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ELECTROREFLECTANCE OF SINGLE CRYSTAL METALS

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Electroreflectance of single crystal metals

by

Thomas Elton Furtak

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Electroreflectance of single crystal metals*

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Measurements of the normal incidence, polarized light electroreflectance of clean, strain free (110) and (100) Ag, from 3 eV to 4.2 eV, and (110) Au, from 1.6 eV to 4.0 eV, were performed using the electrolyte technique in a novel drop configuration. At 3.9 eV in Ag a dramatic reproducible anisotropy in the negative peak in $R^{-1} \Delta R / \Delta \Phi$, that was unquestionably correlated with the orientation of the crystal, was observed only on the (110) face. No anisotropy was detected in the electroreflectance of Au. A detailed study of the anisotropic spectrum was conducted as a function of surface preparation, solution composition, sample bias potential, and modulation amplitude.

The results of this research have demonstrated beyond doubt that the electroreflectance on the (110) surface of Ag involves a modulation of electron states that possess the crystal surface symmetry. The most plausible interpretation, excluding such exotic mechanisms as intrinsic surface states or an anisotropic electron gas, involves a combined effect of a McIntyre-Aspnes-like charge modulation, which is responsible for the gross details, and field assisted indirect interband transitions which add an anisotropic contribution.

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CHAPTER I. INTRODUCTION

Preamble

Traditionally liquid materials science has been the interest of chemistry and solid materials science has been in the realm of physics. Electroreflectance of metals using the electrolyte technique implies the presence of the junction of a solid and a liquid at an interphase boundary. To understand properly and interpret such studies requires a background in solid state physics as well as electrochemistry.

This dissertation is presented with a bias toward solid state physical ideas but it is meant to represent the complete multi-disciplinary effort. To aid the understanding of concepts and definitions which are peculiar to chemistry or physics, Appendices B and C have been included. They give a tutorial discussion of what is appropriate from each of these fields to the interpretation of this research. I will assume that the reader is familiar with the material in these appendices. However specific referral will be made in several places for emphasis.

Although some effort has been directed at the experimental and theoretical study of metallic electroreflectance (ER), it has remained a poorly understood phenomenon. Involving, as it does, a multidisciplinary approach, its interpretation has not received the attention of either chemistry or physics. In the current surge of activity concerning surface studies it is becoming more important to decipher the mysteries of the solid/solution boundary. Metallic ER holds a promise

of revealing information on the electronic structure of the interface as well as the energetics of catalysis and chemical bonding. It may be one of the few ways to modify and thereby study the surface region of metals where intrinsic or more complex surface states might exist.

It was the purpose of my research project to perform properly controlled electrochemistry and surface preparation on metal single crystals in utilizing the electrolyte method of studying electroreflectance. It was planned to use normally incident, polarized light to try to observe the symmetry breaking character of the field. An attempt would be made to identify ER due to electronic interactions with the periodic lattice, thus demonstrating the participation of bound electrons.

Electroreflectance^{1,2}

Modulation techniques³ have proven useful in optical studies by their ability to enhance structure. Electric field modulation of the reflectivity, or electroreflectance (ER), aids the assignment of critical point energies in semiconductors with its uncommonly high resolution. With other modulations such as strain and heat, electron momentum is still a good quantum number, to within a reciprocal lattice vector, even when the symmetry is lowered by the modulation. The electric field ($\vec{F}$) imposes a contribution to the one electron Hamiltonian which is not translationally invariant. The electron momentum parallel to the field is no longer a good quantum number in an electric field perturbed crystal. This causes mixing of the one-electron Bloch

functions. The result is equivalent to spreading a formerly sharp transition over a range of initial and final momenta. If $\vec{F}$ is small, the mixing is restricted to wave functions with momenta near that of the originally vertical allowed transition. This produces a complicated perturbation in the dielectric function, ϵ , that approximates its third derivative with respect to photon energy.⁴ For this reason ER in semiconductors and insulators displays extremely sharp spectra. For higher fields, changes in the dielectric function can be expressed in terms of electro-optic functions that are derived using the now classic Franz-Keldysh theory.⁵ This field-assisted absorption is an even function of the field -- independent of the sign.

Experimentally, two basic techniques are employed to apply an electric field to a solid.³ Provided the material has a high enough resistivity, the field can be imposed by brute force transversely, perpendicular to the direction of the incident photon beam, via ohmic contacts or capacitive coupling. The advantage of this configuration is that the photon field can be aligned perpendicular or parallel to the perturbing field making possible a variety of symmetry studies. The second technique is to apply the perturbing field normal to the sample surface by employing some type of optically transparent electrode. One way to do this is with a capacitor-like package using an insulator, a native or deposited oxide, to separate the field electrode from the sample. The magnitude of the electric field possible with the capacitor package is limited by the breakdown strength (about 10^5 V/cm) of available insulating materials. The other longitudinal

method uses the intense electric field at the interface between a solid and an electrolytic solution. The "transparent electrode" in this configuration is a layer of ions in the electrolyte which come very close to the solid surface. It is possible to achieve fields up to 10^7 V/cm by applying only a few volts across the interface. The electrolyte method is limited by the transparency and temperature range imposed by the electrolyte, and by interfering complications due to the electrochemistry of the system. It is, nevertheless, the only way to apply such intense electric fields to a large, flat optical surface and is the most effective technique in the extension of electroreflectance to metals.

The quantity of interest that is experimentally accessible is the logarithmic derivative of the reflectivity, $\Delta R/R$. The most commonly used procedure is to impose a periodically varying field by one of the previously mentioned methods. The periodic component of the reflected intensity, which is proportional to ΔR , is extracted with phase sensitive electronics. By dividing this by the average value of the reflected intensity, which is proportional to R , $\Delta R/R$ is obtained.

Electroreflectance in Metals

The penetration depth of the electric field beyond the surface of an absorbing semiconductor is of the same order of magnitude as the penetration depth of incident photons. In metals, however, due to the high density of mobile electrons, a static electric field is screened out within a short distance of the surface. The Thomas-Fermi screening

length for typical metallic parameters is less than 1 Å. Since the photon penetrates up to 10,000 Å, it was not expected to be an effective probe of any perturbation due to a static field at the surface of a metal. However, apparently due to the importance of the surface in determining the reflectivity, experimentally observed electroreflectance is a reality. An excellent review of the situation up to 1972 is offered by McIntyre,⁶ who himself has contributed extensively to the understanding of this phenomenon.

Experimental evidence

Well-documented electroreflectance experiments have been performed on Au, Ag, Cu, Pb, and Pt. Most of the work employs the electrolyte technique on thin film samples. Many investigations involved poor or unspecified chemical technique. All the ER studies on bulk metals have been performed with polish-damaged surfaces.

The first spectroscopic report of metallic ER was by Feinleib.⁷ He looked at polished bulk Ag, and films of Au. Using an aqueous KCl electrolyte and applying a 2 V p-p modulation between the sample and a Pt auxiliary electrode, he observed a $\Delta R/R$ of the order of a few tenths of a percent. Peaks in $\Delta R/R$ vs photon energy were reported at 3.9 eV in Ag and at 2.35 eV in Au. The quantitative significance of this work is in doubt since the modulation potential excursions probably encompassed conditions where reactions were modifying the interface. Since proper techniques were not followed it is dangerous to base any conclusions on his data. The appearance of Feinleib's paper, however, attracted the interest of chemists and physicists alike.

Buckman⁸ and together with Bashara⁹ applied the technique of modulated ellipsometry to the ER of Au and Ag films in 1 M KCl. The output of their experiment was a spectral representation of the changes in the dielectric function. Their data were not causally (Kramers-Kronig) consistent however, which can be blamed on the sensitivity and assumptions that go into ellipsometric analysis.

The most reliable ER experiments till now were performed by McIntyre, who established carefully controlled electrochemical conditions. Figure 1a shows his ER of a thin film of Ag¹⁰ using photons incident on the sample at an angle of 45°. The photon field was polarized perpendicular ($\perp$) or parallel ($\parallel$) to the plane of incidence. There is a sharp peak at 3.9 eV and some weaker structure near 3.3 eV. The ER of a Au thin film as measured by McIntyre¹¹ is shown in Figure 1b. This spectrum is dominated by a broad peak at 2.5 eV and some smaller structure near 3.5 eV. Although it is not indicated in Figure 1, the peaks are in the negative direction. That is, the reflectivity is a decreasing function of electrode potential.

Yeager and co-workers measured reflectivity in a multiple reflection cell as a function of electrode potential (Φ) then numerically calculated $R^{-1} dR/d\Phi$.^{12,13} Their samples were Au films in electrolytes of HClO_4 , H_2SO_4 , and NaClO_4 . By performing their analysis at various photon energies they obtained spectral information. Due to the uncertainty involved in this technique compared to the electronic derivative method, their results are tenuous. They observed the broad peak near 2.5 eV and reported that it shifted to lower photon energies

Figure 1. Electroreflectance of metallic thin films as measured by McIntyre with 45° incident light polarized parallel ($\parallel$) and perpendicular ($\perp$) to the plane of incidence. (a) Ag film in 1 M NaClO_4 , $\Phi_{\text{DC}} = -0.5$ V (SCE), $\Phi_{\text{AC}} = 100$ mV rms at 27 Hz; (b) Au film in 1 N HClO_4 , $\Phi_{\text{DC}} = 0.16$ V (SCE), $\Delta q = 1.91$ $\mu\text{coul/cm}^2$ at 270 Hz, dotted line calculated with McIntyre-Aspnes model.

a

b

as the average value of the electrode potential increased. They also noted the similarity between the ER spectra and a difference spectrum calculated between an oxidized and a clean Au film.

