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A POLARIZED LOW ENERGY ELECTRON DIFFRACTION STUDY OF Cu₃Au(001)

by

KEITH DOUGLAS JAMISON

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

DOCTOR OF PHILOSOPHY

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April 1984
ABSTRACT

A POLARIZED LOW ENERGY DIFFRACTION STUDY OF Cu₃Au(001)

by

Keith Douglas Jamison

The first PLEED measurements of an ordered two component system (Cu₃Au(001)) are reported. Using this data an attempt is made to determine the long range order parameter as a function of the crystal temperature.

A polarized electron source with an electron spin polarization of 27% and delivering a current of 0.3μA to the crystal surface is described in the first section. This source uses photoemission from negative electron affinity GaAs(001) to produce an electron beam whose polarization can be easily modulated without changing other characteristics of the beam by changing the helicity of the photoemission light.

Once operational, the source is used in an attempt to determine the long range order parameter of the (001) face of Cu₃Au. Polarization vs. Energy (P–V) curves were taken at room temperature at a number of angles (Θ) to obtain usable P–V curves for theoretical modeling. Next, P–V curves were measured for the 00 beam at 13 degrees and the 01 beam at normal incidence as a function of temperature. As the crystal was heated through the order–disorder tranition temperature no large change in the P–V curves was noted.
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INTRODUCTION

Polarized Low Energy Electron Diffraction (PLEED) was pioneered in this laboratory with the successful study of a number of surfaces.\textsuperscript{1–4} In the PLEED method used for these studies, an unpolarized electron beam struck the surface, and the polarization of the diffracted beams was measured via Mott scattering.\textsuperscript{1} This method, although successful, is tedious, very time consuming, and not very accurate because of the extremely low efficiency of Mott spin analysis.

Another method of doing the same experiments, that under proper symmetry conditions yields the same results in much less time and with more accuracy, is to have the incident electron beam polarized and measure the change in intensity of the diffracted beams when the polarization of the incident beam is reversed. This method requires a source of polarized electrons having both high spin polarization and intensity and with the polarization direction easily reversible without affecting the beam geometry or trajectory. Until recently no suitable source of polarized electrons existed.

During the past year a GaAs polarized electron source was constructed, modeled after that built by Pierce et al.\textsuperscript{5}, and added to our present PLEED system. This source, based on photoemission from GaAs(001), provides an electron beam at the sample with a polarization of \( \pm 27\% \) at 0.3\( \mu \text{A} \). Also, the direction of the electron spin polarization can be easily reversed without changing any other beam characteristics. In addition, the polarized electron beam can be directed into the Mott analyzer for direct polarization measurement and the original PLEED method can be employed for comparison to verify that
both methods yield the same results. This is the first experimental setup where both PLEED methods can be compared simultaneously using the same crystal.

Since its inception, polarized LEED has proven its usefulness in a number of surface physics experiments. Among these are studies of surface magnetism, surface geometrical structure determination, and investigation of the density of unoccupied states of magnetic materials using Inverse Photoelectron Spectroscopy. One area of interest, that has until now been left unstudied using this spectroscopy, is that of surface order–disorder transformations.

The order–disorder transition in Cu\textsubscript{3}Au is a perfect candidate for a prototype study of these systems. The transformation in the bulk alloy has been thoroughly investigated. The surface transformation has been studied by conventional LEED but not with unambiguous results. Since gold (Au) is a high atomic number (Z) material while copper (Cu) has a relatively low Z, polarization effects arising from spin-orbit interaction in LEED might be expected to be particularly sensitive to the distribution of gold atoms at the surface. The Cu\textsubscript{3}Au system also serves as a prototype for PLEED studies of binary alloys for subsequent theoretical analysis. It is hoped that this data will motivate dynamical LEED calculations on the ordered state of Cu\textsubscript{3}Au, including the effects of spin.

Intensity of the 00 and 01 LEED beams was measured as a function of energy and polarization of the primary beam, for temperatures above and below the bulk transition temperature. Substantial structure was observed in polarization-energy (P–V) profiles for both specular (00)
and (01) beams. Using this data, an attempt is made to determine surface order-disorder transformation behavior by analyzing the polarization profiles as a function of temperature.

This thesis is presented in two parts: The theory, design and operating characteristics of the polarized electron source, and the study of the order-disorder transition of Cu$_2$Au(001).
I. POLARIZED ELECTRON SOURCE

In 1976 Pierce and Meier\textsuperscript{13} demonstrated the feasibility of a high current source of spin polarized electrons based on photoemission from GaAs(110). Later Pierce et. al.\textsuperscript{5} developed this source into a practical polarized electron gun suitable for use in LEED experiments. The theory behind the polarized electron source, and the design and performance characterization of the polarized electron gun built at Rice University, will be presented.

A. Electron Spin Polarized Photoemission

Photoemission of electrons from a semiconductor is a three step process involving photoexcitation from the valence band, transport to the surface, then escape into vacuum. This process for the GaAs photocathode has been described in detail elsewhere;\textsuperscript{5,13} therefore, only a brief description will be given here.

The material property of GaAs that allows the realization of a polarized electron source is the valence band splitting arising as a result of spin-orbit coupling (figure 1). It is known from band structure calculations and experiment\textsuperscript{13} that the valence band maximum and conduction band minimum have $P$ and $S$ type symmetry respectively. At the valence band maximum (Gamma point), the degenerate $P$ band is split by spin orbit coupling into a fourfold degenerate $P_{3/2}$ level and the twofold degenerate $P_{1/2}$ level, which is 0.34 eV lower in energy.\textsuperscript{14} Also GaAs is a direct gap semiconductor, meaning the conduction band minimum
Figure 1. The energy bands of GaAs near the center of the Brillouin zone (Γ point) are shown at the left of the figure. The band gap is 1.52 eV and the spin-orbit splitting of the valence bands is 0.34 eV. On the right, the allowed transitions between $m_j$ sublevels for circularly polarized light, $\sigma^+$ (solid lines) and $\sigma^-$ (dashed lines), are shown. The circled numbers give the relative intensities; thus the $P_{3/2} - S_{1/2}$ transition with one helicity light gives three times as many excited electrons of one spin as of the other spin. Changing the helicity of the light reverses the spin direction of the excited electrons. After Pierce et al. 5
is directly over the valence band maximum. Therefore, by selecting the proper excitation energy, only transitions from states of well defined angular momentum $P$, those from the valence band maximum (Gamma 8,7) to the conduction band minimum, are energetically possible.

The excitation of polarized electrons to the conduction band can be described using the following arguments. The selection rules for transitions using circularly polarized light are

$$\Delta M_j = M_f - M_i = +1 \text{ for right hand circularly polarized light (RHCP)}$$

$$\Delta M_j = M_f - M_i = -1 \text{ for left hand circularly polarized light (LHCP)}$$

By studying figure 1, it can be seen that for RHCP light with $h\nu=Eg$, the allowed transitions are from $M_j=-3/2$ to $M_j=-1/2$ and $M_j=-1/2$ to $M_j=1/2$. The transition from $M_j=-1/2$ to $M_j=1/2$ is not allowed because of energy considerations. The net polarization of electrons excited to the conduction band is given by the relative transition probabilities of the two allowed transitions as shown in figure 1. The maximum theoretical polarization is 50% for both RHCP and LHCP light. With higher energy light, electrons from the remainder of the spin split band (Gamma 7) are excited into the conduction band, bringing the polarization to zero. The maximum polarization is obtained for photon energies less than 0.1eV greater than the minimum band gap energy of 1.58 eV.
With proper surface treatment, photocathodes of high efficiency can be prepared. Specifically, application of cesium and oxygen to the GaAs surface lowers its function below the vacuum level yielding a negative Electron Affinity (NEA) photocathode from which electrons excited into the conduction band can readily escape. Figure 2 shows an energy level diagram of the GaAs surface that has been treated with Cs and O₂ which displays an effective surface NEA. It is clear from the figure that while electrons excited to the bottom of the conduction band at the surface cannot escape, those excited in the bulk and subsequently transported to the surface without significant energy loss can escape.

One important aspect of this type of polarized electron source (PES) that makes it very attractive for many experiments is that the polarization of the electrons excited into the conduction band is easily reversible, simply by changing the helicity of the excitation light, while the intensity and the direction of the emitted electrons are not affected.

