak-ups several days later) take a very long time, >4-5 hours.

d) When depositing oxygen, start by opening the variable leak valve until the photocurrent starts to rise rapidly (about 14 turns), then optimize very shortly after by closing by approximately 1/4-1/3 turns. As a general rule, the more patience one shows between changes of oxygen flow rate, the better. If the photocurrent is continuing to rise at a steady rate, don't change it! It is also advisable to change the flow rate in small increments, either 1/4 or 1/3 turn at a time. This type of activation will have an almost linear monotonic rise with few bumps and almost never turns over and starts down.

e) The best activations end almost flat and seem to take a very long time to start down. They peak to between 7-10μA and sometimes higher.

f) Pierce's test for the ratio of photocurrent with a red filter (RG715) to total white light photocurrent (where it should be noted that I have switched the ratio from his) gives a value greater than or equal to .45 for a good activations.

g) Turning off the oxygen has either a negligible effect on the photocurrent, or causes it to plummet precipitously. (Both have given very good activations.)

h) The activation should be allowed to decay approximately 15 to 20 percent after the oxygen valve is closed, while adding additional Cs. When the Cs is turned off the photocurrent should repeak usually to about the same level or slightly higher than the maximum while deposition was in progress. The photocurrent should remain rather flat with time, (i.e. less than a 2% decay in five minutes; sometimes the photocurrent of the best activations even goes up with time!) Don't turn Cs completely off but down to approximately 2A for about a half
hour or so. This seems to more fully cesiate the chamber and give longer photocathode life.

i) Under the laser (with 40mA laser power) a good activation will initially have over 13-15μA photocurrent and often over 20μA.

Post-Activation Photocathode Characteristics: Up to a certain breakdown power (which will be discussed shortly) the photocathode will provide a reasonably unlimited electron flux, and this flux is proportional to the incident light flux on the cathode. Up to 30-35μA photocurrent with laser excitation have been obtained easily in our electron source, and probably more is available. The maximum flux available has never been tested; 20-30μA is very sufficient for our needs.

a) During actual photocathode use, the more intense the focused laser spot is on the cathode, the faster the Cs–O₂–Cs overlayer seem to be burned off that local spot! However moving the photocathode laterally under the laser spot will illuminate another region of the photocathode on which the Cs–O₂–Cs overlayer is more completely intact, and it will emit well. The electron transport optics then must be reoptimized slightly to compensate for the position of the photoemitting spot.

b) The Cs–O₂–Cs overlayer can also be easily protected by simply cutting back on the laser power under operating conditions, so that the local heating of the photocathode is not too severe. Laser power sufficient for approximately 8-10μA photocurrent is found to give the most current to the sample, and the longest photocathode lifetime.

c) Driving the photocathode to higher photocurrents requires higher laser power, and the laser is itself a light emitting diode (tuned to a very tight bandwidth, but a diode nonetheless), and can easily be destroyed by driving to high current. The laser power supply, which has a manually adjustable current limiter, can thus easily be driven to the point where it BURNS OUT THE GaAlAs DIODE LASER, which has a reasonably low breakdown current.

d) Driving the photocathode to higher photocurrents is generally counterproductive in any case, because useful current to the
target does not scale linearly with photocurrent, but is space-charge limited. At maximum, the photocurrent transported to the sample is about three percent, at an operating point of about 8µA total photocurrent.

e) The measured beam polarization from the GaAs(001) photocathode is very stable at 28 ± 2%. It is believed that most of the measured variation in beam polarization is due to beam steering and alignment effects in the Mott accelerating optics, and not in actual polarization changes. While the beam polarization has been measured for a large range of activation and beam conditions, the beam polarization of GaAs photocathodes seems to be totally insensitive to the method of activation, to the photocurrent used, or to photocathode history.
APPENDIX C: The Relative Merits of GaAs and GaAs$_{1-x}$P$_x$ Photocathodes

While the photoemission of polarized electrons from GaAs(001) is used as the source of the electron beam used for most of the present study, a modification of the electron source to utilize photoemission from the (001) face of GaAs$_{1-x}$P$_x$ has been tested in this laboratory and shows great promise. The band structure of this semiconducting compound is very similar to that of GaAs, except that the band-gap is widened from 1.52eV (as in GaAs) to 1.96eV by the substitution of phosphorus for arsenic. Reichert and Zähringer note that '...the energy gap of GaAs$_{1-x}$P$_x$ compounds increases with increasing content x of phosphorus.' This should give the possibility of tuning a GaAs$_{1-x}$P$_x$ source of spin-polarized electrons to an available laser light source by choosing the appropriate x-value. The energy shift of GaAs$_{1-x}$P$_x$ is tuned such that the band-gap just matches the 632.8nm line of the HeNe laser. This choice of photocathode band-structure provides a spin-polarized electron source with very nice electron-optical operating characteristics, many of which are a reflection of the excellent laser-optical characteristics of the readily available and turn-key simple HeNe lasers.