Russian electrochemists^{14,15} investigated the influence of Φ on the ER of Au and Pt bulk samples in 1N H₂SO₄. They experienced contamination problems which caused unreproducible results. On a given sample they report the peak at 2.5 eV in Au but it did not shift with changing Φ . The differential capacitance of the double layer (C_{dl}), which they also monitored as a function of Φ , showed no obvious similarity in form to the $R^{-1} \Delta R(\Phi)$ data. This they interpreted as implying that the ER effect did not scale with charge. A secondary structure appeared in the Au spectral results near 3.6 eV for Φ greater than zero volts SCE which disappeared when the electrode was cathodically treated. This was explained as an oxide effect.

A considerable effort of doubtful value has been contributed by Garrigos and associates. Over a period of four years they have investigated ER of bulk samples of Ag¹⁶ and Au.¹⁷ They have always mechanically polished their surfaces, even with single crystal samples, and have rinsed them in "degreaser" just prior to placing them in their cell. They make no attempt to eliminate the work damage. Earlier experiments were performed under undefined electrochemical conditions. Even more recent, properly controlled work shows evidence of severe contamination.¹⁸ A Kramers-Kronig inversion was used in one paper¹⁷ to attempt an extraction of the effective change in the dielectric function due to the perturbing field. They assumed that the

semiconductor data analysis techniques were applicable. However, since these equations apply only to a uniform, deeply penetrating perturbation, their extension to ER in metals is clearly incorrect.

Anderson and Hansen¹⁹ exploited the attenuated internal reflection (ATR) scheme on thin films ($< 200 \text{ \AA}$) of Au and Cu in $0.1 \text{ M Na}_2\text{SO}_4$. They reported broad structure at 2.5 eV in gold but the data quit at 3.0 eV. It is difficult to assess the significance of their work since almost no information was offered on their experimental procedure.

A very recent description has appeared by Abelès et al.²⁰ of reliable ATR experiments utilizing the excitation of a non-radiative surface plasma resonance at 2.034 eV between a Au film and electrolytes of H_2SO_4 and HClO_4 . By observing how changes in the surface plasmon wave vector with electrode charge varied between the two solutions, they claim to have separated the effect due to the metal from that occurring in the electrolyte. The analysis depends on an oversimplified treatment of the optical effect of the double layer due to Stedman (see next section).

One early attempt was made to perform metallic ER without resorting to the electrolyte technique. Stadler²¹ tried evaporating thin films of Au on the surface of a ferroelectric crystal (BaTiO_3). The atomic displacement in this material causes locally intense electric fields (10^8 V/cm) which are available at the Au interface. The photon beam was incident from the air side and supposedly sampled the electric field perturbed region on the ferroelectric side of the Au film. Piezoelectric effects were eliminated as a cause of the structure at

2.5 eV by comparing the effect of a one-signed driving voltage with that of the symmetric waveform used to reverse the ferroelectric displacement.

In view of the variety of methods and levels of sophistication which have been employed to study ER in metals, it is remarkable that the data are so similar. Virtually every attempt using Au as a sample has revealed some structure in $\Delta R/R$ near 2.5 eV while the work on Ag always shows something at 3.9 eV. A closer study of the conditions which apply at the electric field perturbed metal surface suggests an explanation for this resemblance. The thin perturbed region of the metal imposes an effective intermediate phase between the bulk metal and the solution. The reflectivity of the system is a function of the optical properties of all three phases, and in particular, of the optical coupling at each phase boundary. At 2.5 eV in Au and 3.9 eV in Ag, the bulk metal optical properties are changing rapidly with photon energy. It seems logical that, in such a multiphase assembly, these are the locations of structure, regardless of the modulation mechanism in the intermediate layer. This makes a theoretical interpretation difficult.

Theoretical interpretations

Early ideas The first attempt to explain metallic ER was proposed by Feinleib.⁷ That model, however, was based on a two phase optical system which is not valid since it ignores the existence of the double layer in the electrolyte or the metal. A phenomenological

description was presented by Prostak and Hansen²² based on a field induced rigid shift in energy of the optical properties of a 0.5 Å layer of metal. No justification for the shift was given. Later, Hansen and Prostak²³ explained that a change in electron density in the surface region induces a shift of the Fermi level with respect to the bulk band structure. This, they argued, was the source of the rigid shift. This formalism predicts $\Delta R/R$ of both signs for a material such as Ag, which experimentally exhibits only a negative peak (Figure 1a).

Electrolyte effects Stedman²⁴ has calculated the optical effect of changes in ionic concentration in the diffuse layer of the electrolyte due to changes in electrode charge. There was no spectral information in her results, which predicted a contribution to normal incidence $\Delta R/R$ of up to 3×10^{-5} for a charge variation of $10 \mu\text{coul/cm}^2$. A "speculative" extension²⁵ of the theory to include inner layer effects was based on the compression of water and an addition to the concentration mechanism due to specifically adsorbed ions. This added a $\Delta R/R$ as high as 10^{-3} for oblique incidence, mainly due to the adsorption contribution. The model on which these conclusions were based contained many doubtful assumptions, including the use of ion refractivities derived from measurements on dilute bulk solutions.

Assuming no special mechanism but employing the linear approximation (LA) theory (Appendix D) for a three phase system, McIntyre⁶ has shown that a simple discrimination between metallic and solution effects can be made. If the modulation occurs in the electrolyte, with an angle of incidence of 45° , $\Delta R/R$ is small and finite for

s-polarization (perpendicular to the plane of incidence) but zero for p-polarization (parallel to the plane of incidence). The reason for this is that the Brewster angle²⁶ between two transparent media with nearly the same optical constants is very near 45° . The modulated electrolyte layer becomes "invisible" under these conditions with p-polarized light. Whereas, using the LA theory, if the modulation occurs in a layer which has optical properties which slightly deviate from the metallic values, then at 45° , $\Delta R/R$ for p-polarization is approximately twice the value of $\Delta R/R$ for s-polarization. This applies regardless of the modulation mechanism. From Figure 1 it is evident that, if these arguments apply, the change occurs in the metal, not the electrolyte. It is expected that electrolyte effects are not important.

Surface state theory Cahan, Horkans, and Yeager¹² proposed an explanation of ER in Au that hypothesized the existence of intrinsic surface states. These states were claimed to be present due to the truncation of the lattice and were said to be caused by a distortion of the d-band toward the Fermi level in the surface region. They offered as proof, the presence of a tailing of absorption in unmodulated Au to lower energies than the expected d-band to Fermi level gap. (This, however, can be attributed to lower energy inter-band transitions in the bulk. Appendix B) Their idea for modulation comes from a shifting of these surface states with Φ . It is more likely that any surface states are caused because of a complex interaction between the metal and solution sides of the double layer. These

are best referred to as extrinsic surface states.⁶ The energy specification of surface states, whether intrinsic or extrinsic, is a complicated problem and cannot be treated by simply assuming bulk band distortion in the surface region.

The McIntyre-Aspnes theory The most successful theory of metallic ER has been formulated by McIntyre and Aspnes^{6,11,27,28} (M-A). The basic assumption is that the bound electrons are either "stiff" or well shielded by the free-electrons so that, to 1st order, the only modification of the optical properties of the metal in the surface region involves the free electron component. Their evidence for this is that d-states have small orbits compared to sp-states of comparable energy. There are errors of constant factors in the presentation of the M-A theory in references 6 and 28. A correct reproduction of the basic ideas is presented here.

The linear approximation (LA) theory for a spatially varying perturbation of a substrate (s) in contact with an ambient medium (a) is used to describe the optical interaction with the interface. Eqs. (D-1), (D-2), and (D-4) apply. This yields a formula for $\Delta R/R$ in terms of the spatially averaged change in the substrate dielectric function, $\langle \Delta \epsilon_s \rangle$. The substrate free electron dielectric function $\epsilon_s^f(\omega)$ for photon energy $\hbar\omega$, which depends on the electron density, N , through the plasma frequency, ω_p , is given by Eq. (B-5). According to the theory, the only source of modulation is $\Delta\omega_p/\omega_p = (1/2)\Delta N/N$. When the fluctuation in electron density is expressed in terms of a change

in the charge on the electrode, a concise form for the M-A $\langle \Delta \epsilon_s \rangle$ is obtained.

$$\langle \Delta \epsilon_s \rangle = (1 - \epsilon_s^f) \Delta q (N |e| A d)^{-1} \quad (1)$$

When this is substituted into the LA theory, the result is

$$\frac{\Delta R}{R} = - \frac{4\omega_n \Delta q}{cN |e| A} \text{Im} \left[\frac{1 - \epsilon_s^f}{\epsilon_s - \epsilon_a} \right] . \quad (2)$$

The final form is independent of the screening length, d , and scales with the charge modulation amplitude. When τ in Eq. (B-5) is small, as is the case for the noble metals in the visible and uv regions of the spectrum, ϵ_s^f is dominated by its large, negative real part. Under these conditions, for $\omega \ll \omega_p$, $\Delta R/R$ is negative. Since ϵ_s^f is devoid of structure, the main source of the experimentally observed peaks, according to the M-A theory, is due to $-\text{Im}(\epsilon_s - \epsilon_a)^{-1}$. It follows that the ER spectra should have a similarity with the loss function, $-\text{Im}(\epsilon_s)^{-1}$.