The actual polarization and yield of electrons emitted from the surface may be less than the theoretical value of 50% for a number of reasons. Since the incident polarized light penetrates 1 micron into the surface and the electron diffusion length for bulk GaAs is ≈0.5 microns, the emission of electrons is limited by their diffusion length. Depolarization of the electrons may occur in the transport process as a result of spin relaxation in scattering from defects. Also spin exchange scattering with the cesium overlayer may reduce the effective polarization. A more detailed discussion of the various depolarization mechanisms is given in reference 13.
Figure 2. The valence and conduction bands of p-type GaAs bend downwards in energy at the surface. A negative electron affinity (vacuum level lower than the bulk conduction band minimum) is obtained by activation with Cs and O$_2$. Electrons excited across the band gap $E_g$ by photons of energy $h\nu$, thermalize to the conduction band minimum, and diffuse to the surface to escape into the vacuum. Very high quantum yields can be achieved. After Pierce et. al. 5
B. Construction of PES

For a usable polarized electron gun, the polarized electrons must be produced, formed into a well defined and approximately monoenergetic beam, and transported to the target. The transport of the polarized electrons involves designing multiple lens electron optics. Wherever possible the electron optics and light optics used for the Rice polarized electron source are exact duplicates of those used by Pierce et al.\textsuperscript{5}

1. Polarized Electron Source Chamber

The polarized electron source is contained in an independent vacuum chamber made from a commercial 4 inch cross with additional ports cut into it (Figure 3). The chamber is pumped by a 50L/S DI ion pump and has a base pressure of \(1-2\times10^{-10}\) Torr as measured with a nude ion gauge. During crystal activation oxygen can be admitted to the chamber through a leak valve. Cesium is applied to the crystal by means of a SAES Cs dispenser.\textsuperscript{16} Also, a partial pressure analyzer is mounted to the chamber for diagnostic and leak checking purposes.

The GaAs crystal is mounted on the front of a molybdenum can which serves as a crystal holder. The holder is water (or LN\(_2\)) cooled and can be heated to 700°C by electron bombardment using an electrically isolated tungsten filament mounted inside the can. Also, the entire crystal holder is electrically isolated so the crystal can be floated to
Figure 3. Schematic drawing of the polarized electron source. Modulating the handedness of the circular polarized light incident on the GaAs produces a constant-intensity photoelectron beam with modulated spin polarization at the sample surface. The ac component of the intensity of the electron beam scattered from the sample to the Faraday cup measures the spin-dependent scattering.
accelerate the photoelectrons. The mount in turn is attached to an XYZT crystal manipulator. This manipulator is used to position the crystal below the spherical mirror analyzer (SMA) for polarized electron emission and to retract the crystal for Cs–O activation (Figure 3). The crystal temperature is measured with a chromel–alumel thermocouple spotwelded to the tab that retains the GaAs crystal.

The light optics are mounted on a vertical axis above the PES chamber. Laser light enters through a 2.75 inch viewport above the spherical mirror analyzer and illuminates the crystal through a hole in the spherical mirror analyzer as indicated in figure 4. A 2.75 inch viewport is also mounted below the SMA to aid in optical alignment of the laser beam. During activation, the crystal is in the retracted position where white light can enter through a 1.33 inch viewport shown in figure 3.

An improvement over the original PES design of Pierce et. al. is that all of the electron optics are mounted on two flanges to minimize alignment problems. The electron optics in the source chamber are mounted on the 6 inch flange that is part of the isolation valve and the electron optics in the LEED chamber are mounted on a 2.75 inch flange at the base of the LEED apparatus. The two sets of optics are connected together by a sliding lens. This lens slides through the isolation valve when it is open and can be retracted to shut the valve.
Figure 4. A detailed schematic of the electron optics from the photocathode to the target showing the beam envelope calculated by Pierce et. al. The upper part of the figure can be considered the 'source' and takes electrons up to the isolation valve. The lower part of the figure which follows the valve consists of the LEED gun and the lenses which focus the beam to the 0.5-mm aperture at the entrance of the LEED gun.
2. Light Optics

Electrons are photoemitted from GaAs(100) using light from a commercial GeAlAs laser (Figure 3). The photodiode laser operates at 790nm and the emitted light is formed into a parallel beam by a 52mm aspheric lens. The beam is then collimated and linearly polarized. Next the laser light goes through a Pockels cell and is focused onto the GaAs crystal. A Pockels cell is an electrooptic device that induces birefringence proportional to the voltage applied to it. Linearly polarized light, whose electric field vector is oriented along an axis 45 degrees to either axis of the Pockels cell, can be changed to RHCP or LHCP light by applying an appropriate voltage to the Pockels cell. Modulating the polarization of the laser light in this way allows the direction of the polarization of the photoemitted electrons to be modulated from RHCP to LHCP electronically; therefore lockin techniques can be used to measure small spin dependent effects.

3. Electron optics

When the circularly polarized light of the proper energy strikes the NEA GaAs crystal surface, polarized electrons are emitted. The light that strikes the crystal is focused to a small spot and the electrons are emitted in a 5-15 degree cone in the direction of the light normal to the surface. These electrons are then accelerated to 250 volts, aperture and sent into a spherical mirror analyzer (SMA) (Figure 4). The SMA has two purposes. First, it changes the
polarization direction of the electrons from parallel to their momentum (longitudinal) to perpendicular (transverse). Second it moves the electrons out of the path of the incoming light. The spherical mirror analyzer is tuned for a 250 eV pass energy.

Once the electrons exit the SMA they pass through a series of steering plates to correct for misalignments and then are accelerated to 1000 eV where they form a parallel beam. The optics just described form the GaAs part of the source. At this point the electrons pass through an isolation valve and into the LEED electron gun.

Once in the LEED electron gun optics, the electrons are decelerated and focused through a 0.5 mm aperture shown in figure 4. This aperture simulates the point source of the filament that usually is employed. From this aperture the electron beam can be restereed, sent through the last two lens elements and then to the sample crystal.

The electron optics were designed so all lens elements in the region from the cathode to the 0.5mm aperture of the LEED gun are kept at a constant potential relative to the GaAs photocathode. Therefore, when the energy of the cathode is changed only the potentials of the last two lens elements and last set of steering plates are varied relative to the cathode potential. The ratio of these lenses was chosen to be a constant 2:1.5
C. Operation of the Polarized Electron Source

Detailed below is the crystal cleaning, activation, and operation procedures for the GaAs polarized electron source. These procedures are not necessarily optimal but they have served up to now. A systematic study of the procedures to optimize them would be useful.

1. Cleaning the GaAs Crystal

Polished GaAs(100) crystals were purchased from Laser Diode Laboratories. The GaAs was p doped with $1.0-2.0 \times 10^{19}$ cm$^{-3}$ to allow NEA. The crystals are cut to fit in the crystal holder (0.5x0.5cm) and then cleaned in a two step process before activation.

The first cleaning step is a chemical etch before insertion into the vacuum chamber. This etch is necessary for crystals grown in the bulk to remove carbon introduced during growth, which has been shown to be the main surface contaminant. First the crystal is degreased in a combination of trichloroethylene and methanol baths. After that, it is put into a solution of $H_2SO_4:H_2O_2:H_2O$ for etching; then into a base solution to passivate the surface until it can be put into vacuum. The detailed cleaning procedure used is outlined in appendix 1 of reference 5.

After chemical cleaning, the crystal is placed immediately into the vacuum chamber. To achieve the UHV conditions the chamber must be first baked at 175°C for 30 hours. During this time the crystal is held at 300°C to prevent contaminants from condensing on the crystal. After
bakeout, the chamber has a base pressure in the low \(10^{-10}\) Torr range. At this point additional cleaning under vacuum is performed by heating the crystal to 640\(^\circ\)C (GaAs(100) melts at 660\(^\circ\)C) where the Ga and As evaporate congruently, removing any contaminants in the first few layers. The procedure used most often is to heat the crystal to 630\(^\circ\)C for 5 minutes then to 640\(^\circ\)C for approximately 2 additional minutes. The exact crystal temperature is not known since the thermocouple is not directly attached to the crystal. The procedure used is to attempt activation at progressively higher temperatures until the crystal activates (or melts). Argon ion bombardment has also been found to clean the GaAs surface but it decreases the photoemission sensitivity, hence is avoided.\(^20\)

2. Activation

After the heat cleaning, the GaAs crystal is cooled rapidly to 30\(^\circ\)C for activation. Rapid cooling is accomplished by flowing liquid nitrogen through the cooling lines for 2 minutes. The crystal reaches 30\(^\circ\)C in less than 10 minutes.