The discussion which follows will focus first on a comparison of the operating characteristics of GaAs$_{1-x}$P$_x$ and GaAs polarized electron sources, then on the differences and similarities in cathode preparation of these two types of photocathodes, and finally on some of the curious puzzles associated with this entire class of electron sources.

Comparison of GaAs$_{1-x}$P$_x$ and GaAs Electron Sources: Many of the excellent electron-optical characteristics of a GaAs$_{1-x}$P$_x$, as well as its ease of implementation, are directly related to the superior laser-optical characteristics of the Helium-Neon laser:

a) the alignment of the laser optics, and the obtaining of a parallel laser beam through the Pockels cell (which is necessary for good circular polarization of the light), are orders of magnitude more easily achieved with visible (bright
red) HeNe laser than with the invisible (near infra-red) GaAlAs diode laser used with the spin-polarized GaAs electron source.

b) The HeNe laser also provides a very tightly collimated beam of illuminating radiation, with only a small amount of beam divergence, while the GaAlAs diode laser has very large beam divergence, and requires a very large aspheric lens to collect even a reasonable fraction of the useful laser light intensity. Because of this severe beam divergence, it is also very difficult to obtain parallel light through the Pockels cell or focus the GaAlAs laser to a tight spot due to of spherical aberration in the GaAlAs diode laser optics.

c) The difference in ability to align for parallel light through the Pockels cell with the two lasers means that the smooth, symmetric, and perfectly sinusoidal variation of optical polarization through the cycle RHCP→LP→LHCP→LP→RHCP, which is necessary for the sinusodial variation of electron polarization between spin-down and spin-up, is more completely and easily obtained with a HeNe laser.

d) The HeNe laser may be focussed to a very tight spot on the photocathode, while the focussing of laser light from the GaAlAs laser gives at best a diffuse spot of well over a millimeter in diameter. This means that the electron photoemission from the GaAs$_{62}$P$_{38}$ electron source may be treated as from a point source, while the electron beam emitted from the GaAs source is much broader and more diffuse. As a result, the electron transport characteristics are much better for the GaAs$_{62}$P$_{38}$-photocathode/HeNe-laser source than for the GaAs-photocathode/GaAlAs-diode-laser source.

e) Because the obtaining of a well collimated LEED beam requires the introduction of a number of small apertures along to electron transport optics, a significant fraction of the initial photoemitted electron flux is lost before reaching the target crystal. But the tightly focussed point source of the GaAs$_{62}$P$_{38}$/HeNe source allows a larger fraction of the beam to make it through. The average absorbed flux to the target from the GaAs/GaAlAs source obtainable is typically .15-.20 μA, and
.25–.30 µA is about the maximum current obtainable. For comparison, the average current to the target crystal from the GaAs \( \text{GaAs}_{62\text{P}_{38}} \) HeNe source is .30–.35 µA, and a maximum absorbed target current of \( \lambda \) .45 µA is easily obtainable.

f) The beam polarization of an electron beam from a GaAs \( \text{GaAs}_{62\text{P}_{38}} \) photocathode, measured under equivalent beam transport and activation conditions to the polarization measurements of photoelectrons from a GaAs photocathode, is found to be 26 ± 3% for a photocathode newly activated to NEA that has been freshly prepared and inserted into our chamber. This beam polarization is, for all practical purposes, the same as that for the GaAs/GaAlAs source.

NOTE: As has just been stated, this is true for 'new' cathodes, but it has been found that the beam polarization is not this high for the 'older' GaAs \( \text{GaAs}_{62\text{P}_{38}} \) cathodes that have been activated several times, and this decay is the single most serious drawback of these photocathodes. This problem will be the focus of a later section.