McIntyre¹¹ has extended this theory to non-normal incidence and has compared it to his measured ER on Au. The dotted lines in Figure 1b are the result of that calculation. The agreement, with no adjustable parameters, is surprisingly good. The 2.5 eV peak is experimentally broader and extends to lower energy. McIntyre has identified this extra structure with surface plasma modulation (see Appendix B). In the Au/solution system, the conditions for surface plasma

oscillations are met at about 2.5 eV. The surface plasma mechanism was also blamed for the structure near 3.2 eV in Ag (Figure 1a). The agreement between experiment and theory is better yet for Ag near 3.9 eV but poor for Cu.

Bewick and Robinson²⁹ have identified the region of applicability of the M-A theory in very carefully performed experiments on Pb. They demonstrated that $\Delta R/R$ scaled with Δq with an angle of incidence of 45° (where no electrolyte effects should be visible). A deviation from this behavior was observed for large negative charge changes which was identified by them as being caused by bound electrons.

Other theories Hansen together with Anderson¹⁹ has attempted to improve on the M-A theory by including the contribution of bound electrons. As in previous theories influenced by Hansen, they were looking for a way to "shift" the optical properties. A band-bending which affects the interband energy separation $\hbar\omega_{n'n}$ was hypothesized but improperly exploited. The formula they employed for the dielectric function was obtained from the work by Ehrenreich and Philipp³⁰ where the oscillator strength is used but not defined. In an earlier paper Ehrenreich and Cohen³¹ have shown that their oscillator strength actually depends on $\omega_{n'n}$. Hansen and Anderson have apparently overlooked this, since they treated the oscillator strength as a constant. They also let the damping parameter, τ , go to zero before taking the real and imaginary parts of Ehrenreich's result. This means they lost information about any modulation of the imaginary part of the dielectric function. In addition, they neglected the $\vec{k}$ -space dependence of

$\hbar\omega_{n'n}$. Their final computer-generated result had so many adjustable parameters that they were able to fit their own data.

Relying on band shifting as a source of structure, even when properly employed, seems experimentally unjustified. A superficial study of the band structures of the noble metals (Appendix B) in the region of the first strong interband transitions reveals that any change in interband energy must come about by a shift in the bands with respect to each other or by a shift of the Fermi level. With both cases, transitions from the Fermi surface to higher states are affected oppositely than transitions from lower lying states to unoccupied states at the Fermi level. This will in general cause peaks of both sign in the differential optical properties. One can get an idea of this effect by looking at thermomodulation^{32,33,34} at low temperature, where the major modification is a broadening of the Fermi level. This produces peaks of both sign in $\Delta R/R$. The prime example is Ag, whose ER is one sided and located at 3.9 eV. This is the energy location for the onset of transitions from the Fermi level ($p \rightarrow s$). There is no significant structure in the energy region where the much stronger (producing a greater contribution to the interband joint density of states) transition to the Fermi level ($d \rightarrow p$) should produce a peak of opposite sign.

Garrigos et al.³⁵ have presented an obscure theory which appears to have no logical interpretation. They calculated the modified reflectivity of a metallic surface with a phenomenological surface current. Their justification was that the static electric field

induces a charge density which is acted upon by the electric field of the sampling light, thus producing the surface current. Due to the large number of parameters, they were able to fit their own data.

Bower³⁶ has attempted to include bound electron effects by developing a theory for a spatially dispersive dielectric constant. His conclusions, however, were based on improper reasoning connected with the use of spatially dependent response functions.

Preface to This Research

Symmetry consideration³⁷

The electric displacement, $\vec{D}$, is related to the electric field of the photon, $\vec{E}$, by the dielectric tensor of the medium, $D_\mu = \sum_\nu \epsilon_{\mu\nu} E_\nu$. The dielectric tensor must transform into itself when operated on by the symmetry operations of the point group of the lattice. If the point group has a symmetry at least as high as the orthorhombic system, then with the proper choice of coordinate axes, $\epsilon_{\mu\nu}$ can be diagonalized. In a medium of $m3m$ symmetry, such as a face-centered cubic crystal, all three diagonal components are equal. The optical interaction, described by the displacement, is isotropic under these conditions.

In the surface region of a normally isotropic crystal, the symmetry is lower due to the presence of a preferred direction perpendicular to the surface. This situation may exist for only a few atomic layers beyond which the bulk symmetry applies. The surface symmetry, and therefore the dielectric tensor in the surface region, depends on

the particular crystallographic plane which forms the surface. Table 1 summarizes the situation for the three principal cubic directions.

Table 1. Surface dielectric tensor in cubic crystals

Crystallographic surface	Surface symmetry	Surface dielectric tensor diagonal ^a
(100)	4mm	$\epsilon_x, \epsilon_x, \epsilon_z$
(111)	3m	$\epsilon_x, \epsilon_x, \epsilon_z$
(110)	mm2	$\epsilon_x, \epsilon_y, \epsilon_z$

^a $\hat{z}$ is perpendicular to the surface.

With normally incident light, $\vec{E}$ is always parallel to the surface. For the (100) and (111) surfaces, $\vec{D}$ is still isotropic. However, on the (110) surface the symmetry is low enough that $\vec{D}$ in the surface region depends on the orientation of $\vec{E}$.

This argument implies that even in a cubic single crystal, the optical properties of the (110) surface are inherently anisotropic. The contribution of the surface region is so small that the effect is normally unobservable. However, if any change in the surface region that maintains the crystal symmetry is imposed, and the optical effect of that change detected, then anisotropy will be observed only on the (110) surface or one of lower symmetry for normal incidence.

These are the conditions that apply to ER of single crystals. The (110) surface or one of lower symmetry must be used if effects due to the lattice potential orientation are to be studied.

Structure of the interface

The junction of a metal and an electrolyte is characterized by a distribution of charge carriers (in the metal, electrons; in the electrolyte, ions) which differs from that of the bulk phases. Figure 2 illustrates a hypothetical union of a metal and an electrolytic solution; the so-called double layer. The various regions in the solution are discussed in Appendix C. Here, comments will be restricted to the metal phase. All the pictured zones may or may not exist depending on the conditions. The distances are only hypothetical and are subject to variation and reversal.

Penetration of perturbing field This is the depth to which the metal has knowledge of coulomb forces due to the presence of solution ions and dipoles. Its extent reflects the ability of electrons in the metal to screen a static charge. In a free electron gas the electron density falls from 90 percent to 10 percent of its bulk value over a distance of 0.34 Fermi wavelength³⁸ (about $1.8 \text{ \AA}$). Electrons that participate in the screening are also expected to participate in interactions with the metal cores.

Intrinsic surface This is the depth to which the metal knows about the lattice termination. According to some calculations³⁹ these effects are still present beyond 20 atomic layers. Certainly

Figure 2. Schematic representation of the hypothetical structure of the metal/solution double layer showing the approximate extent of various characteristic regions.

the first several layers are involved. Three dimensional reciprocal space is not expected to be strictly valid in approximating the electron wave functions here since lattice periodicity is limited perpendicular to the surface.

Photon penetration The photons probe a region which can be characterized by α^{-1} , the inverse of the absorption coefficient. This is the depth at which the light intensity has dropped to e^{-1} of its incident value. It is usually over 100 Å and may be a micrometer or more.

CHAPTER II. EXPERIMENTAL

Solid Electrodes⁴⁰

Solid electrodes are characteristically influenced by chemical interactions. They have a tendency to acquire anodic films involving oxygen and layers of cathodically adsorbed hydrogen. There is still some doubt whether an ideal double layer region exists. Specific adsorption is a more critical factor, and the geometry on the molecular level is often unknown. For these reasons, electrochemistry has been based on studies of the mercury electrode. It is physically smooth and homogeneous, renewable, and chemically inert. It is possible to work with solid electrodes, however, the utmost care must be adopted.

The first criterion should be reproducibility. Minute impurities may be strongly adsorbed and thereby concentrated at the interface leading to errors. These impurities tend to fall into one of two categories.

1. Inorganic impurities. These may be oxygen or heavy metallic cations that could undergo oxidation or reduction resulting in a steady flow of direct current. The electrode is then no longer ideally polarized. Although dramatically affecting the $I(\phi)$ results, this type of impurity should not affect the capacity measurements.

2. Surface active contamination. This category includes specifically adsorbed ions or organic molecules. Even concentrations below normal detection levels are enough to ruin the surface.

In addition to the inherent difficulties involved with solid electrodes there is the haunting problem of how to provide for an inert electrical connection. This is combined with the necessity of mounting the sample in a molecularly tight mount. The criterion of inertness is quite restrictive. The only trustworthy construction materials are quartz and teflon. Even these have limitations. By the time the demands of optical studies are added to the list, the experimental difficulties have become quite formidable. On top of all this, when single crystal electrodes are studied, the requirements become almost incompatible.

With single crystals, mounting is particularly critical. The sample cannot be squeezed since this would induce a lattice perturbation in the form of strain. In addition, the surface must be prepared in such a way that all the work-damaged material produced in the polishing process is completely removed. In order to exploit the single crystal to advantage, it must be accurately oriented with respect to the experimental measurement.