Activation is done with the crystal in the retracted position. A beam of white light from a tensor lamp illuminates the crystal to photoemit electrons. The first aperture is biased to +150 volts to collect the electrons thus providing a measure of the current leaving the crystal.
To activate the GaAs, cesium is first evaporated onto the crystal surface. In 3-20 minutes, a photocurrent is detected. Cesium application is continued until a photocurrent maximum is reached (0.12μA for our lamp). The current is then allowed to drop to 70% of its maximum value. At this point, oxygen is applied along with the cesium (Figure 5). The oxygen and cesium continue to be applied simultaneously, adjusting the oxygen flow so a maximum rise in photocurrent is obtained. When the current will not rise further regardless of the combination of cesium and oxygen, both are turned off and the photocathode is ready for use. The maximum photocurrent is approximately 2-3μA using a tensor lamp as the source of photons. With a properly activated photocathode, an emission current of 20μA should be achieved with 1mW of 790nm laser light. Also, this current typically decays with a half life of about 6 hours on a freshly activated crystal. The current can be peaked up with the application of more cesium. An activation usually lasts a week but with continued cesium 'peak ups' the photocurrent drops more rapidly.

Attempts were made to measure the quantum yield curves of the GaAs crystal to determine whether the characteristic knee of NEA photocathodes was obtained. Unfortunately, there is still controversy as to what actually constitutes NEA. The results obtained were mixed and will not be presented here. Although a quantum yield of 3% at 790nm was routinely obtained, electron spin polarizations of around 27% were always measured regardless of quantum yield therefore quantum yield studies were discontinued in favor of doing the experiment with an electron spin polarization of 27%.
Figure 5. Typical activation curve for GaAs using a white light source.
After activation, the crystal is moved into place below the SMA, where a beam of polarized electrons is photoemitted using laser light. The electrons are brought through the sphere and eventually strike the 0.5mm aperture shown in figure 4. At this point the beam is maximized using the steering plates. An electrometer is used to measure the current. When the current is maximized the electrometer is placed on the other side of the aperture where the transmitted current can be read and maximized. Next, the last set of steering plates is used to direct the beam through the final apertures and to the crystal where the beam current is again maximized. A total transmission of 3-5% through the optics is routinely obtained.

This procedure is usually done at an arbitrary beam energy of 90eV. In practice, this means the maximum transmission is at 90 volts with the transmitted current falling off above and below this energy. Other energies can be maximized but the transmission is not constant with energy and falls off rapidly below 50eV.
II. LEED THEORY

There are many excellent review articles and books covering dynamical LEED theories. The LEED theory section of this thesis will not attempt to give a comprehensive overview of LEED theory but rather a brief description of how diffraction occurs and a summation of the theories used to model this effect.

It can be determined from the deBroglie relationship

$$\lambda(A) = (150/E(\text{eV}))^{1/2}$$ (1)

that low energy electrons ($\sim 5 - 200$ eV) have wavelengths of 1 to 5 angstroms which, like x-rays, are on the order of the lattice spacings of most crystals. Therefore, low energy electrons elastically scattered from a single crystal should form diffraction patterns similar to those found in X-ray diffraction. Unfortunately, the characteristics of the diffraction patterns are not the same, the difference arising because there is a strong interaction between the electron and the crystal lattice which is absent with X-rays.

In general, LEED theories assume an incident plane wave with a given wavevector $\vec{k}$ is incident on a single crystal surface which is ideally flat and infinite in extent. Thus, the atomic structure of the surface is perfectly periodic in two dimensions, and the crystal is assumed to fill the half space behind the surface. The solution in vacuum half-space is a superposition of the incident wave with the diffracted waves including the effects of damping. A wave matching procedure uses a model of the transition region between the vacuum and
the bulk crystal to connect the vacuum solution to the crystal solution continuously.

Described below is the kinematic LEED theory which assumes only single scattering and dynamical LEED theory which takes into account multiple scattering of the electrons. These theories address how the electrons interact with the lattice to predict the backscattered intensities of the electrons.

A. Kinematic LEED Theory

In kinematic LEED theory, electron diffraction is described in terms of a modified version of classical X-ray diffraction theory. When electrons or X-rays are incident on the crystal surface, the waves elastically scattered from the surface atoms interfere with each other forming a diffraction pattern. This is known as Bragg diffraction and gives rise to the Laue equations\(^{27}\) that determine the energies and directions for which elastic scattering occurs

\[ \hat{a} \cdot \Delta \hat{K} = 2\pi h, \quad \hat{b} \cdot \Delta \hat{K} = 2\pi m, \quad \hat{c} \cdot \Delta \hat{K} = 2\pi n \]

(2)

where \(\hat{a}, \hat{b}, \hat{c}\) are the lattice basis vectors, \(\Delta \hat{K}\) is the change of the wave vector due to scattering, and \(h, m, n\) are integers.

Kinematic LEED theory assumes that only the incident wave produces diffracted waves while the re-diffraction of the diffracted waves (multiple scattering) is neglected. Multiple scattering is suppressed in the theory by incorporating a large absorption term in the crystal
potential. This effectively inhibits multiple scattering by not letting the different layers in the lattice interact with each other. This restriction, in addition to the small penetration of the electrons into the crystal, leads to a relaxation of one of the Laue equations.

Assuming \( \mathbf{a} \) and \( \mathbf{b} \) are the basis vectors of the surface and \( \mathbf{c} \) defines the interlayer spacing (Figure 6), then the conditions \( \mathbf{a} \cdot \mathbf{A} = 2\pi \mathbf{n} \) and \( \mathbf{b} \cdot \mathbf{A} = 2\pi \mathbf{n} \) hold strictly, defining the diffraction pattern. The third Laue condition \( \mathbf{c} \cdot \mathbf{A} = 2\pi \mathbf{n} \) does not hold strictly; therefore electrons emerge from the surface in energy regions instead of at discrete energies. These energy regions become narrower as the depth of penetration becomes deeper (higher energies); i.e. more layers interact, therefore increasing the rigidity of the third Laue condition. The maxima in the diffracted beam intensity that exist when the third Laue condition holds are called Bragg peaks of order \( n \). (Figure 7)

Although kinematic theory predicts spot locations accurately, it does not generally predict the energy dependence of beam intensities well except in the few cases where there is little multiple scattering. The failure of this theory is caused by not taking into account multiple scattering which is responsible for most of the structure in LEED intensity spectra.

B. Dynamical LEED Theory

The formation of the additional Bragg peaks not predicted by kinematic theory can be understood using the following argument. If \( \mathbf{k} \) is the direction of the primary beam which is scattered in a 3-D
Figure 6. In kinematic theory, intensity maxima occur through constructive interference between waves scattered from consecutive layers of atoms. A wave with wavevector \( \mathbf{k} \) is incident on the crystal while the elastically scattered wave has wavevector \( \mathbf{k}' \). If \( \mathbf{c} \) is the relative displacement of the layers and \( \mathbf{a} \) and \( \mathbf{b} \) are the lattice vectors of the surface, the Laue equations for constructive interference are: 
\[ \mathbf{a} \cdot \Delta \mathbf{k} = 2\pi n, \quad \mathbf{b} \cdot \Delta \mathbf{k} = 2\pi m, \quad \mathbf{c} \cdot \Delta \mathbf{k} = 2\pi n. \]
Figure 7. Intensity vs. voltage curve for the 00 beam of Ni(001). The diffracted intensity is divided by the intensity of the incident beams and the positions of the Bragg peaks predicted by Kinematic theory are shown by arrows. 33
periodic crystal, then the interference will take place in the
directions $\vec{k}'$ which obey the condition

$$\vec{k}_{0} - \vec{k}' = \lambda \vec{g}$$  \hspace{1cm} (3)

In this case $\vec{g}$ represents a reciprocal lattice point, since the third
Laue condition must also be satisfied. The scattered beam $\vec{k}'$ is now
able to interfere for a second time in a new direction $\vec{k}$ before it
leaves the crystal. If

$$\vec{k}' - \vec{k} = \lambda \vec{g}$$  \hspace{1cm} (4)

the directions of the backscattered beams are then given by the new
direction $\vec{k}$. An example of this for the 00 beam is shown in figure 8.