\( \text{GaAs}_{62\text{P}_{38}} \) Photocathode Preparation: Many of the steps in the preparation of GaAs \( \text{GaAs}_{62\text{P}_{38}} \) photocathodes parallel the methods used in preparation and activation of GaAs cathodes, described earlier in Appendix B and by Pierce et al. However, there are some differences that are worthy of note:

a) The material for the GaAs \( \text{GaAs}_{62\text{P}_{38}} \) cathodes used in this study is an epitaxial layer of n-type GaAs \( \text{GaAs}_{62\text{P}_{38}} \) approximately 1–3 microns thick, grown on a (001)-oriented substrate of GaAs. The samples used in this study were grown by and obtained from Siemens AG of West Germany.

b) The preinsertion cleaning of these samples followed the same degreasing, etching, rinsing and drying procedure described earlier for GaAs, except that only one etchant step was taken, rather than three, and used an 8:1:1 mixture of \( \text{H}_{2}\text{SO}_{4}, \text{30%H}_{2}\text{O}_{2} \), and \( \text{H}_{2}\text{O} \) in which the crystal was placed for 15 seconds, following the procedure outlined by Conrath et al.

c) The pre-activation heating of the cathode to remove
contaminants is only to 610°C for 5 minutes and 620°C for 30 seconds, rather than the higher temperatures and longer cycles used for GaAs. The remainder of the activation process duplicates techniques used for GaAs photocathodes.

d) The photo-yield for white light activations of GaAs\textsubscript{62P,38} cathodes is comparable to that obtained with GaAs. And as noted above, the electron transport characteristics here are superior to GaAs source characteristics.

The Decay of Electron Beam Polarization: The problem with GaAs\textsubscript{62P,38} photocathodes is that the electron beam polarization decays progressively with successive activations. It is believed that this decay is due to the degradation of the epitaxial phosphorus-rich layer by successive heating cycles. The depletion of phosphorus, either by preferential boiling off into vacuum or by diffusion into the bulk causes a decrease in the semiconductor band-gap of the cathode. Because the photo-exciting energy is held constant, this means that with continued depletion of phosphorus, the laser energy probes deeper into the valence band, which causes a mixing into the photoemitted electron flux of electrons photo-excited from the lower \Gamma\textsubscript{7} valence band into the conduction band (See Figure 8 and the discussion of spin-polarized photoemission in the text.), and thus a degradation of the beam polarization as the cathode becomes more GaAs-like. It should be noted that this shift in GaAs\textsubscript{1-xP-x} band structure provides only minor changes in photo-yield or electron-optical characteristics, but severely changes the beam polarization.

Maintenance of the GaAs\textsubscript{62P,38} Epitaxial Layer: There are several potential methods for eliminating, or at least minimizing, the degradation of the GaAs\textsubscript{62P,38} epitaxial layer, but they must be the focus of further investigations, for they are beyond the scope of the present study. Several comments on possible lines of approach are, however, in order here:

a) The simplest solution to the degradation of the epitaxial layer is to find some method of effectively cleaning the surface to be free of hydrocarbons and other contaminants
without heating to the point where phosphorus is lost. This may be accomplished by repeated heating cycles to lower temperatures (possibly in the range 350°–450°C, for that is the cleaning method used by Conrath et al.\textsuperscript{194}), or by the deposition of oxygen and subsequent heating to desorb CO as suggested in appendix B for GaAs.

b) Another potential epitaxial-layer preserving option is to omit the etchant step in preinsertion cleaning process, combined with gentle heating. This method has potential for improving photocathode 'polarization-maintenance' because the etching of the crystal significantly thins down the epitaxial layer, and thus provides less phosphorus in the near-surface region to start with. It should be noted that investigations leading to the maintenance of the epitaxial layer in these photocathodes could be of great importance, because every other characteristic of the \( \text{GaAs}_{0.62}\text{P}_{0.38} \) photocathode/HeNe-laser spin-polarized electron sources indicates that this type of source provides the highest quality polarized-electron LEED beams available. An investigation of the above-mentioned potential, but as yet untested, cleaning techniques indicates that there remain avenues available for eliminating or minimizing the one remaining 'bug' in these sources.

c) Alvarado\textsuperscript{195} reports that the negative electron affinity 3–5 photocathodes used at Julich, which are grown in situ in the experimental chamber, maintain very high beam polarization and show no evidence of noticable decay with time, and that these photocathodes require almost no cleaning because they are grown in vacuum and never see atmosphere. Thus it would seem that the best photocathodes are those that can be grown epitaxially in the chamber in which they are actually used.