Surface Preparation

Mechanical polishing

It is known that spark cutting induces deformation to a depth of 100 micrometers, even with medium energy sparks.⁴¹ The resulting surface must be ground flat with a suitable abrasive such as 600 grit SiC paper. It is important in this step to provide a flowing stream of water across the surface of the paper to carry away abrasion debris

which could cause additional damage beyond that produced by the 0-40 micrometer particles. This treatment must then be followed by a series of successively finer abrasives imbedded in a polishing cloth. The polishing time for each grade is much longer than that required to remove the visible scratches left by the previous grade. Particularly with softer metals, such as the noble metals, polishing is a combined process of erosion and filling. An apparently smooth surface actually contains plastically deformed regions where "valleys" have been filled in. These show up in a chemical etching treatment that preferentially attacks such regions. Even with 500 Å size particles the damage can range up to 11,000 Å.⁴¹

The surface treatment followed in my experiment is shown in Figure 3. The description is for Ag, which was studied more extensively than Au, however the mechanical polishing techniques were identical.

The sample of Ag was an ingot of 99.99% purity, oriented with the [110] direction parallel to the long axis. The Au crystal was not measured for composition but it was assumed that it was of at least routine purity. Back reflection Laue x-ray studies assisted in the orientation before cutting to expose the (110) and (100) planes of Ag, and the (110) plane of Au.

After spark cutting the samples into 1/8" wafers, they were ground flat using the technique described above. A short Ag wire was attached to the back side with radio solder. This stub was later used as a projection for making electrical contact. I performed the

PRELIMINARY TREATMENT			
ORIENTED Ag INGOT	→	SPARK CUT DISC SAMPLE	→
		GRIND FACES FLAT #600 SiC	→
			SOLDER ELECTRICAL CONNECTION
MECHANICAL POLISH			
VIBRATORY POLISH 3000Å ALUMINA	→	ULTRASONIC CLEAN IN ACETONE	→
		HAND POLISH 500Å ALUMINA	→
			RINSE IN DOUBLE DISTILLED WATER
ETCH-ATTACK CHEMICAL POLISH		ELECTROCHEMICAL POLISH	
5 PARTS NH ₄ OH 3 PARTS (30%) H ₂ O ₂ BY VOLUME 500Å ALUMINA SLURRY 1. SKID POLISH ~ 5 MIN 2. ETCH RINSE ~ 15 SEC		KCN 37 g/l IN AgCN 35 g/l DOUBLE K ₂ CO ₃ 38 g/l DIST. H ₂ O Ag CATHODE; ROOM TEMP ($\phi_{\text{Ag}} - \phi_{\text{SCE}}$) = -0.25 VOLTS 1. SLOW STIR ~ 10 MIN C.D. ~ 60 MA/CM ² 2. STILL ~ 5 MIN C.D. ~ 15 MA/CM ²	
HEAVY FLUSH WITH DOUBLE DISTILLED WATER			
INTO NITROGEN CHAMBER			

Figure 3. Technique for preparing smooth, strain free single crystal surfaces of Ag.

preliminary fine polishing on a Beuler "Vibromet" vibratory polishing machine using a slurry of 3000 Å alumina. In some of the runs an additional fine polishing step was added in 500 Å alumina slurry by hand. At this point a longer thin Cu wire was fastened to the projecting wire on the back of the samples using a conductive glue ("Duco" cement and Ag paint).

Removal of surface damage

Noble metals, because of their inert character, are difficult to chemically or electrochemically polish. Ag is particularly temperamental. After many unsuccessful methods were tried, including thermal annealing, a potentiostatically controlled electropolishing technique and an etch-attack polishing method were adopted.

As shown in Figure 3, the etch-attack involves simultaneous chemical action and mild abrasion by using the etchant instead of water in the slurry. It is very tricky since the chemical reaction heats up the surface and drives the system into conditions which promote the formation of contaminating films. With care it can produce a surface of considerable crystallographic perfection.⁴² I used a final wash of the crystal in the etchant to ensure that all traces of abrasion were eliminated.

It was necessary to employ potential control in the argentocyanide electropolishing of Ag⁴³ (Appendix C). I used a saturated calomel reference electrode (SCE) and a Ag wire counter electrode in a conventional, air saturated electrochemical configuration. A control

circuit similar to that utilized in the ER measurements (described later) maintained the desired Ag sample potential with respect to the SCE. The whole operation was conducted in a ventilation hood due to the extreme toxicity of the electropolishing solution. The composition of that solution as well as the operating conditions for satisfactory polishing are outlined in Figure 3.

The Au sample was electropolished under the less sophisticated, standard current control configuration. The electrode potential was not monitored so the SCE was not needed. I used a solution of 10 parts glacial acetic acid to 3 parts sulfuric acid in a stainless steel beaker that acted as the cathode. A current density of about 4 A/cm^2 was passed through the cell for about 15 seconds. This rather high current density caused vigorous oxygen evolution which seemed to be required for satisfactory polishing. Ultrasonic stimulation to break up the oxygen bubbles resulted in a less perfect surface.

The samples appeared very clean and bright after the final treatment. The Ag crystals had a few microscopic pits presumably due to crystallographic imperfections. This was more pronounced on the etch-polished samples. The Au crystal exhibited some minor irregularities which I attributed to action due to the oxygen evolution. This was verified by different agitation schemes.

Grazing-incidence electron diffraction was performed on an etch-polished Ag sample. The spot pattern indicated the surface was free from strain.⁴²

It is expected that the microscopic topography of these surfaces was far from the ideal single crystal plane. Any orientation error would have produced a stepped plane. More serious is the result of the mechanical and electropolishing procedure. Even if the surface appeared unstrained by electron diffraction, there might have been high and low spots. I do not believe that the non-uniformity was severe, but the surface was certainly not ideally planar. I do feel that the single crystal surface perfection achieved in this research represented the state of the art in electrochemical studies.

Electrochemical Methods

Drop technique

Instead of the usual method of studying electrodes, I employed a technique whereby the electrolyte was confined to a single drop which rested on the sample top surface.⁴⁴ This had the advantage in single crystal studies of leaving the sample completely free on all sides without the strain-inducing mount. Only one face was exposed to the solution so that well defined crystallographic studies could be made. Electrical contact could be made to the back of the sample without fear of contamination. However, the most attractive feature was that the solution-volume-to-electrode-area ratio was greatly reduced. If any contamination were present in a minute concentration, the total amount available, even if it were all adsorbed, would have no noticeable effect on the measurements.

Figure 4 shows my realization of this technique. The sample (a), which was about 1/2" dia., was provided with electrical contact via a thin Cu wire (b) which was attached to the back side. It rested freely on a hollow teflon pedestal (c) which was secured to an overflow basin (d) with a hollow Kel-F screw (e). The electrolyte contacting the sample was restricted to a drop (about 0.1 ml) resting on the horizontally exposed upper face. The drop was flattened by a quartz optical window (f) that was supported from the side by a quartz rod extension (r). Electrical contact with the drop was achieved with solution-bearing, thin bore glass capillaries. Capillary-g led, through a closed stopcock (h), to a small reservoir in which a Beckman asbestos fiber junction reference electrode (i) was dipped. Capillary-j led, through a medium-porosity fritted glass membrane (l), to a closed compartment which contained the counter electrode. The counter electrode was the coiled extension of a Pt wire (n) that was sealed in the outer half of a small standard taper joint (m). The entire counter electrode chamber could be filled with solution, then sealed shut, to prevent solution from streaming into the drop by capillary action, through a fill port and teflon cap (k). Tube-p led to a 100 ml all-glass syringe filled with fresh solution (not shown) and tube-q led to a similar empty syringe (also not shown). This system was designed to enable the drop to be renewed without wetting the sides of the crystal. In some trials tube-q was eliminated and the excess solution allowed to drop over the sides of the crystal into the

Figure 4. Capillary electrode placement and sample mount (shown with a (110) Ag sample) used in the drop electrochemistry configuration. The components marked with letters are identified in the text.

overflow basin. The light was incident from above and was focused to a spot (s) which was 1x5 mm in extent.

This entire assembly was made to fit inside a plexiglas box with a quartz window in the top. The front of the box, provided with a silicone rubber seal, was removable to permit access to the interior. Although other investigators of metallic ER⁴⁵ reported no affect due to oxygen in the solution on the $\Delta R/R$ spectra, I believe it is important to eliminate oxygen to avoid its interference in electrochemical monitors and because in the elimination process, one also gets rid of other airborne contamination. The plexiglas box was supplied with a flowing atmosphere of purified, water-saturated nitrogen.

Electrolyte

A suitable electrolyte must meet several criteria. It should be of high conductivity. It should be easily purified. The pH value should allow a wide range of electrode potentials without solution breakdown. Finally, it should contain an anion that has a low tendency for specific adsorption.

Ideal choices from the chemical point of view are NaF (which is the electrolyte with the least known tendency for adsorption) and NaClO_4 . These have rather low conductivities that cause stability problems with the control circuitry (described later). In this research I have chosen KOH and HClO_4 .

KOH is a base. It permits a moderate negative polarization of the electrode without hydrogen evolution. The hydroxyl ion does not

specifically adsorb to any great extent, and the solution displays a high conductivity. In addition, solutions with OH^- as the anion are particularly suitable for optical studies of the electrode. The molar polarizability and molar volume of OH^- are similar to water,⁴⁶ the chief constituent of any aqueous electrolytic solution. Hence, the refractive index of an OH^- layer, if such a layer exists, would be close to that of water.

HClO_4 is an acid with an anion of low adsorption capability. The conductivity is very high, and the allowable electrode polarization range to positive values is appreciable.