The effects described above can be incorporated in multiple
scattering model calculations. Described below is an overview of how
multiple scattering is incorporated into LEED theory. This overview
will follow closely a clear review on the subject given by Pendry.\textsuperscript{28}

This LEED theory approach is known as the layer method and was
first introduced by Kambe\textsuperscript{22} and McRae.\textsuperscript{23} In this approach the solid is
divided into layers parallel to the surface, where the first step of the
calculation is finding the reflectivity of a single layer. The plane
wave incident on the layer is represented by,

$$\exp(i\vec{k}^+ \cdot \vec{r})$$  \hspace{1cm} (5)

where $\vec{k}^+ = \vec{k}_{//}$ and $\vec{k}^z = + (2E - 2iV_{oi} - |\vec{k}^+|^2)^{1/2}$ and $E$ is the energy of the
Figure 8. Diagram illustrating the formation of the specular beam a) by single diffraction (kinematic) and b) by multiple diffraction.\textsuperscript{33}
wave in Hartrees, \( \hat{k}_{//} \) is the momentum parallel to the surface which effectively defines the angle of incidence together with the energy and \( V_{oi} \) is the inverse lifetime of the electron, measured in Hartrees, due to decay through plasmon or Auger excitation processes. The plane wave can be decomposed into spherical waves centered on some atom arbitrarily chosen as the origin. This can be written as

\[
\exp(i\hat{k}_{/}r) = \sum_{\ell m} A_{\ell m}^0 Y_{\ell}(|\vec{K}|r) Y_{\ell m}(\hat{r})
\]

(6)

where \( Y \) are spherical harmonics, \( J_{\ell} \) are Bessel functions and

\[
A_{\ell m} = 4\pi i^{\ell} (-1)^m Y_{\ell - m}(\hat{K}).
\]

(7)

The potential of the atom will scatter these spherical waves to give

\[
\sum_{\ell m} t_{\ell m, \ell' m'} A_{\ell' m'} Y_{\ell' m'}(|\vec{K}|r) Y_{\ell m}(\hat{r})
\]

\[
t_{\ell m, \ell' m'} = \delta_{\ell \ell'} \delta_{m m'} \exp(i\delta_{\ell}) \sin(\delta_{\ell})
\]

(8)

(9)

where \( \delta_{\ell} \) are the phase shifts determined from the atomic potential. Inaccuracies in the atomic potential limit the accuracy of the calculations.

Each atom also receives additional incident waves due to scattered waves off their neighbors. The total wave field scattered from the origin atom is given by

\[
\sum_{\ell m} t_{\ell m, \ell' m'} A_{\ell' m'} Y_{\ell' m'}(|\vec{K}|r) Y_{\ell m}(\hat{r})
\]

(10)
with \( h_{\chi} \) a Hankel function of the first kind and

\[
A_{\chi m} = A_{\chi m}^{(\text{scatt})} + A_{\chi m}^{(0)}
\]  

(11)

\( A_{\chi m}^{(\text{scatt})} \) is the scattered wave from other atoms incident on the atom at the origin and is given by the expression

\[
A_{\chi m}^{(\text{scatt})} = \sum_{m', L'} H_{\chi}^{m m'} t_{\chi}^{m'} y_{\chi}^{L L'} A_{L L'}^{m m'}
\]  

(12)

where

\[
H_{\chi}^{m m'} = \sum_{\ell \ell'} 4\pi (-1)^{1/2} (\ell - \ell' - \ell'') (-1)^{(m' + m'')} h_{\chi}^{\ell} (|R| R) y_{\chi}^{\ell', -m'} (|\hat{R}| \hat{R})
\]  

\( x \exp (i \hat{R} / |\hat{R}|) / y_{\chi}^{L L'} (|\tilde{R}| \tilde{R}) y_{\chi}^{\ell, m'} (|\Omega| \Omega) y_{\chi}^{\ell', m'} (|\Omega| \Omega) d\Omega
\]  

(13)

The coordinates of other atoms within the layer are given by \( \hat{R}_j \) and for simplicity it is assumed that each layer is a Bravais lattice. Having obtained the scattered waves in the spherical wave representation, the expression can be transformed into the plane wave representation and the reflectivity matrix thereby obtained.\(^{28}\) In the scattering process the symmetry of layers changes \( \tilde{\chi} \) to discrete units, \( \tilde{g} \). Therefore the forward and backscattered matrices can be defined as

\[
M_{\tilde{g} \tilde{g}} = 8\pi^2 \frac{i}{|K| \tilde{g} \tilde{g}^+} \sum_{\ell \ell' m' L M} [i^0 y_{\ell m} (K^+) i^0 t_{\ell} y_{\ell'}^{m'} L M (1 - H t) y_{\ell m}^{-1} [i^0 (-1)^m y_{\ell m}^{L M} (\tilde{K}_g^+)]
\]  

(14)
\[
\tilde{q}_G = \left[ \pm (2E-2iV_{\text{oi}}) \frac{r}{|\tilde{K}_{/+G}|^2} \right]^{1/2} \tilde{K}_{/+G}.
\]

In the above equation, the reflection coefficients are referred to an origin with respect to the center of a layer. Often, a more convenient method is to define two separate origins, one on each side of the layer then refer the reflected wave to the origin on its own side of the layer. New origins half way between the layers are defined which are taken to have a spacing \(c\). The reflectivities and transmissivities of the layer are now defined by

\[
Q_{EE}^{++} = (\delta_{EE} + M_{EE}^-) \exp[i(\tilde{K}_{E}^+ + \tilde{K}_{E}^-)c/2]
\]

\[
Q_{EE}^{+-} = M_{EE}^+ \exp[i(-\tilde{K}_{E}^+ + \tilde{K}_{E}^-)c/2]
\]

\[
Q_{EE}^{-+} = M_{EE}^+ \exp[i(\tilde{K}_{E}^+ - \tilde{K}_{E}^-)c/2]
\]

\[
Q_{EE}^{--} = (\delta_{EE} - M_{EE}^+) \exp[i(\tilde{K}_{E}^+ - \tilde{K}_{E}^-)c/2]
\]

Having obtained reflectivities for the layers individually, it is easy to stack the layers together; for example, the reflectivity of a pair of layers is given in terms of the single layer reflectivity by

\[
Q^{++}_2 = Q^{++}(I-Q^{+-}Q^{-+})^{-1}Q^{++}
\]

\[
Q^{+\pm}_2 = Q^{-+}Q^{+-}Q^{-+}(I-Q^{+-}Q^{-+})^{-1}Q^{++}
\]
\[ Q_2^{+-} = Q^{-+} + Q^{-+} (I - Q^{-+} Q^{+-})^{-1} Q^{+-} \]  \hspace{1cm} (22)

\[ Q_2^{--} = Q^{--} (I - Q^{-+} Q^{+-})^{-1} Q^{--} \]  \hspace{1cm} (23)

and in this way the layers continue to add to the thickness of the composite layer until, after about eight layers, the reflectivity of an infinitely thick surface is reproduced.

Using the theory outlined above and including something like 5 phase shifts and some 20 diffracted beams in an energy range of 0–100 eV, very good reproduction of experimental data have been obtained.\(^2\)

The surface structure is determined by a trial and error method. Many calculations are made for slightly different, physically plausible surface structures then each one is compared to experimental results. The set of assumptions that consistently leads to a 'best fit' with experimental results is then assumed to have the correct parameters such as surface layer contraction, and position and orientation of adsorbates. At the moment the basic limitation of the calculations is the accuracy of the atomic potential used. Figure 9 shows an example of the fit obtainable between theory and experiment.

C. Electron Spin Polarization

The LEED theories described in the last section analyze the intensities of the diffracted beams but totally ignore an equally important aspect, the electron spin polarization. The basic theory of
Figure 9. Comparison of theoretical and experimental LEED spectra taken at normal incidence for a C(2x2)Na/c(2x2)S/Ni(001) surface structure: (a) 00 beam; (b) 1/2 1/2 beam; (c) 10 beam; (d) 11 beam. From Pendry.\textsuperscript{28}
spin polarization in atomic scattering and how the electron spin polarization can be determined (Mott scattering) will be discussed first. A discussion of polarization effects in LEED follows that.

1. Spin Polarization from Atomic Scattering

The orientation of the electron spin can effect how an electron is scattered. This is illustrated in figure 10, which shows electrons scattered to the left and right by a positive charge. In the rest frame of the electrons, the current represented by the moving charges produces a magnetic field \( \vec{B} = \vec{E} \times \vec{v}/c \) which interacts with the magnetic moment \( \vec{\mu} \) of the electron giving rise to a spin-orbit interaction \( (\vec{\mu} \cdot \vec{B}) \) term in the Hamiltonian. As a result, the scattering potential will be higher or lower depending on the relative orientation of the magnetic field \( \vec{B} \) to the electronic moment (figure 10). The gradient of the scattering potential constitutes an additional force on the electron that changes the deflection of the electrons to that illustrated by the dashed lines in Figure 10. For an unpolarized incident beam the number of spin down and spin up electrons scattered in a particular \( \theta \) direction will therefore, in general, be different resulting in non-zero polarization in the scattered beam. Since the number of electrons scattered at angle \( \theta \) is proportional to the differential scattering cross-section, the polarization can be written

\[
P = \frac{N^+ - N^-}{N^+ + N^-} \tag{24}
\]
Figure 10. Above: The scattering of electrons in a central electric field illustrate the various effects that arise. Below: An atomic potential. The dotted lines illustrate how the potential is modified when spin-orbit coupling is added to the potential. From Kessler.30
Conversely, for an initially polarized electron beam, the total number of electrons scattered into a given angle will be dependent on the incident beam polarization. The effective scattering asymmetry between beams of opposite polarization scattered into an angle $\theta$ is given by the asymmetry parameter

$$A = \frac{N^+ - N^-}{P_o (N^+ + N^-)}$$  \hspace{1cm} (25)$$

where $P_o$ is the polarization of the incident beam and $N^+$ and $N^-$ are the number of electrons scattered into an angle $\theta$ for either a spin up or spin down incident beam.