The Advantages of Photocathodes Grown Epitaxially in situ in the Experimental Chamber: Discussions with the German experimenters whose work parallels ours indicate that there are significant advantages in the use of GaAs, GaAs\(_{1-x}\text{P}_x\) and Al\(_x\text{Ga}_{1-x}\text{As}\) photocathodes grown by epitaxial methods in the experimental chamber. (The last of these, the
$\text{Al}_{x}\text{Ga}_{1-x}\text{As}$ cathodes, are equivalent to the $\text{GaAs}_{1-x}\text{P}_x$ cathodes, and may be tuned to optimized beam polarization at a particular excitation energy, and $\text{Al}_{0.37}\text{Ga}_{0.63}\text{As}$, for instance, also has its band-gap energy at the HeNe photon energy.) There are a number of polarized electron beam characteristics reported for such photocathodes that seem to justify this assessment that epitaxially grown systems are better:

a) The photocathode lifetimes and photo-yield decay time-constants reported for epitaxially grown cathodes are significantly longer than for comparable cathodes that require cleaning at atmosphere. This implies that the cathodes cleaned and etched at atmosphere contain residual trace contaminants or surface imperfections, introduced (or at least not eliminated) by the cleaning and etching process, that are not present in the epitaxially grown surfaces, and that such defects contribute to the photocathode decay. This decay may also be exacerbated by the simple process of cycling the chamber to atmosphere, for it is known that the background gas environment of a photocathode strongly influences its activation, and that activations are progressively improved the longer the cathode is maintained in the relatively clean UHV environment.

b) Defects in the crystalline lattice, which are thought to contribute to the depolarization of the electron spins during the photoemission process\textsuperscript{196}, are significantly reduced for epitaxially grown photocathode surfaces. This may be the reason why the reported electron beam polarizations for such epitaxially grown photocathodes are significantly higher than comparable atmosphere-processed cathodes. (A 44.1 ±1.3% beam polarization, for example, for photoemission from epitaxial $\text{Al}_{0.37}\text{Ga}_{0.63}\text{As}(001)$ photocathodes when excited by a HeNe laser is reported by Alvarado et.al.,\textsuperscript{197} and comparable (i.e. ~40\%) polarizations are reported for epitaxially grown GaAs photocathodes. Lower beam polarizations are measured for comparable atmosphere-processed cathodes in this laboratory\textsuperscript{198} and for the GaAs photocathodes in use by Pierce and coworkers at NBS,\textsuperscript{199} each of which have beam polarizations on the order of ~ 27–29\%.)
c) In addition, cathodes grown in situ do not require the severe high temperature cleaning procedures used here, because they are never subjected to the atmospheric pressure of contaminants that other cathodes, preprocessed at atmosphere, endure. Thus the reasonably fragile epitaxially-grown films need only be cleaned with a reasonably low temperature annealing cycle, which provides for a longer and more stable cathode lifetime.
APPENDIX D: The Magnetization and Characterization of Ni(111)

Because SLEED uses spin-polarized low-energy electrons as a probe of surface properties, the probe itself places a number of special constraints on the studies of ferromagnetic systems, and these include limits on possible diffraction geometries, the requirement of reversible saturation sample magnetization, and severe limitations on the stray fields allowable in the experimental region. The restriction to certain high symmetry geometries, which allows for the separation of exchange and spin-orbit asymmetries, has been discussed at some length in the text, and thus need not be dealt with here. On the other hand both the requirements for sample magnetization and stray field reduction will be the focus of discussion here.

The characteristics of a low-energy spin-polarized electron beam work both to the experimenter's advantage and disadvantage in studies of ferromagnetic systems. Because the exchange interaction between electrons in the incident electron beam and ground state electrons in the sample is strong in the energy range of LEED, a spin-polarized electron beam has the potential of being a sensitive probe of sample magnetization near the surface. But because both run-to-run reproducibility and any meaningful comparison with theory (which itself is formulated to align all spins in one direction, studies of surface magnetization by probes such as SLEED are most easily quantifiable when the sample is repeatably and symmetrically magnetizable to saturation in some chosen direction along with its antiparallel direction. All of the following are important characteristics of the sample magnetization: to be able to repeatedly magnetize the sample into a single large domain of constant magnitude and direction, which is symmetric in both opposite directions, and to be able to null any stray magnetic fields that may persist in the experimental region without demagnetizing the sample.