Chemical procedure

All the glassware and teflon parts which contacted the solution were treated with 400°C concentrated sulfuric acid then rinsed with twice-distilled water till no trace of the hydrogen ion was detected in the rinsings. Suction, provided with a syringe, was used in this process to insure thorough cleaning of the fritted glass membrane. After the acid treatment, only the outside surfaces of the pieces were handled, and those with neoprene rubber gloves.

The nitrogen was collected from the boil-off of a large liquid nitrogen storage tank. It was passed through an activated charcoal filter then over Cu turnings at 200°C . The Cu had previously been activated by heating it to 400°C in the presence of molecular hydrogen. The final gas treatment was a presaturation with water in a gas wash column. The resulting gas should have been free from oxygen and organic impurities.

The water for preparation of the solution and final rinsing of the apparatus was twice-distilled from an alkaline permanganate solution of deionized water in a closed, quartz still. The absolute purity of the product was not known. However, this water was acquired from a laboratory engaged in surface studies of the Pt electrode. These investigators found the same water quite satisfactory for their critical applications.

The electrolyte was prepared from Fisher "Reagent ACS" grade 70% HClO_4 and "Certified ACS" grade KOH without further purification. Although trace impurities might be expected without pre-electrolytic treatment of the prepared solutions, it was not deemed necessary with the small solution volume actually allowed to contact the sample. The solutions were pre-saturated with N_2 before the syringes were filled.

With the HClO_4 electrolyte it was necessary to fill the salt bridge chamber of the calomel reference electrode with saturated NaCl rather than saturated KCl solution to avoid the formation of a precipitate at the fiber junction. When this electrode was used it has been reported as SCE (NaCl). The equilibrium potential of this reference did not differ appreciably from the conventional KCl filled type.

Optics and Electronics

Optical system

I placed the plexiglas box inside a light-tight enclosure which contained the focusing and detection optics. This was a multi-braced steel frame covered with rubber sheeting and sealed with putty. The

entire front of the enclosure was removable for access to the experiment.

Figure 5 is a schematic illustration of the interior of the light enclosure showing the path of the light. Not shown in the figure is the compressed air cooled 900 watt Xenon arc lamp which was a source for the Leiss model 9100 double monochromator. Quartz prisms were used over the entire spectral energy range. The monochromator was calibrated from 1.6 eV to 4.5 eV using Osram spectral lamps. Using a slit width of 500 μ meters my spectral resolution (defined as the width of an atomic emission line at half maximum) was 0.025 eV in the region of 3.64 eV. The resolution is better at higher photon energies and worse at lower energies for the constant slit width used in this experiment.

The exit slit of the monochromator is shown in Figure 5 (a). The light was collected by a 5 inch diameter, f/6.4 spherical mirror (b), which was masked to a 2 inch diameter, and directed to a planar mirror (c) which deflected the beam downward. A 2 inch diameter Polacoat thin film polarizer was mounted in a rotatable mount at position (d). A gear and index mechanism allowed the orientation of the plane of polarization to be controlled from outside (e) the light enclosure. In some experiments a mechanical drive was added in place of the manual crank at (e). The plexiglas box (k) is also shown with a simplified interior (no controlling electrodes) for clarity. The light passed into the nitrogen atmosphere through the quartz plate (f) to the sample (g). The return beam was collected, as soon as there was

Figure 5. Interior cross section of the light enclosure showing the optical components (identified in the text).

a spatial separation of the incident and reflected beams, by a beveled diagonal mirror (h). A quartz lens (i) introduced enough convergence to concentrate the beam so that it was slightly larger than the photocathode of the detector (1 cm dia.). The photomultiplier (j) was an EMI 6256B and is characterized by a S-13 response (usable from 2 eV to 7.5 eV).

In this diagram the position of the fresh solution (l) and used solution (n) syringes is also shown, as is the nitrogen gas inlet (m).

Control electronics

The entire control and detection electronic system is illustrated in block form in Figure 6.

The main component of the control circuit was the potentiostat (POT). A schematic of this device is shown in Figure 7. A bipolar operational power supply (Kepco 72-1.5M) (BOP) served as the adding amplifier as well as the power booster. The high impedance operational amplifier (Analog Devices AD506L) was employed in the buffer mode to protect the reference electrode (SCE). In operation the BOP adjusted its output to the counter electrode so as to keep the difference between its inputs equal to zero. The sum of the AC and DC inputs and the feedback voltage was present at the inverting input. Since the non-inverting input was grounded, the output was adjusted so that the feedback (which was minus Φ_{SCE}) was minus the AC and DC inputs.

The sample current was monitored by the voltage developed across a one ohm load resistor. The variable feedback elements served to

Figure 6. Block diagram of the control and detection electronics.

Figure 7. Schematic diagram of the control potentiostat.

control the gain and stability of the control system. External input to the potentiostat was supplied by one (or both) of two signal generators. The high frequency modulation potential was developed with a sine waveform (Hewlett-Packard 200 CD). The DC potential was scanned with a triangular waveform (Wavetek 142). Not shown is a low voltage regulated power supply⁴⁷ which was the source of the non-varying DC bias potential.

Various potential and current monitors were employed to achieve operation versatility.

- Potential
1. An x-t recorder (Varian G-14A-1) provided a continuous record of the DC potential of the sample.
 2. Visual readout on a digital voltmeter (Fluke 8000A) (not shown) monitored the DC potential.
 3. The x-axis of an x-y recorder (Moseley 2D) was driven as a function of DC potential for $I(\Phi)$ measurements.
 4. The x-axis of another x-y recorder (Hewlett-Packard 7001AM) was driven versus DC potential for $R^{-1} \Delta R(\Phi)$ measurements.
 5. AC potential waveform was monitored on an oscilloscope (Tektronix 535A).
 6. AC potential rms values were recorded with a VTVM (Hewlett-Packard 4000H).

Current The voltage across the load resistor was monitored.

1. DC values were recorded with a milli-micro voltmeter (Keithley 149). This had an amplified output which was fed to the y-axis of 3 above.
2. AC values were monitored by 5 above and by another VTVM (Hewlett-Packard 400D). The output of this instrument could be fed to the y-axis of 3 above for capacitance versus Φ measurements.

The electrochemical cell, which was a load for the control system, acted like a low pass filter that handed back to the BOP, through the feedback loop, only the low frequency component of the voltage delivered by the counter electrode. The cutoff frequency (f_{co}) was approximately $(2\pi C_{dl})^{-1} \cdot (R_{solution}^{-1} + R_{faradaic}^{-1})$, where C_{dl} is the double layer capacitance, and the resistances are in the solution from the counter electrode to the reference electrode, and in the double layer due to faradaic chemical activity. The faradaic resistance was usually high when double layer operating conditions held. In this case f_{co} was determined, outside of uncontrollable variables, by the solution resistance, and the electrode area. In a given configuration the area, which was large in my case, was fixed. It was desirable then to work with highly conductive solutions. In practice my control system would not pass a square wave to the electrode without distortion when operating at $f < 40$ Hz in 0.5M HClO₄. To enable operation at higher, noise free frequencies, a sinusoidal waveform was used. The modulation was conducted at 1000 Hz in most cases.

Detection electronics

A second home-made, regulated, DC power supply⁴⁷ provided voltage to a 10 turn rheostat mounted on the monochromator drum. This was set to provide a 1 volt/turn output which was fed to the x-axis of the HP recorded for $\Delta R/R$ versus photon energy runs. The resolution of this technique was limited by the size of the voltage steps due to the windings on the rheostat. This amounted to 2 mV or about 0.025 eV at a 3.0 eV photon energy.

The monochromator drum was driven by a 10 rpm synchronous motor coupled through a gearbox which usually was set at a speed reduction ratio of 1/100. The result was a scan rate of 1 turn per 600 sec. At this speed it was possible to set the time constant of the lock-in amplifier to 300 msec, which is 1/4 the time resolution imposed by the rheostat windings.

Figure 8 is a schematic of the electronic servo⁴⁸ used to maintain the average anode current of the photomultiplier equal to a preset value. The high voltage was supplied by an operational power supply (Kepco OPS 2000), through the 60 k Ω protection resistor, to the dynode chain which controlled the gain of the detector. The anode current, proportional to the light intensity, was sent to ground through a 100 k Ω load across which a voltage was developed. The AC portion of this signal was sent directly to the lock-in amplifier via a small capacitor. The DC signal was isolated by a low-cutoff filter and a buffer operational amplifier. It was monitored at this

Figure 8. Schematic of the electronic gain servo used to maintain a constant DC signal from the photomultiplier.

point as well as sent, in a feedback mode, to the open loop input of the OPS. The operating level of the system could be adjusted by either of the variable resistors. I used a picoammeter (Keithley 741) in a voltmeter mode to monitor the DC signal. This was accomplished by feeding the output of the buffer amplifier through a 1 megohm resistor to the ammeter. The advantage of this instrument was a variable zero suppression which was not available on other conventional voltmeters at my disposal.

The entire detection and control electronic system had only one continuous ground. All the AC power connections were made without grounding connections. In coaxial cable that was connected to an already grounded chassis the shield connection was broken. Even the individual electronic instruments were insulated from the mounting rack in an effort to eliminate ground loops. The main system ground was connected to the high voltage end of the photomultiplier

Operating Procedure

The final sample pre-treatment for Ag was simply a heavy rinse in twice-distilled water, for gold a quick dip in concentrated nitric acid was followed by the water rinse. After this the samples were mounted on the teflon pedestal and the atmosphere box was placed in position within the light enclosure. The system was allowed to saturate with nitrogen before the drop was created.