The differential cross sections used in the equation 20 can be found by solving the Dirac equation. This is done by analogy with non-relativistic scattering theory. The procedure is described in many texts; therefore only the results will be presented here.

The solutions to the Dirac equation, have the form:

$$\frac{d\sigma}{d\Omega} = (|\mathbf{f}|^2 + |\mathbf{g}|^2) (1 + i \frac{\mathbf{g}^* \cdot \mathbf{\mathbf{\hat{n}}} - \mathbf{f}^* \cdot \mathbf{\mathbf{\hat{n}}}}{2})$$  \hspace{1cm} (26)$$

with

$$f(\theta) = \frac{1}{2iK} \sum_{l=0}^{l+1} \left( \exp \left( 2i\delta_{l,-1} \right) + \mathbf{l} \exp \left( 2i\delta_{l,-1} \right) - 1 \right) P_\mathbf{l} \left( \cos \theta \right)$$  \hspace{1cm} (27)$$

and

$$g(\theta) = \frac{1}{2iK} \sum_{l=0}^{l+1} \left[ \exp \left( 2i\delta_{l,-1} \right) - \exp \left( 2i\delta_{l,-1} \right) \right] P_\mathbf{l} \left( \cos \theta \right)$$  \hspace{1cm} (28)$$
Where \( P \) are Legendre polynomials. This can be rewritten

\[
\frac{d\sigma}{d\Omega} = (|f|^2 + |g|^2)(1 + S(E, \theta) \hat{P} \cdot \hat{n})
\]  

(29)

with \( P \) the initial polarization of the beam and the Sherman function \( S(E, \theta) \) defined as

\[
S(E, \theta) = \frac{i(fg^* - f^*g)}{|f|^2 + |g|^2}
\]  

(30)

For an initially unpolarized beam, the polarizations of the scattered beam can be shown to be:

\[
\hat{P} = i \frac{fg^* - f^*g}{|f|^2 + |g|^2} \hat{n}
\]  

(31)

or

\[
\hat{P} = S(E, \theta) \hat{n}
\]  

(32)

where \( \hat{P} \) = polarization of the scattered beam and \( \hat{n} \) is the normal to the beam direction.
2. Mott Scattering

One of the useful features of our experimental apparatus is the ability to directly measure the electron spin polarization of the source beam. This is accomplished using an experimental technique called Mott scattering.\(^{31}\) The theory described above gives the general framework for the Mott scattering effect which is further developed below.

The component of the electron spin polarization transverse to the beam is measured by scattering from gold nuclei at high energy (\(\sim 100\text{KeV}\)). As noted above, for a polarized beam the spin-orbit interaction gives rise to a left-right scattering asymmetry from the gold target, and its measurement is used to determine beam polarization. The electron beam is accelerated to high energies in order to assure that the scattering is from the bare target nucleus, with negligible perturbation by the surrounding electron cloud. The method is based on theoretical predictions by Mott.

To determine the polarization, equation 29 is used. The Sherman function \(S(E,\theta)\) has been accurately calculated for zero target thickness. Multiple scattering in the real gold foil target reduces the scattering asymmetry but an effective Sherman function can be determined for a given target thickness.\(^{31}\) Therefore the polarization is determined by measuring the scattering asymmetry. Because \(n\) has opposite sign for the left detector and the right detector in the scattering asymmetry measurement, equation 29 can be rewritten in terms of the scattering asymmetry.
\( \frac{N_L}{N_R} = \frac{1 + \text{SP}}{1 - \text{SP}} \)  

(33)

thus lending to easy polarization determination from the measured scattering asymmetry once an effective Sherman function is known.

3. Polarized LEED

Until recently, the effects of spin–orbit coupling had not been included in LEED calculations. But especially with higher Z materials it has been shown that relativistic effects do influence the LEED I-V curves and also cause the diffracted beams to become polarized.\(^1\)\(^,\)\(^3\)\(^2\) To incorporate this into LEED theory, the spin orbit term in the Hamiltonian must be considered.

\[ V_{so} = \frac{1}{2c^2r^2} \frac{dV}{dr} \hat{L} \cdot \hat{S} = \frac{\sigma(\alpha+1/2,\beta+1/2)}{2c^2r^2} \frac{dV}{dr} \]  

(34)

With the addition of this term, spin polarization of the LEED beams can be calculated. This effect was first experimentally verified in this laboratory by measuring the polarization of the diffracted beams from tungsten.\(^1\)

Because of spin–orbit coupling, a single phase shift for each orbital angular momentum is not sufficient, and the quantum number \( j \) (total angular momentum) must be considered through the equation

\[ \hat{L} \cdot \hat{S} = \frac{(J^2-L^2-S^2)}{2} \]  

(35)
which defines the value of $\mathbf{L} \cdot \mathbf{S}$. The quantum number $j$ can take the value of $\pm 1/2$ and therefore for each value of $j$ there are two phase shifts $\delta_{\mp \ell}$ according to whether the spin is parallel or antiparallel to the orbital angular momentum. Unfortunately $j$ is not the quantum number with which the electron is supplied to the crystal. This is more likely to be $s$, the orientation of the spin (for example, with respect to the surface normal). The scattering matrix transformation for the atom in the $j$ representation is

$$t_{\ell m j', m', s} = \delta_{\ell L'}, \delta_{j J'}, \delta_{s s'} \sin(\delta_{\ell}) \exp(i\delta_{\ell})$$

into a representation in which $s$ is a good quantum number. This is done as follows:

$$t_{\ell m s, L'M's'} = \sum_{LMJ} U_{\ell m s LMJ} t_{LMJ L'M'J'} U_{L'M'J' s'}$$

where

$$U_{\ell m s, LM=0} = 0$$

unless $\ell = \ell_0$, $M = m + s$, $J = \pm 1/2$. Otherwise,

$$U_{\ell (m-1/2), 1/2, \ell, m, (\ell+1/2)} = (\frac{\ell + M + 1/2}{2\ell + 1})^{1/2}$$

$$U_{\ell (m+1/2), 1/2, \ell, m, (\ell+1/2)} = (\frac{\ell - M + 1/2}{2\ell + 1})^{1/2}$$
\[
U_{\chi(m-1/2),-1/2,\chi,m,(-1/2)} = \left(\frac{\xi-M+1/2}{2\xi+1}\right)^{1/2}
\]

\[
U_{\chi(m+1/2),-1/2,\chi,m,(1/2)} = \left(\frac{\xi+M+1/2}{2\xi+1}\right)^{1/2}
\]

Note that the spin-orbit coupling has introduced spin flip terms which are not present in the non-relativistic theory.

In equation 9 for the amplitudes of waves incident on the atom at the origin which have been scattered from other atoms, the spin quantum numbers must be added to the orbital quantum numbers to define the electron state, so the amplitudes become

\[
A_{\chi}^{\text{scatt}} = \sum_{\chi' m' s'} H_{\chi' m' s'} A_{\chi m s} L M s L M s'.
\]

Propagation of the spin-up or spin-down scattered waves from one atom to the next is not affected by relativistic considerations. The final formula for the spin-dependent scattering matrices is

\[
M_{gg} = \frac{8\pi i}{g} \left[ K^{-1}_{g} A K^{+}_{g} \right] \sum_{\chi' m' s' L M s} \chi' m' s' L M s (1-Z)^{-1} L M s, \xi L M s [i (-1)^{m} \xi m^{-1} (K_{g})]
\]

where

\[
Z_{LM s}, m = H_{LM, m} m^{*} m^{*}, m s.
\]

It can thus be seen that the theoretical computer programs can be easily modified to take into account relativistic effects with the main
calculational difference being the doubling of the matrix size which significantly increases the computation time.