Because low energy electron beams are easily deflected by the presence of magnetic fields, and because the spin-polarization vector of polarized electron beams are rotated away from their nominal direction by the presence of stray magnetic fields, and thus it is important to
eliminate if possible, or reduce at very least, any magnetic fields that
may be found in the experimental region. Great care must be taken to
reduce stray fields especially around the sample itself, which may be a
significant source of stray magnetic flux if the two ends of the
effective magnetic dipole which it creates are not terminated properly
by some type of 'keeper' made of a high permeability material.

The present discussion will focus on the magnetization and
characterization of the Ni(111) sample investigated in the present
study, and will be structured as follows: First there will be a brief
overview of the technique used to characterize the amount and quality of
the sample magnetization, which is called the magneto-optical Kerr
effect (MOKE). Then the Moke measurement of the Ni(111) crystal is
presented. The implications of the hysteresis will be discussed, and
the procedure used for magnetizing the sample and reducing stray
magnetic fields will be outlined. Two tests for stray magnetic fields
around the sample will close the discussion.

Magnets Sample Characterization using MOKE — An Overview: When a beam
of linearly polarized light is reflected from the surface of a
ferromagnetic sample, the reflected beam is elliptically polarized with
the major axis of the ellipse rotated relative to the plane of
polarization of the incident light (i.e. the plane that includes the the
electric field vector and the propagation vector of the linearly
polarized magnetic wave). This effect is the combination of two
magnetization-dependent phenomena, both of which cause changes in the
light polarization that are proportional to the net magnetization of the
sample (but neither of which is affected by an external magnetic
field).200 The first of these phenomena is the rotation of the linear
polarization direction from in the plane of incident polarization to a
plane containing the major axis of the ellipse, and is called the
magneto-optical Kerr effect, or more simply Kerr rotation. The second
phenomenon is the coherent generation of a small component of the
orthogonal linear polarization to that of the incident light, which
leads to the elliptical output beam polarization, and is called
reflectance magneto-circular dichroism (RMCD). These effects are
generally small, but nonzero for any light reflection from a
ferromagnet. The size and relative contribution of the two phenomena is dependent on the energy, and angle of incidence of the light, on the magnetization of the sample, and on the details of the conductivity and polarizability tensors that couple light reflection to the characteristics of the ferromagnet. The physics underlying these effects is described in detail in the literature and a lucid presentation is given by Hart.

Experimental Measurement of the Magneto-Optical Kerr Effect: For our purposes either of these phenomena (MOKE or RMCD) may be thought of as an arbitrary parameter that scales linearly with the net magnetization of the sample, and may thus be used to track the magnetization with changing external magnetic field. By continuously varying the current through magnetizing coils which in turn drives the applied magnetic field through the sample, one can continuously magnetize the sample to saturation in one direction and then in the other. If simultaneous measurements are then taken of both the magnetizing current and the Kerr rotation (which is linearly proportional to the sample magnetization), a hysteresis curve for the sample can be obtained. The method employed to take these measurements uses a photoelastic modulator (also called a piezo-birefringent modulator) and lock-in techniques to obtain the very tiny Kerr-signal, and is based closely on techniques developed by Sato (See Figure D1.)

![Diagram of Magneto-Optical Kerr Effect](image)

**Figure D1. Magneto-Optical Kerr Effect alignment.**

*[After Sato, ref.200, fig.1, p.2403.]*
Although the methods used here are described more fully in Sato's work, several notes on the implementation of Sato's technique are in order:

a) The light path from the laser into the sample and back out should match as nearly as possible normal incidence conditions. Sato's configuration, for example, has the angle ~4°.

b) The alignment used here is set to duplicate that of Sato:
P = linear polarizer
Mo = piezo-birefringent modulator
S = sample
A = analyser (a second linear polarizer)
D = photodetector

c) The alignment of the optical elements is important:

- The first linear polarizer should be aligned so that the polarization direction is tilted at 45° with respect to the plane of scattering (which contains the y-axis) and with respect to the vertical x-axis which is perpendicular to the scattering plane. The z-axis is the light propagation direction.

- The optical axis of the piezo-birefringent modulator should be aligned with either the x-axis or y-axis, and must be at an angle of 45° with respect to the linear polarizer.

- The sample magnetizing axis may be aligned with either the x-axis or y-axis, but not at some arbitrary angle between them.