It was necessary, with the electropolished Ag samples, to reduce cathodically the contaminating viscous layer left from the

electropolishing action⁴⁹ (Appendix C). This was accomplished in situ by holding the conditions at the electrode surface at the point where atomic hydrogen evolution was just beginning. A one half hour treatment was usually sufficient, after which the drop was renewed. Without the reduction treatment, anomalous results were observed (Appendix A). This was not necessary with the electropolished Au, which had an acid treatment prior to mounting in the apparatus, nor with the chemically polished Ag.

Cyclic voltammetry was performed. The characteristics of the $I(\Phi)$ curves identified the ideally polarizable region for each sample and indicated when electroactive impurities were present (Appendix C). A slow triangular voltage waveform was delivered to the potentiostat input on top of a steady DC bias value. The output was recorded directly on the Moseley x-y recorder. Due to a zero drift problem in the direct current detection system there was an absolute error of $\pm 2 \mu A$.

For capacitance measurements, a small (30 mV rms), high frequency (1000 Hz), sinusoidal component was added to the slow triangular sweep. The alternating current, which was proportional to the double layer capacitance, was detected with one of the VTVM's and the output fed to the y-axis of the recorder, while the x-axis was still scanning the potential. I could easily detect a change of $0.5 \mu F$ with this technique. However the absolute capacitance may be off by as much as 2 or 3 μF . In addition, there is an uncertainty in determining the

coverage of the electrode by the drop which enters into the determination of the capacitance per unit area.

In capacity data I looked for the absence of frequency dependence, the absence of hysteresis with respect to the potential, and similarity with other published results. When these criteria were satisfied, I was reasonably sure that the surface was free from films or absorbed material.

The operating procedure for taking optical data was as follows: The potentiostat maintained a constant bias with respect to the SCE reference. A sinusoidal modulation of frequency f , was applied on top of that. This produced a sinusoidal polarization of the interface. Photons interacted with the modulated interface and carried information to the detector. The signal from the detector was split into a DC component, which was fed directly to the DC monitor, and an AC signal, superimposed on background noise. The lock-in amplifier (PAR 186), which was referenced to the modulation potential, extracted the component of the AC signal channel which was in phase with the modulation at frequency f . The only source for the AC signal was a modulation on the reflectivity of the interface. On dividing the AC signal by the DC signal, all constant factors canceled leaving $\Delta R/R$ directly. Since the electronic gain servo on the detector maintained a constant DC signal, the output of the lock-in versus a scanned parameter had the same shape as $\Delta R/R$ versus that parameter.

Several modes of operation were employed:

Mode A The scanned variable of the most interest was the photon energy, $\hbar\omega$. The monochromator drum was mechanically scanned. The voltage, proportional to the drum position, was connected to the x-axis of the HP recorder, and the lock-in output was delivered to the y-axis. The result was a plot of $R^{-1} \Delta R (\hbar\omega)$.

Mode B With the monochromator set at a fixed photon energy, the slow triangular sweep was imposed on the potentiostat as the scanned variable. The DC potential was delivered to the x-axis of the HP recorder and the lock-in output directed to the y-axis. The output on the recorder was $R^{-1} \Delta R (\Phi)$ for the fixed photon energy.

Mode C The monochromator setting and the bias potential were held constant in this mode, while the orientation of the light polarization was mechanically rotated as a function of time. The lock-in output was directed to the y-axis of the recorder while the x-axis was being scanned with time (a feature of the HP 7001AM recorder). The chart output was $\Delta R/R$ as a function of the orientation of the polarization of the light.

CHAPTER III. RESULTS

Single crystals of Ag were studied much more extensively than those of Au. I believe the results for silver, based on the criterion of reproducibility, are better than any metallic electroreflectance data previously published, crystal or thin film. The results for Au, while recorded under the same operation conditions, were not numerous enough to establish their reliability. I expect that the Au data, by reason of comparison to the literature, are at least as good as the majority of previous work.

A summary of the reported data under the differing conditions of crystal orientation, surface preparation, and solution composition is given in Table 2. The numbers indicate the figure where the indicated type of data appears.

Electrochemical Results

Silver

The voltammetry, $I(\Phi_{DC})$, for the Ag (110) surface is shown in Figure 9. All potentials are expressed versus the saturated calomel electrode (SCE). In $HClO_4$ the NaCl filling solution was used. The potential axis is plotted with Φ increasing negative to the right in accordance with electrochemical convention. Cathodic current is at positive ordinates. This is the condition where electrons are leaving the electrode. The zero error is $\pm 2\mu A$.

In curve a, the double layer region is identified as the location of zero current. It is displaced toward positive potential due

Table 2. Summary of results and the figure numbers where data are located

Sample	Solution ^a	$\hat{F}$ ^b	Prep. ^c	$I(\Phi)$	$C_{dl}(\Phi)$	Mode A ^d	Mode B ^d	Mode C ^d	Peak ^e
Ag	HClO ₄	[110]	etched	9		13			22
Ag	KOH	[110]	etched			A1			22
Ag	KOH	[110]	e'pol.	9	10	14, A2	18, 19, 21	16, 20	22
Ag	KOH	[100]	e'pol.		10	14		16	
Au	HClO ₄	[110]	e'pol.	11	11	15		16	

^a1 molar.

^b $\hat{F}$ = direction of the modulating field, normal to the surface.

^cSurface preparation by etch-polish or electropolish.

^dOperating modes are described in the previous section.

^eA record of peak position as a function of Φ_{DC} .

Figure 9. Cyclic voltammetry on clean (110) Ag. Exposed top area = 0.8 to 1 cm^2 . (a) 1 M HClO_4 , etch-polished, 40 mV/sec; (b) 1 M KOH, electropolished and reduced, 20 mV/sec; (c) 1 M KOH, electropolished and reduced, wetted bottom in electrical contact with top, 50 mV/sec.

to the high concentration of H^+ ions in the acid. Hydrogen evolution was beginning at the negative end of the region as H^+ was converted to atomic hydrogen. This can be identified from the small cathodic upturn near -0.45 V. Due to the low concentration of OH^- in the acid solution, it was much harder to form the oxide. The anodic trend that is shown beginning near +0.27 V is an indication of some process involving oxygen. This curve exhibits ideal behavior. The double layer region is characterized by an almost undetectable current, all of which can be attributed to charging of the interface.

In b, basic solution allows a more negative excursion of potential, due to the low concentration of H^+ , but makes the risk of oxide formation on the positive end greater as a result of the increased OH^- concentration. The features of this curve are a slight slant toward the cathodic direction with decreasing Φ , indicating the presence of some trace amount of oxygen in the solution, and a larger current in the charging region, although still less than $5 \mu A/cm^2$.

Curve c displays a structure that I have identified with a wetting problem that was troublesome with the KOH electrolyte. In many samples the solution, due to the superior wetting ability of strong bases, crept around so as to cover the entire surface of the crystal including the sides and bottom where the radio solder contact was located. It seems as though one of the main advantages of the drop method, inert electrical contact, had been compromised. I believe this current behavior to be a characteristic only of reactions that occurred at the solder/solution interface. The justification for

this conclusion is that before wetting occurred, I observed ideal voltammetry behavior as in b. This behavior instantly changed to type c, which always displayed the same shape, when drop renewal allowed increasing coverage of the sides. When dry nitrogen was pumped through the atmosphere box to allow evaporation on the wetted sides of the crystal, thus breaking electrolytic contact with the bottom, ideal behavior was restored. The size of this structure is much less than impurity peaks in voltammetry reports in conjunction with ER studies by other investigators, where the entire solution was homogeneous and contacting the electrode.^{17,18} Nevertheless, when this behavior was present the risk of misinterpreting charge flow data and the risk of leached impurities passing into the solution from the solder was real. I do not think this was a problem with the optical measurements because the contaminating reaction occurred on the bottom of the crystal whereas the top, which was diffusion isolated from the bottom, was the only surface sampled by the light.

The $C_{dl}(\Phi)$ for several representative samples of Ag is shown in Figure 10. The solid lines with superimposed solid symbols are my data, extracted from I_{AC} . The comparison with two studies of C_{dl} from the literature^{50,51} are also shown as dotted lines. These are two of the few results available on Ag solid electrodes in concentrated solutions. Both of those studies were conducted on renewable surfaces (by scraping) with meticulous attention to purity in a standard electrochemical apparatus.

Figure 10. Double layer capacitance of Ag in 1 M KOH, electropolished and reduced; 1 kHz; ▲ (110), area = 0.8 cm², Φ_{AC} = 30 mV rms; ■ (110), area = 1 cm², Φ_{AC} = 10 mV rms; ● (100), area = 0.8 cm², Φ_{AC} = 30 mV rms. Literature comparison, renewable polycrystalline Ag, + Zelinskii et al.;⁵⁰ x Nechaev and Pautov⁵¹ in 1 N NaClO₄.

My data require an estimate of surface coverage. I used values of 1 to 0.8 cm^2 . There is a 20 to 30% margin of uncertainty in this estimate. The shape of the C_{dl} curves should be true, however the absolute value is in some doubt. The literature comparisons were strained polycrystals due to the scraping technique. The data shown as a crossed (+) dotted line were in 1 M KOH, the same as that which I used.