D. Thermal Effects

When the temperature of a sample crystal is raised, two consequences are apparent in the I-V curves. First, the intensity of the diffracted beams decreases and the intensity of the background between the diffraction spots increases although the total scattered flux remains about the same.

Plotting the logarithm of the diffracted intensity at an intensity peak as a function of temperature usually results in a straight line with the slope dependent on the electron energy. In the simplest approximation, this effect can be described by a kinematic theory where the intensities of the diffracted beams are attenuated by the Debye-Waller factor, $\exp(-2W)$ where

$$2W = \frac{12h^2 (\cos \phi)^2 T}{mk_b \lambda^2 \Theta_d}$$

(44)

with $m$ the mass of the atoms, $k_b$ the Boltzmann's constant, and $\phi$ the scattering angle of electrons of wavelength $\lambda$. $\Theta_d$ is the characteristic Debye temperature. While it is true that the kinematic approximation does not work well for LEED intensity predictions, the Debye-Waller factor does do well in most cases predicting the intensities as a function of temperature even for those diffraction peaks not accounted for by kinematic LEED theory.
As previously mentioned, not only do the intensities of the diffracted beams decrease as a function of temperature, but the background between the beams increases with increasing temperature due to thermal diffuse scattering. Thermal diffuse scattering is caused by the incident electrons interacting with the crystal lattice creating and destroying phonons.\textsuperscript{34} These interactions can change the direction of the electron scattering taking the electrons out of the LEED beams but with energy loss of only a few meV; therefore these electrons cannot be experimentally distinguished from true elastic electrons. The probability of these electron-phonon interactions occurring increases with temperature according to the Boltzmann factor. Basically the diffracted electrons can be divided into three categories: a) The zero-phonon portion corresponding to the electrons which have been scattered purely elastically; b) The one-phonon part, arising from electrons which have been scattered once by a phonon; c) The multi-phonon part comprising all electrons which have interacted with more than one phonon. Figure 11 shows the proportions of these effects as a function of the Debye-Waller exponent.

The effect of crystal temperature in PLEED is not as well studied or modeled theoretically. There have been attempts to predict the effect of temperature on the polarizations of diffracted LEED beams using the multiple scattering theory of Feder\textsuperscript{32} but, unlike LEED intensity spectra, there is no simple kinematic approximation that gives accurate predictions. In fact, the kinematic approximation for PLEED predicts the polarization to be independent of temperature.\textsuperscript{32}
Figure 11. Distributions of back-scattered 'quasielastic' electrons into zero-phonon, one-phonon and multi phonon parts, depending on the Debye-Waller factor $2W$. After Lagailly and Webb.\textsuperscript{34}
Feder states that in multiple scattering theory the polarization of the diffracted beams will decrease or increase with increasing temperature depending on the primary beam energy, the diffraction geometry and the diffracted beam under consideration. This seems possible since the increasing temperature modifies the weights of the spin-dependent higher order contribution of the scattering amplitudes relative to each other and the first order (kinematic) contribution. Larger thermal lattice vibrations reduce the atomic scattering amplitudes and thereby the amplitudes of atoms further down the multiple scattering path. Higher-order scattering amplitudes thus are reduced more strongly than the single-scattering amplitudes. Polarization features which are due to multiple scattering will thus be modified and the high temperature limit should be kinematic. The effects can be measured experimentally provided that the thermal diffuse scattering is eliminated from the experimental data.

There have been some experimental studies of the polarization dependence of LEED beams on temperature. These studies show that the polarization features shift slightly with temperature and the magnitude of these features can either increase or decrease with temperature. None of these experiments attempted to eliminate the thermal diffuse scattering contribution to the diffracted intensity; therefore their results are difficult to model theoretically, although shifts in the peak positions can often be explained in terms of thermal contraction and expansion.
III. ORDER-DISORDER TRANSITION OF Cu₃Au

Cu₃Au is a classic example of a two component system which exhibits an order-disorder transition. Below the transition temperature Tc, Cu₃Au has a face centered cubic (FCC) structure with alternate (001) layers having a 50%-50% copper-gold then 100% copper composition. This structure is shown in figure 12. Above the transition temperature, the copper and gold atoms are randomly distributed on the FCC sites.

The amount of disorder below the transition point (in this case the number of copper atoms where gold atoms should be or vice-versa) can be described by an order parameter which is a measure of the long range correlation between similar atoms. Experimentally, the surface order parameter is obtained by measuring the size and shape of the LEED beams resulting from the copper (or gold) superstructure or, in some cases, the size and shape of the specular or integral beams. The behavior of the order parameter near the transition is characterized by a critical exponent which is found by measuring the order parameter at a number of temperatures around the transition, then fitting the measurements to the equation

\[ S = (T - T_c)^\beta \]  \hspace{1cm} (45)

where \( S \) is the order parameter, \( T \) is the temperature, \( T_c \) is the critical temperature and \( \beta \) is the critical exponent providing the best fit to the data. This critical exponent can be compared to predictions of various theoretical models to determine which best describes the system being
Figure 12. Structure of bulk $\text{Cu}_3\text{Au}$ below $T_c$. 

$\text{Cu}_3\text{Au}$ (ORDERED)

(001) PLANE

\[ \text{Cu} \quad \text{O} \quad \text{Au} \]
A. Theory

Qualitatively, order-disorder transitions can be understood using thermodynamic arguments. The requirement that the Gibbs free energy of a given system must be a minimum determines the stability of the ordered or disordered state at any given temperature. The free energy $G$ is defined as

$$G = E - TS + PV$$

where $E$ is the internal energy, $T$ is the temperature and $S$ the entropy. The pressure ($P$) and volume ($V$) can be assumed constant. At low temperatures, the temperature entropy ($TS$) contribution to an ordered alloy is negligible, and the stable state is the one where the free energy is a minimum: the ordered state.

As the temperature increases, the atoms become more mobile and start to interchange places, increasing the entropy. With more atoms acquiring sufficient energy to interchange, it becomes easier for them to do so because the nearest neighbors are no longer all dissimilar. At some point, the $TS$ term in the free energy equation becomes dominant, and, to keep the free energy a minimum, the stable state becomes the one with the most internal energy, the disordered state. This transition is rapid, with the temperature where the transition occurs called the critical temperature $T_c$. 
Phase transitions are usually classified by their order $n$. A transition is considered to be of the $n$th order when derivatives lower than the $n$th derivative of the free energy $G$ are continuous at the transition temperature while the $n$th derivative is discontinuous. \textsuperscript{37} This criterion is somewhat limited for this study because experimentally the quantities are not always easy to measure. In fact, the surface order-disorder transition of Cu$_3$Au has characteristics of more than a single type of transition.\textsuperscript{12}

The order-disorder transition can be quantitatively understood through statistical mechanics using an Ising model\textsuperscript{38} in which two kinds of atoms are distributed in a regular three dimensional array. When a particular atom of one kind is substituted for an atom of the other kind, the energy changes by an amount which depends upon the kind of neighbors and their arrangement. The thermodynamic state of this type of system can be obtained by finding the partition function

$$Z_g = \sum \exp(-E_\tau/kT)$$

(47)

where $\tau$ is the configuration, $k$ the Boltzmann constant, and $E_\tau$ is the energy of the system for that configuration. The sum is taken over all possible configurations.

The Ising model has yet to be solved rigorously in three dimensions but the two dimensional solution has been found.\textsuperscript{39} Approximate solutions can be found for the three dimensional case by making certain approximations in the energy term of the partition function and using Monte Carlo techniques to calculate the ensemble of states. For
example, assuming that only the nearest neighbors interact, the energy of a configuration \( \tau \), \( E_\tau \) can be written as

\[
E_\tau = J_1 \sum_{i,j} S_i S_j - \varepsilon \sum_{i=1}^{n} S_i
\]  

(48)

where \( J_1 \) is the nearest neighbor interaction constant, and \( \varepsilon \) is the chemical potential of the alloy. The first summation is taken over the nearest neighbors and the second over the second nearest neighbor. In this equation, \( \sum S_i \) is a direct measure of the long range order parameter \( S \), if the summation is made appropriately with respect to one particular sublattice.

From this assumption the bulk order-disorder transition of \( \text{Cu}_3\text{Au} \) has been modeled within the limits of the Monte Carlo calculation.\textsuperscript{40} The critical behavior of the \( \text{Cu}_3\text{Au}(001) \) surface has been predicted using a Bragg-Williams approximation where no short range order is assumed.\textsuperscript{41} This is a rather unphysical assumption, and there are other more sophisticated approximations currently used to solve the Ising model in three dimensions.\textsuperscript{42} To check the validity of these various approximations, the theoretical critical behavior is often compared to the experimental results.\textsuperscript{43}

It is interesting to note that, if \( J_1 \) is negative and \( \varepsilon = 0 \), then equation 48 corresponds to the case of superlattice formation in binary alloys or antiferromagnetism.\textsuperscript{44} In equation 48, \( \varepsilon = \mu H \) is equivalent to an antiferromagnet in a magnetic field.\textsuperscript{44} This equivalence implies that very different systems (magnetism and order-disorder) can be theoretically understood with the same models and are manifestations of
the same underlying phenomena.