- The analyser should have a linear polarization in the vertical (x-axis) direction.

d) Because the piezo-birefringent modulator is driven at 50kHz and the magnetic Kerr-rotation signal is picked up at 2f, the Kerr rotation signal should be detected at 100kHz.

e) The amplitude of the modulation of the photoelastic modulator should be such that it retards at most only up to λ/4 retardation. This will sinusoidally cycle the light polarization through lp-rhcp-lp-lhcp-lp, where lp stands for linear polarization and r(l)hcp stands for right(left) hand circular polarization of the light. For a HeNe laser, λ/4 retardation is obtained at a modulation of 371. Driving the photoelastic modulator to higher amplitudes strongly introduces higher harmonics into what before was a purely sinusoidal variation between right-hand and left-hand circularly polarized light. This introduces a spurious signal at 100kHz that severely distorts the measured hysteresis.
**Figure D2.** Hysteresis curves obtained for the Ni(111) sample (solid loop) and the soft iron c-magnet (dotted curve) by MOKE. The curves are described in detail in the text.

**Experimental MOKE from Ni(111):** The Magneto-Optical Kerr Effect signal obtained from our sample is shown in Figure D2, and is superimposed on a comparable signal typical of those from the soft iron C-magnet used to retain flux from the sample in the vacuum chamber. The hysteresis for the Nickel (111) sample magnetized in the [110] direction is shown as a closed solid loop, and the hysteresis for the soft iron C is a dotted curve. The shape of these two hysteresis curves tells us a number of things about the magnetic character of the sample we are to study:

a) First, both curves are symmetric about the origin. This implies that the sample magnetizes symmetrically in both directions.

b) The sample does not start to magnetize, or demagnetize, until at least 3 amps are flowing through the magnetizing coils. (Remember that the sample and manipulator are configured with a 19-turn magnetizing coil.)

c) The sample reaches saturation magnetization $M_s$ at about 9-10 amps, which is equivalent to ~180-190 Gauss.

d) The sample retains magnetization (at least within our experimental accuracy) essentially equal to saturation magnetization after the current is turned off, and even if a current is back-driven through the coils up to ~3 amps. This implies not only that the sample is magnetized primarily in one
large domain, but that that domain remains constant in magnetization direction and magnitude. The 'squareness' of the hysteresis is a good indication of a good 'hard' magnet - ideal for our study.

e) The C-magnet, on the other hand, shows a very 'soft' hysteresis curve. The hysteresis never, even at the highest currents driven, turned over flat, implying that it didn't truly saturate. Further the zero-field 'remanence' magnetization was much smaller than the peak magnetization with driving field. And finally, with only about one amp back-driving current, the magnetization could be driven to zero. There are several implications of this particular form for the iron "C" hysteresis. First, the "C" could retain a much higher magnetic flux than could the sample. And further, that the remanence magnetization in the C-magnet could be driven to zero with rather small demagnetizing currents, small enough not to affect the magnetization in the sample. Another note on the Magneto-Optical Kerr Effect measurements is in order, and that is that the relative vertical scale of the two MOKE hysteresis curves are arbitrarily scaled and that the measured signal from the iron was orders of magnitude larger than from the nickel, due primarily, it is assumed, to the relatively much stronger optical matrix elements in the conductivity and polarizability tensor in iron.

Sample Magnetization Procedure: The sample magnetization characteristics, obtained from the hysteresis curves, indicated that the following procedure could be used to magnetize the sample and then demagnetize the excess magnetic flux from the soft iron C-magnet:

a) Manually ramp the current through the sample magnetizing coils up to 10-12 amps, and then ramp it smoothly back down to zero.

b) Reverse the polarity of the current source and very carefully ramp the current up to between .95 - 1.03 Amps and then return it to zero.

c) When magnetizing in the opposite direction, follow the same procedure, but with each of the current flows in the opposite sense, forward-driving to ten amps and then back-driving to one amp.

The ability to magnetize the sample by this procedure was confirmed by MOKE of the sample, taken out on the benchtop, with simultaneous Hall probe measurements, and confirmed that stray fields in the near-sample region could routinely be reduced to below ~30 milliGauss, although the
precise magnitude or even direction of these small stray fields was
difficult to control.

In addition to the Hall probe measurements, small stray-
field beam steering effects in LEED were a sensitive measure of
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141. S.F. Alvarado, R. Feder, H. Hopster, F. Ciccardi, and H. Pleyer,
    Z.Phys. B49, 129 (1982);
    See also the three references in ref 13.

142. Tamura et.al., ref. 13, p. 5457.

143. ibid. p. 5457.