The two (110) surface curves from my work (square and triangle) agree well in shape. The (100) surface (circle) curve is displaced to positive Φ in accordance with theories of the double layer.⁸⁷ This would be explained as due to a shift of the potential of zero charge (PZC) to more positive values as the packing density of atoms on a single crystal surface increases. In all my data I observed no Φ hysteresis.

I believe that the electrochemical results show that I had achieved a clean surface with only water dipoles and solution ions near the uncontaminated Ag sample.

Gold

This material was observed only in HClO_4 since the PZC lies in a potential range accessible with acid electrolytes, and the conductive properties of the acid promote efficient operation of the control circuitry.

In the $I(\Phi)$, shown in the bottom portion of Figure 11, one can notice several features. The hydrogen evolution reaction starts at a

Figure 11. Electrochemical monitors on Au versus Φ , SCE (NaCl). Electropolished (110) surface, in 1 M HClO₄, 0.8 cm² coverage; bottom, voltammetry, 400 mV/sec; middle, double layer capacitance, 1 kHz, Φ_{AC} = 100 mV rms; top, Carr and Hampson⁵² in 0.45 M H₂SO₄.

less negative potential than for the Ag/HClO_4 system in agreement with the overpotential differences for this reaction between the two metals (0.2 V). It is also possible to polarize the Au to a more positive potential before oxygen involvement becomes a problem. This is due to the more inert chemical character of Au. Finally, the voltammetry displays some structure, most of which can be attributed to double layer charging since the potential was being swept at a rather high rate (0.4 V/sec). This is verified by the current increase in the region where C_{dl} is big.

My measured C_{dl} is displaced downward from the only comparison, in concentrated acid (H_2SO_4) solution, available in recent literature.⁵² This discrepancy may be accounted for by my area determination errors and a difference in the solution concentrations (0.5 M in C and H; 1 M in this work) I saw no Φ hysteresis, as Carr and Hampson did. Their structure near 0.1 V was dependent on scan direction indicating that they may have had problems.

Electroreflectance Versus Photon Energy

The data in this section were recorded under mode A as described earlier. The photon energy was scanned at fixed bias potential and $\hat{e}$ (polarization direction of the light).

Silver (110)

Figure 12 shows the orientation of the sample with respect to the light beam. The angle of incidence was as close to normal as was possible, limited by the size of the light cone, without using a beam

Figure 12. Orientation of the plane of incidence with respect to the (110) Ag crystallographic axes. Light was incident in a range of angles from 0° to 5° .

splitter. The crystal surface, denoted as (110), has three principle crystallographic directions in its face, $[\bar{1}10]$, $[\bar{1}\bar{1}\bar{1}]$, and $[00\bar{1}]$. The $[\bar{1}10]$ direction was also in the plane of incidence. Notice that p-polarization corresponds to $\hat{e}$ along $[\bar{1}10]$ and that s-polarization corresponds to $\hat{e}$ along $[00\bar{1}]$. Whenever reference is made to the orientation of $\hat{e}$, it is understood that $[110]$, $[111]$, and $[100]$ mean that $\hat{e}$ is oriented along a direction which is a symmetry equivalent, in the bulk crystal, to these directions. The total orientational uncertainty of $\hat{e}$ with respect to the crystal axes amounted to $\pm 3^\circ$.

The ER of an etch-polished sample in 1 M HClO_4 for three orientations of $\hat{e}$ is shown in Figure 13. The ordinate has been normalized by dividing the measured $\Delta R/R$ (largest peak value $-6.00 \pm 0.05 \times 10^{-3}$) by the rms driving potential Φ_{AC} (54 mV). The negative nature of the peaks were verified by monitoring the DC signal from the light detector while the potential was discontinuously stepped by 0.15 V. This check is an important procedure with any modulation experiment since there is a phase ambiguity of 180° between the signal and reference channels of the lock-in amplifier.

The peak position (3.88 eV) agrees with McIntyre's reliable results¹⁰ and is independent of $\hat{e}$. The location of structure occurs just at the onset energy for interband transitions in Ag and dies out at energies where these transitions are strong. The rapidity of the drop-off was dependent on solution composition and Φ_{DC} as described later. The beginning of the peak tails to low energy where no

Figure 13. ER of (110) Ag versus photon energy for three orientations of the light polarization $\hat{e}$. Etch-polished surface in 1 M HClO_4 ; $\Phi_{\text{DC}} = 0 \text{ V SCE (NaCl)}$, $\Phi_{\text{AC}} = 54 \text{ mV rms at 1 kHz}$.

interband effects are expected in bulk unperturbed Ag. There is no evidence of low energy structure near 3.3 eV as seen by other investigators of this using films at oblique incidence^{9,10} and microscopically strained bulk samples.^{7,15,16} I believe the low energy structure is a product of imperfect samples in those reports (Appendix A).

The most significant characteristic of my data, never before observed, is the marked anisotropy in magnitude. This feature appears at all photon energies below 4.1 eV to some degree but is much more pronounced in the peak region.

The anisotropy is a result of the symmetry of the crystal surface and not s- and p-polarization effects on the reflectance for three convincing reasons:

1. The experiment was performed with light incident in a range of angles from 0° to 5°. Under these conditions polarization effects on isotropic surfaces are unimportant. In routine optical experiments angles as high as 15° are treated as normal incidence.
2. Oblique incidence (45°) ER on thin films¹⁰ shows a polarization dependence to $\Delta R/R$ (Figure 1a). However, the effect is just the opposite of what I see. My largest peak occurs for what would be s-polarization which is in contrast to the largest peak for p-polarization in Figure 1a.
3. I have rotated the crystal 90° with respect to the incident beam (normal to the surface). The result is that the

anisotropy follows the crystal, not the s- and p-behavior of the light.

Silver (100)

According to predictions of surface symmetry arguments (Chapter 1), anisotropy should be peculiar to the (110) and lower symmetry planes. Figure 14 shows the result of the ER on the (100) face of Ag together with a comparison of ER on the (110) face measured under similar conditions. Curves b and c were recorded on the (110) face with two perpendicular orientations of the light polarization. Curves a result from measurements on the (100) face with polarization orientations along similar directions. As predicted, there is no anisotropy in any region of the spectrum on the higher symmetry surface.

The peak structure in the (100) data is shifted to higher energy. Also notice that the peak magnitude is larger in this determination. This is a result of sample to sample variation and a higher C_{dl} which, under the same operating conditions, allows a greater charging effect. The appearance of some low energy structure near 3.3 eV is attributed to surface inhomogeneities on this particular (110) sample.

Gold (110)

In contrast to Ag, my results for Au, shown in Figure 15, display no anisotropy. The size of the $\Delta R/R$ structure is smaller than that observed in Ag but still well above the noise (0.5×10^{-4}). As in Ag, the peak is negative. That is, R is a decreasing function of Φ .

Figure 14. ER of Ag for two perpendicular orientations of the light polarization $\hat{e}$ and two orientations of the perturbing field $\hat{F}$, perpendicular to the surface, electropolished and reduced, 1 M KOH, $E_{DC} = -0.6$ V SCE, $I_{AC} = 35$ mV rms at 1 kHz; (a) (100), $I_{AC} = 5.4$ mA; (b,c) (110), $I_{AC} = 4.8$ mA.

Figure 15. ER of (110) Au; electropolished, in 1 M HClO_4 , $\Phi_{\text{DC}} = 0.6$ V SCE (NaCl), $\Phi_{\text{AC}} = 100$ mV rms at 1 kHz.

The broad structure beginning well below 2 eV and topping out at 2.5 eV in addition to the plateau at about 3.6 eV compares favorably with reported thin film ER¹¹ (Figure 1b).

The structure for $\hbar\omega > 3.6$ eV has been a source of some controversy in ER as well as the reflectivity (Appendix B). Other investigators^{14,28} have seen this feature, but it was dependent on the electrode potential to a much larger degree than I observe. My results show that this region of the spectrum scales roughly in the same way as the major peak with Φ .

Summary

To emphasize the polarization dependence in a given sample, mode B was used as an operating procedure. With all other variables held constant the light polarization direction, $\hat{e}$, was scanned with time. Figure 16 is a summary of the results for the cases investigated. The abscissa is labeled for the (110) surfaces but still represents the relative angular orientation on the (100) surface. For that surface, each long tick mark represents a direction of [100] symmetry. The photon energies were located at the maxima in the $\Delta R/R$ major structure.

The anisotropy is only observed on the Ag (110) surface to well within the experimental error. Although these data represent only one photon energy and bias potential, it is significant to note that when the polarization anisotropy was absent, it was absent over the entire range of Φ and $\hbar\omega$ investigated, to within experimental uncertainty.

Figure 16. ER versus light polarization $\hat{e}$; Abscissa labels apply to (110) surfaces and represent the same angular relationships for the (100) surface. For Ag, the same parameters as in Figure 14 apply. Top, $\hbar\omega = 3.88$ eV; middle, $\hbar\omega = 3.93$ eV. For Au, the same parameters as Figure 15 apply. $\hbar\omega = 2.45$ eV.

Electroreflectance Versus Operating Conditions

In the extensive study of Ag (110), several operating parameters and electrochemical conditions were observed in relation to their effect on the experimentally observed ER. The variables of interest in this section were observed to have a minor effect compared to the influence of the three major independent variables; photon energy, electrode bias potential, and light polarization.