B. LEED Experiments

In 1973 Sundaram et. al. made the first LEED study of the surface order-disorder transition of Cu$_3$Au$^{10}$ They measured the integrated intensities of the superlattice beams caused by the ordered gold and copper overlayers as a function of temperature, to determine the type and temperature of the transition.

To analyze the data, they assumed that the electrons only scattered once (kinematic approximation) with the intensity of the diffracted beams having the form

$$I \propto S^2 \exp(-2W).$$

(49)

where $S$ is the long-range order parameter and $W$ the Debye-Waller factor. By correcting for the effect of the Debye-Waller factor, in this model, the spot intensity at any temperature is due entirely to the long range order parameter. The temperature dependence of the long range order parameter is easily determined under these assumptions. Sundaram et. al. concluded that the surface started to disorder $60^\circ$ below the bulk order-disorder transition temperature of $390^\circ$C. There was, and still is however, some controversy as to the correctness of this analysis because it was based on a simple single scattering model and the integrated intensities of the superstructure LEED beams at a given temperature was the only observable measured.
Within the past year, McRae and Malic\textsuperscript{12} repeated the measurements of Sundaram using a more sophisticated analysis technique. In their experiment, not only the integrated intensity of the diffracted beams were recorded, but the angular profiles as well. The angular information is necessary to obtain both the short-range and long range order parameters of the surface.\textsuperscript{45}

In their work, the long range order parameter was determined from a single scattering model based on neutron scattering work by Dietrich and J. Als-Nielsen\textsuperscript{46} for \(\beta\)-Brass, modified for LEED. This model assumes that the diffracted intensities have both a long range order parameter \(S\) and a short range correlation function \(\rho(r)\). Therefore the diffracted intensity takes the form

\[
I \propto \frac{a-b}{2} \exp\left(-2W\right) \left(N^2 S^2 8(q)+N \sum_{\mathbf{r}} [\rho(r)\exp(i\mathbf{q} \cdot \mathbf{r})]\right)
\]

(50)

where \(a\) and \(b\) denote the atomic scattering factors for Cu and Au, \(W\) is the Debye-Waller factor, \(N\) is the number of atoms, and \(\mathbf{r}\) is the distance between two atomic sites. This equation applies specifically to fractional order beams where \(\mathbf{q}\) is the surface parallel momentum. To determine the critical exponents and \(T_c\), intensity profiles both above and below the transition temperature were taken. Any intensity in the diffracted superlattice beam above the transition temperature was attributed to short range order and could be used to eliminate short range order contributions to the diffracted intensity below the transition temperature.
From their analysis, McRae and Malic determined that the surface order-disorder transition occurs at 390°C which is the same as the bulk transition temperature. They also concluded that the surface transition is at least partially continuous which is in agreement with Sundarahan. In addition however, they found evidence for a critical (discontinuous) transition on the surface, which is the same as that of the bulk transition. A critical exponent of 0.31 was measured for the second order transition.
IV. EXPERIMENTAL APPARATUS AND DATA ACQUISITION

The entire polarized LEED apparatus, shown in figure 13, is contained in three separately pumped vacuum chambers. From left to right, the first chamber houses the polarized electron source (PES) whose design and operation was described in section 2. The next chamber is the main experimental region and the chamber on the right is the Mott electron spin analysis region.

A. Description of Experimental Apparatus

A brief description of the polarized electron source will be given here. Linearly polarized light from a GaAlAs laser traverses a Pockels cell, which modulates its sense of polarization between LHCP and RHCP at 500Hz, and is focused onto the GaAs(001) emitter. The laser light photoemits electrons from the GaAs crystal surface when it has been properly treated with cesium and oxygen, with the photoemitted electrons polarized either parallel or antiparallel to the surface normal depending on the helicity of the incident light. Once in vacuum, the electrons traverse a spherical mirror analyzer which bends the beam out of the direction of the incident light and thereby converts the electron spin polarization direction from longitudinal to transverse. Next, the electrons are sent through transport optics, an isolation valve, and finally through the PLEED optics. In normal operation, the source has an electron spin polarization of $27\% \pm 2\%$ and delivers a current of 0.3μA to the target crystal.
Figure 13. Schematic of entire polarized LEED apparatus. Looking from left to right, shown are the polarized electron source, the main experimental (LEED) chamber, and the Mott spin analysis chamber.
The center chamber is the main experimental chamber which contains two independent LEED systems and the sample crystal. The left LEED optics is used for the PLEED measurements where the polarized electron beam is the source of incident electrons. The other LEED optics is normally run in the Auger mode to monitor surface contamination. It can also operate in the LEED mode, for PLEED measurements where the incident electron beam is unpolarized and the polarization of the diffracted beam is measured via Mott scattering. Additionally, this chamber contains an ion gun for surface preparation and a quadrupole partial pressure analyzer (PPA) for diagnostic purposes. The LEED chamber has a base pressure of $3 \times 10^{-10}$ Torr.

The polarized electron beam can be directed through the LEED chamber and into the Mott analysis (right) chamber where the beam polarization is measured. The electrons enter the Mott chamber through a lens system where they are focused and directed to the entrance of a 100KeV accelerating column. The electrons, now at 100keV, then enter the main part of the third chamber where, following further collimation, their polarization is determined by the conventional Mott scattering technique.

The Rice Univeristy Mott scattering chamber has been described in detail in other theses. Briefly, the Mott scattering technique makes use of the left-right scattering asymmetry produced as a result of spin-orbit coupling when high energy electrons are elastically scattered at large angles from the gold nuclei of a thin gold foil. This polarization-induced scattering asymmetry has been accurately calculated, and experimentally verified, for a wide range of electron
energies and scattering angles. The asymmetry is largest for electrons scattered in the plane perpendicular to the total polarization and for 100 keV electrons displays a broad maximum at scattering angles of 120 degrees. Although multiple scattering reduces the asymmetry, the correction appropriate to the 1000A thick gold scattering foils used in this work has been determined previously.1 Electrons scattered at 120 degrees are detected by two symmetrically placed surface barrier detectors. Pulse height analysis enables identification of those electrons which have undergone elastic scattering and these are counted using two scalers which are in turn read by a CAMAC based computer system that calculates the polarization of the electrons. The component of electron spin polarization perpendicular to the scattering plane of the gold foil is measured.

B. Crystal Manipulator

The Cu$_{3}$Au(001) crystal is mounted on a custom designed manipulator$^{50}$ that has three independent rotational motions (figure 14). The crystal face can turn in the standard two crystallographic directions, $\Theta$ and $\Phi$. In addition, the crystal face is offset from the main rotation axis of the manipulator assembly; therefore, by rotating the main axis shaft (the third degree of freedom), the crystal is transported from one LEED system to the other or to an ion gun for sputtering (figure 13). The crystal can be heated by a tungsten filament mounted inside the molybdenum can that serves as the sample holder shown in figure 14. Crystal temperature is measured using a
Figure 14. The crystal manipulator
a chromel-alumel thermocouple attached to one of the tabs that holds the sample to the molybdenum can.

C. Surface Preparation

Our Cu Au(001) sample was purchased from Cornell University$^{51}$ with both faces cut and polished to within 0.5 degrees of the (001) direction as determined using a Laue camera. After insertion into the vacuum chamber and bakeout, the crystal surface is cleaned by argon ion bombardment. Surface cleanliness is monitored using the second (unpolarized) LEED optics in the Auger mode.$^{47}$ Two contaminants were initially present on the surface, sulfur and carbon. Neither posed much of a cleaning problem and after three or four sputter/anneal cycles, no contaminants were observed on the surface.