144. ibid. p. 5457;


146. G. Holzwarth and H.J. Meister, Nucl.Phys. 59, 56-64 (1964)
    and references cited therein;
    H. Boersch, R. Schliepe, and K.E. Schriefl, Nucl.Phys. A1345,
    635-636 (1921).
    N.F. Mott, Proc.Roy.Soc. A124, 425 (1929);
    N.F. Mott, Proc.Roy.Soc. A135, 429 (1932);
    S.R. Lin, N. Sherman, and J.K. Percus, Nucl.Phys. 45, 492 (1963);
    Kessler, ref. 136.


149. The vertical direction for the spin quantization axis is chosen because that is the axis defining the helicity of the laser light photoexciting the electrons in the GaAs crystal. The electrons thus emitted, normally upward, have spin polarization which is longitudinal along the axis of propogation. This axis defines a reference orientation for all further spin-dependent scattering. This choice of spin direction - aesthetically pleasing because it gives "spin-up" and "spin-down" physically relevant meaning - does not, however, follow the standard convention for defining a spin-quantization, (see, for example, S.F. Alvarado, M. Campagna, and H. Hopster, Phys.Rev.Lett. 48(1), 51-54 (1983), discussion p. 51; and Jamison et.al., ref. 7, discussion p. L452.), which defines the spin quantization axis normal perpendicular to the plane of scattering. n = kxx / kxk where k and k are the wave vectors of the incident and scattered electrons, respectively. That choice of quantization axis is not, however, possible here for all of our scattering geometries [for example, the (11) beam] where the scattering plane and spin-polarization are not perpendicular.

150. Pierce et.al., ref. 10.

151. Pierce et.al., ibid., and references cited therein.
D.T. Pierce and F. Meier, Phys.Rev. B13, 5484 (1976);
A.N. Andronov, A.V. Maslevtsov, B.V. Gin, and V.N. Lepeshinskaya, Izvestiya Akademii Nauk SSSR. Seriya Fizicheskaya 40(8), 1627-1632 (1976);
B.J. Stocker, Surf.Sci. 47, 501-513 (1975);
B. Goldstein, Surf.Sci. 47, 143-161 (1975);
T.Luig, M. Rissmann and H. Merz, Solid St. Commun. 58(11), 775-779 (1986) and references cited therein;
An excellent review is given by: W.E. Spicer, Appl.Phys. 12, 115-130 (1977), which also cites much additional work in the field.

152. The presentation here is that of Pierce et.al., ref. 10.


155. ibid., p. 194.

156. See the several references in ref. 15.
    L.R. Bedell and H.E. Farnsworth, Surf.Sci. 51, 165 (1973);

157. R.G. Musket, W. McLean, C.A. Colmenares, D.M. Makowiecki, and
    excellent review of surface cleaning techniques for a wide
    variety of surface systems. The cleaning procedures used
    here are derived from those given in Musket, et.al., p.163-165
    and the references cited therein.

    P.F. Kane and G.B. Larrabee (Plenum, New York 1974), pp. 509-575,
    especially pp. 534-537 and references cited therein.

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    M. Eizenberg and J.M. Blakely, J.Chem.Phys. 71(8), 3467-3477 (1979);
    J.E. Demuth and T.N. Rhodin, Surf.Sci. 45, 249-307 (1974) and
    references cited therein.

160. See references in 157 and 159.

    1460-1474 (1975), and references cited therein.

162. The work functions of all the clean surfaces of the elements may
    be found in: G.A. Haas, in: American Institute of Physics
    New York 1972), ch. 9j pp. 9-172 - 9-180; or in: H.B.
    Michaelson, in: CRC Handbook of Chemistry and Physics,
    E82-E84.
    The values used here for both Cu(001) (i.e. 4.59eV) and Ni(111)
    (i.e. 5.35ev) are taken from Michaelson and references cited therein.

163. R. Feder, Phys.Lett. 78A(1), 103-104 (1980);
    B.I. Dunlap, Solid St.Commun. 35, 141-144 (1980);
and Feder, ref. 12, pp. 2053-2054.

164. Noonan and Davis, ref. 154.

165. See Demuth et al., ref. 161, figure 21, p. 1471; The experimental profiles shown in Demuth et al. were obtained by J.E. Demuth and T.N. Rhodin, Surf.Sci. 42, 261 (1974); and by R.L. Park and H.E. Farnsworth, Surf.Sci. 2, 527 (1964).