The normal cleaning procedure used was to sputter at room temperature for 20 minutes with 750 eV argon ions, then anneal for 30 minutes at 500°. Subsequent LEED and Auger measurements showed good surface order and no contaminants after this procedure. Initially, after sputtering, the copper (56eV) to gold (48eV) Auger peaks showed a preferential sputtering of copper but, after 20 minutes of annealing, the copper/gold ratio changed to the 'normal one' shown in figure 15. This ratio remained constant even after an additional four hours of annealing.
Figure 15. Auger spectra of the Cu₃Au crystal a) before annealing but after sputtering and b) after annealing for 20 minutes at 500°C.
D. Data Acquisition

Polarization and intensity data were taken on a point by point basis with a CAMAC based computer system controlling the experiment. The incident energy of the electrons is first set by the computer using a programmable power supply. Next, the diffracted current is measured by positioning a Faraday cup to collect the maximum current of the diffracted beam being studied. As noted in section two, the helicity of the incident light, hence the electron spin polarization of the incident beam is modulated at 500 Hz. The light modulation signal is also used as a reference source for a lockin amplifier which, in turn, is used to determine the change in intensity of the diffracted beam in phase with the change in polarization of the incident light, i.e. the difference between spin up and spin down diffracted intensities.

The asymmetry parameter \( A \), which is defined as

\[
A = \frac{I^+ - I^-}{P_0(I^+ + I^-)} \tag{51}
\]

where \( P_0 \) is the polarization of the incident beam and \( I^+ \) and \( I^- \) are the intensities of the spin up and spin down diffracted currents respectively, must be measured to determine the effective polarization of the diffracted beam.\(^{32}\) To do this, the current collected by the Faraday cup is converted into a voltage using a current to voltage converter inside the Faraday cup preamplifier (figure 16). The preamplifier then splits the voltage into a 500Hz (difference) component which goes to the lockin amplifier, and a DC (spin averaged) component
Figure 16. Electronics used to determine the diffracted beam polarization and intensity. The current collected by the faraday cup is converted to a voltage. This voltage is split into a high frequency (difference) and a low frequency (sum) component which are fed into a lockin amplifier and voltmeter respectively. A computer reads the outputs of these instruments and calculates the polarization and intensity.
which goes to a voltmeter. The computer can read the spin averaged
diffracted current from the voltmeter and the difference current from
the lock-in amplifier. At each energy the polarization or asymmetry can
be determined using the following formula:

\[ A = \frac{I^+ - I^-}{|P|(I^+ + I^-)} = \frac{\text{lock-in}}{\text{voltmeter} \times 2|P|} \] (52)

with the asymmetry the same as the polarization under our symmetry
conditions. This procedure is then repeated at the next voltage. The
faraday cup was repositioned after each point (even for the 00 beam)
because there were small beam deflections at low energies caused by
stray magnetic fields. Usually data were recorded between 30 and 120
volts in approximately one volt increments.

All intensity data shown is normalized to the incident current.
This is done by recording both the current striking the crystal and the
total diffracted intensity and then dividing one by the other.

E. Sources of Error

The electron energies (V) quoted here, have been corrected for the
contact potential difference between the GaAs source crystal and the
sample, thus giving the mean kinetic energy of the incident electrons in
vacuum, i.e. \( E = eV_{FS} + \phi_f - \phi_s \) where \( V_{FS} \) is measured potential difference
between the GaAs crystal and the sample crystal, \( \phi_f \) is the work function
of the activated GaAs crystal (0.0eV) and \( \phi_s \) is the work function of the
sample (6.3eV). Uncertainties in the work functions lead to an
uncertainty in V of \( \pm 1.0 \) eV.

Error in the absolute asymmetry measurements could arise as a result of improper calibration of the electronics measuring the signal. The polarization is determined by a ratio measurement using voltages from two separate instruments. Miscalibration of one or both of the instruments could lead to a systematic error in the absolute asymmetries. Also, if the polarization of the incident beam \( (P_o) \) is incorrect, the absolute polarization will be in error. To check for these types of systematic errors, the polarization vs. voltage of the 13 degree specular beam was measured using the old method of an unpolarized incident beam and measuring the polarization of the diffracted beam. The agreement between the two methods was good as shown in figure 17.

There are also statistical errors in the polarization measurements introduced when the computer reads the lockin amplifier and voltmeter. These errors have been minimized by reading the value from each instrument 300 times and averaging the results. In the future an estimate of the statistical error should be calculated by taking standard deviations of the measurements. This capability was not available when the data was taken.

Angle resetability affected our ability to reproduce some of our results on a day to day basis with a high degree of accuracy. The resetability of the \( \theta \) angles was estimated to be \( \pm 1.0 \) degree, with the absolute angle of the measurements also \( \pm 1.0 \) degree. It was, however possible to reproduce any result by moving the crystal in 0.5 degree increments around the assumed angle value then taking the best match to
Figure 17. Comparison between P-V curves taken using the polarized electron source (line) and Mott detector (hash). Data was taken at $\Phi=0$ and $\Theta=13$. 
previous results. The $\phi$ angle was never changed but its absolute angle is estimated to be $\leq \pm 1.0$ degrees.
V. EXPERIMENTAL RESULTS AND DISCUSSION

The room temperature polarization and intensity of the specular 00 beam as a function of energy at $\phi=0^\circ$ and $\theta=5,7,9,11,13,15$ are shown in figures 18 through 23 respectively. Polarization and intensity profiles of the 01 beam at room temperature and normal incidence are shown in figure 24. Large polarization features are found that vary significantly with angle as do the intensity features. Additionally, the 01 beam shows large intensities at the high polarization features.

Figures 25 and 26 show the temperature variation of the 00 beam at $\phi=0^\circ, \theta=13$ degrees and the 01 beam at normal incidence, respectively. No significant difference in the I-V or P-V peak positions is observed when the Cu$_3$Au crystal is heated through the order-disorder transition. The polarization reduction as the temperature is increased at the higher energies is, in part due to thermal diffuse scattering which we were unable to eliminate from our experimental data.

Another method of displaying the data that may lead to a better insight of the order-disorder transition of Cu$_3$Au is to plot the intensity and polarization of a polarization feature at one particular energy as a function of temperature. This method was first introduced by Sundararamam$^{10}$ who noticed a variation in the linearity of the temperature dependence of the intensity peaks. This deviation in linearity predicted by the Debye-Waller factor was ascribed as the onset of disordering of the surface.
Figure 18. P-V / I-V Curves theta=5°.

Figure 19. P-V / I-V Curves theta=7°.
Figure 20. 00 Beam, theta=9°.

Figure 21. 00 Beam, theta=11°.
Figure 22. 00 Beam, theta=13°.

Figure 23. 00 Beam, theta=15°.
Figure 24. O1 Beam, normal incidence.
Figure 25. Temperature dependence of 00 Beam $\theta=13^\circ$
Figure 26. Temperature dependence of 01 Beam.
Figures 27 and 28 show intensities and polarizations of the 00 beam at 13 and the 01 beam at normal incidence respectively at constant energy as a function of temperature. The same effect found by Sundaraaham is seen in the intensities, a break in the linearity approximately 60 degrees below the bulk order disorder temperature at 390°C. The polarization also shows the same tendencies but there are no simple models from which to draw similar conclusions in PLEED theory. 32

In hindsight there are a number of reasons why PLEED may not be sensitive to the order disorder transition of Cu$_3$Au(001). Recent experiments using ion scattering 52 have shown the top layer is composed of 50%-50% CuAu even for temperatures substantially above Tc. This implies that though the top layer may have intralayer disorder, the mixing between layers is minimal at temperatures just above the order-disorder transition. At extremely high temperatures (~800°C) ion scattering experiments 52 revealed that there is good layer-to-layer mixing at the surface, but the Debye-Waller factor and thermal diffuse scattering make PLEED measurements difficult at such high temperatures. In conclusion, to the extent that PLEED might be sensitive to the total gold coverage, one might expect little difference above and below Tc in the PLEED spectra, except at very high temperatures.

The recent LEED experiment of McRae and Malic 12 measured both intensities and angular profiles of the diffracted beams. They made estimates of the critical exponents and order of the transition. It is doubtful that PLEED can add any more to this information until the theory is better developed.
Figure 27. 00 Beam E=68.1 V I-T Curve, P-T Curve
Figure 28. O1 Beam E=56.4 Volts, P-T Curve.
Conclusions

A GaAs polarized electron source was designed, constructed and installed on the Rice PLEED apparatus. P-V curves obtained using the source were identical to those curves taken by the old method, in which the polarization of the LEED beams were measured for an unpolarized incident beam. The source polarization of 27% is low compared to other polarized electron sources but it was high enough for this experiment and with additional work, this value may increase.

This was the first measurement of the PLEED spectra of an ordered two component system. It is hoped that this data will encourage further theoretical interest in PLEED. In contrast to expectations, no dramatic effects caused by the order-disorder transition in the P-V spectra were observed. Possible reasons for this are discussed in the previous section. Fortunately, there is still a wealth of experiments, especially with surface magnetism, where PLEED can yield additional insight into the physics of the processes involved.
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