166. Jona, ref. 74, p. 4292, gives many of the arguments for and against this visual inspection technique.


168. Van Hove and Koestner, ref. 3.

169. See refs. 2 and 3.

170. See ref. 153.

171. Van Hove, Tong, and Elconin, ref. 3.

172. Davis and Noonan, op.cit. ref 153.

173. Feder, ref. 12, p. 2071; Feder, Pol.El.in Surf.Phys. ref. 13, pp. 179-184, especially p. 181; Although R-factors are begining to be used by Feder and co-workers; See: W. Hosler, W. Moritz, R. Feder, and E. Tamura, "Influence of the Scattering Potential Model on Low-Energy Electron Diffraction from Cu(001) - c(2x2) - Pb" (in press).


175. See ref. 153.
176. See Luig et.al., ref. 151, p. 775, where a negative electron affinity of $\chi_{\text{eff}}$-0.18eV is obtained for a cathode prepared by standard techniques for maximum photoyield. This electron affinity is considered very typical.

177. See discussion, ref. 162.

178. See ref. 176 above.

179. See ref. 10.

180. SAES Getters/USA Inc., 1122 Cheyenne Mountain Blvd., Colorado Springs, CO 80906.

181. Pierce et.al., ref. 10, pp. 483-485.

182. ibid.

183. MACOR is the trade name of Code 9658 Machinable Glass-Ceramic (MCG) made by Corning Glass Works, Corning, New York. This material is an excellent insulator to use in UHV research applications because of its high dielectric strength, low outgassing characteristics, and ease of machinability into a wide variety of useful shapes.


185. Pierce et.al., ref. 10, citation on p. 485.

186. ibid.

187. ibid.

188. See Spicer, ref. 151; and;
D. Conrath, T. Heindorff, A. Hermanni, N. Ludwig, and E. Reichert, Appl.Phys. 20, 155-157 (1979), and references cited therein;

189. Reichert and Zahringer, ibid., p. 191.

190. A.G. Thompson, M. Cordona, and K.L. Shaklee, Phys.Rev. 146, 601-610 (1966);
J.J. Tietjen and J.A. Amik, J. Electrochem. Soc. 113, 724-728 (1966);
A. Onnen, in: Festkorpereprobleme, Advances in Solid State

191. Pierce et.al., ref. 10, p. 483-485.

192. Siemens Allis, Inc.: Measuring Systems Mktg. Div., 100 West Ave. South, Iselin, NJ 08830. The samples studied here were obtained for us through the kind help of Dr. Carl Rau, who obtained the sample used here from the Siemens semiconductor division in Germany.

193. Conrath et.al., ref. 188, p. 155.

194. ibid.

195. S.F. Alvarado, private communication; see also Alvarado, et.al., ref. 149, p. 51.

196. The high crystalline quality of epitaxially grown layers is one of the reasons for the wide increase in the use of MBE in semiconductor fabrication. Pierce et.al., ref. 10, p. 487-488, comments on possible depolarization mechanisms; A comparison of the reported electron beam polarizations from epitaxially grown cathodes and bulk cathodes reported by workers in refs. 151, 188 and 195 indicates a trend toward much larger, beam polarization values for the epitaxially grown cathodes, presumably because of the increased crystalline perfection for these surfaces.

197. Alvarado, Campagna and Hopster, ref. 149, p. 51.

198. See, for example, Jamison et.al., ref. 7.

199. The earlier, higher polarizations reported by Pierce and co-workers in ref. 10, were inferred indirectly from data comparison. When the beam polarization became directly measurable in their apparatus with the addition of a mini-Mott analyzer, polarizations in the 28-29% range were measured.


245-247 (1979);
D.J. Mapps, Contemp.Phys. 19(3), 269-281 (1978);
G.S. Krinchik and V.A. Artem’ev, Sov.Phys.JETP 26(6), 1080-1085 (1968);
G.S. Krinchik and G.M. Nurmukhamedov, Sov.Phys.JETP 21(1), 22-25 (1965);
J.L. Erskine and E.A. Stern, Phys.Rev.Lett. 30(26), 1329-1332 (1973);
B.R. Cooper, Phys.Rev. 139(5), A1504-A1514 (1965);
J. Kranz and Ch. Schrodter, Phys. A (1983);
In addition, much recent work by S.D. Bader and co-workers at Argonne has extended MOKE measurement to the monolayer magnetism regime.

   Much of the discussion of this section follows Hart.

204. Sato, ref. 200.

205. Morvue Photoelastic Modulator, Hinds International,
   P.O. Box 4192, Portland, OR 97208.

206. See Kittel, ref. 19, and;
   Howard, ref. 21.