Modulation amplitude

A convenient way to express the effect of a variable which is not expected to modify the measurement is through the polarization ratio $\Delta R (\hat{e} \text{ parallel to } [100]) / \Delta R (\hat{e} \text{ parallel to } [110])$. The result of this analysis as a function of the modulating potential amplitude applied to the interface is shown in Figure 17. The region of amplitude independent effects lies below 35 mV rms. Most of the reported data were recorded in this region. The onset of amplitude dependent behavior is attributed to the extent of the modulation encompassing a potential region over which the double layer properties vary appreciably, or to more complicated perturbations of the electron transitions responsible for absorption.

With all other variables fixed, $\Delta R/R$ scaled linearly with Φ_{AC} , which is directly proportional to Δq , the charge modulation for amplitudes below 35 mV rms.

Figure 17. Ratio of $\Delta R/R$ on (110) Ag for two perpendicular light polarizations versus modulation amplitude (rms); same operating parameters as Figure 13.

Modulation frequency

I did not believe that it was worth a large investment of time to study the frequency dependence of the signal. The upper limit of the potential control circuitry was about 1.5 kHz, depending on the solution. This is a relatively low frequency for making any determinations as to the dynamic orientational effects of the water dipoles.

A cursory study of the frequency dependence over the limited region of possible variation revealed no change in the polarization ratio $\Delta R_{100}/\Delta R_{110}$ (40 to 1000 Hz). This indicated that the double layer could respond effectively over this frequency range and that no long time constant adsorption or reaction processes were involved. This information is largely redundant to that provided by the double layer capacitance.

Surface preparation

No major effect was observed which may have depended on the differences between the etch-attack polished and the electropolished surfaces. This was true for properly prepared and cleaned surfaces (Figures 13 and 14). On samples that still retained some surface strain after the final treatment, anomalous low energy structure appeared (Appendix A). With electropolished samples that were not subjected to the cathodic reduction pretreatment, anomalous high energy structure was seen that replaced the normal ER lineshape (Appendix A).

Solution composition

In previous studies of electric field modulation of metal surfaces, only Abelès *et al.*⁵³ with his ATR configuration on Au at low photon energy was able to observe changes attributable to the composition of the electrolyte. Other investigations^{12,28} show no major difference in ER structure due to different electrolytes. Among my results, Figure 13 represents ER in 1 M HClO₄ and Figure 14 b,c represents the characteristics of the 1 M KOH solutions. One observes different behavior for $\hbar\omega > 4.0$ eV as previously mentioned. In addition, the peak height in KOH solutions never achieved the maximum height obtainable in the HClO₄ solutions.

These two solutions are quite different and might be expected to affect the metal interface differently. The KOH is a strong base with a high proportion of OH⁻ ions whereas the HClO₄ is a strong acid with a large concentration of H⁺. The OH⁻ anion does not undergo specific adsorption whereas, while still possessing a weak tendency, the ClO₄⁻ may adsorb to some degree. It has already mentioned that OH⁻ is expected to behave like water optically while ClO₄⁻ may not.

Oxygen effects

By opening the atmosphere box which contained the exposed drop of solution, I could observe the effect of oxygen, which has the largest concentration in air, after nitrogen. The $\Delta R/R$ structure increased uniformly across the spectrum of photon energies by about 10 percent under these conditions.

The explicit effect of an electrochemically generated oxide layer was briefly investigated. A short anodic treatment in the potential region for the formation of Ag_2O resulted in the disappearance of the $\Delta R/R$ signal. When the potential was returned to the double layer region, after the current peak associated with cathodic reduction of the oxide, structure returned situated roughly at the same energy as before but severely broadened. There was no polarization dependence to this broadened structure. This test reinforces the claim that the Ag was originally clean and oxide free before the anodic treatment.

Electroreflectance Versus Electrode Bias Potential

The data in this section were recorded under mode C. With all other variables constant, the electrode bias potential, Φ , was scanned over the region of ideal double layer behavior. This technique was the best for Φ studies since it insured reproducible electrochemical conditions at all photon energies for a given Φ . I recorded data on the scan toward more positive potentials only, to make certain that the electrode was in a clean, freshly reduced state.

Results are reported for the (110) surface of Ag only, since that material was the only one exhibiting anisotropy. The potential was scanned from -1.5 V (SCE) where atomic hydrogen evolution is just beginning. Before recording data, the sample was maintained at this negative potential to electrochemically reduce the surface layer due to electropolishing as previously described.

Figure 18 shows representative results for three photon energies; before the peak (3.4 eV), very near the peak maximum (3.9 eV), and after the peak (4.07 eV). Note that Φ increases to the left. The width of the noise in the final $\Delta R/R$ spectrum was 0.1×10^{-3} . Several features are worth pointing out:

1. There is a big variation in peak height with Φ . This reflects the ability of the electrolyte to deliver charge to the metal surface. The charge modification during a half cycle of the 1000 Hz sinusoidal modulation is related to the experimentally measured I_{AC} (rms) by, $\Delta q = 4.5 \times 10^{-4} I_{AC}$. This quantity is plotted in Figure 19 together with the 3.9 eV curves from Figure 18. The optical signal scales roughly with the delivered charge but it is clear that some additional change due to Φ is also affecting the ER.
2. The scaling of $\Delta R/R$ with capacitance is only apparent at photon energies near and beyond the peak maximum.
3. The polarization anisotropy of the peak disappears for negative potentials (< -0.9 V), and reverses character at the positive end of the Φ axis. This behavior can be expressed by the polarization ratio which is plotted in Figure 20. This graph dramatically illustrates the potential region and sense of the anisotropy.
4. For $\hbar\omega = 3.4$ eV the polarization dependence reverses near $\Phi = -0.5$ V. and for $\hbar\omega = 4.07$ eV the anisotropy is constant with respect to Φ .

Figure 18. ER of (110) Ag versus electrode potential for two perpendicular light polarizations $\hat{e}$, and three representative photon energies. Electropolished and reduced surface, 1 M KOH, $\phi_{AC} = 30$ mV rms at 1 kHz.

Figure 19. Comparison of ER on (110) Ag to experimental charge delivered during a half cycle of modulation; $\Delta R/R$ replotted from Figure 18 for $\hbar\omega = 3.90$ eV; $\blacktriangle$, $\hat{e} \parallel [110]$; $\blacksquare$, $\hat{e} \parallel [100]$.

Figure 20. Ratio of $\Delta R/R$ on (110) Ag for two perpendicular light polarizations versus electrode potential; same operating conditions as Figure 18.

The data recorded with mode C for the two perpendicular polarization orientations and for a variety of photon energies were replotted with $\hbar\omega$ as the abscissa for a selection of constant potentials. This information appears in Figure 21. The region of anisotropy in the peak magnitude is clearly displayed, as is the reversal of the low energy anisotropy.

An additional characteristic of the data shows up in this figure. The energy position of the maximum of the peak is observed to shift with Φ . To most accurately study this behavior, mode A was employed. The location of the maximum in the peak of $\Delta R/R$, for $\hat{e}$ parallel to [100] under a variety of conditions, versus electrode bias potential is shown in Figure 22. Each type of symbol represents a given day's run. The parameters are listed in the captions of the referred figures. The data exhibit some uncertainty from day to day. The peak shift, clearly discernable on a single sample, is very small -- at the limits of my resolution capability. Going from zero volts toward negative bias potential, the position first shifts slightly to lower energy then bottoms out and shifts toward higher energy. The behavior of this effect is similar for all samples in KOH but occurs over a smaller potential range in HClO_4 .

Cahan et al.¹² have reported a peak shift in the ER of Au films. As the electrode was made more positive, the peak was seen to broaden and shift rather dramatically to lower energy. However, McIntyre's²⁸ more reliable data on Au exhibited no such shift within the limits of his resolution.

Figure 21. ER of (110) Ag versus photon energy and electrode potential for two perpendicular light polarizations; this graph was reconstructed from data taken under the conditions that apply to Figure 18.

Figure 22. Photon energy location of the maximum in the major structure of $\Delta R/R$ for (110) Ag versus electrode potential. For all cases $\hat{e} \parallel [100]$. Each type of symbol represent one day's results under conditions that apply to Figure 13 (●), Figure 14, (■,▲), and Figure A2. (x).

Kramers Kronig Analysis

A Kramers-Kronig inversion of the experimental $\Delta R/R$ was performed following standard modulation reflectivity techniques³ to get the differential Fresnel coefficients. These were used with the linear approximation theory (Appendix D) to get values for $\Delta\epsilon_2^b$ at the surface. This inversion depends very strongly on assumptions concerning the optical structure of the double layer. It also requires knowledge of the optical properties of the bulk metal, which vary rapidly in the region of interest.

In view of the many uncertainties surrounding the understanding of metallic ER, I have decided against basing any conclusions on the KK results. Although $\Delta R/R$ is not directly proportional to quantum mechanical absorption processes, it does represent the true experimental phenomenon. Any data processing which depends on tentative assumptions is no better than an analysis of $\Delta R/R$ itself. The experimental results will always be available for comparison to theory when more complete interpretations become available.

CHAPTER IV. DISCUSSION

The results of this investigation represent the first reproducible electroreflectance measurements on properly prepared, strain free single crystal metal surfaces. The drop technique avoided most of the sample mounting and solution purity problems experienced when conventional electrochemical procedures are employed. The improved method enabled a study of the photon energy and electrode potential dependence of $\Delta R/R$. In addition, the application of careful single crystal surface preparation techniques made possible a detailed study of the light polarization dependence which before had never been attempted.

Any explanation of the electroreflectance of Ag and Au must satisfy a number of experimental features. These are summarized in the following list. Several of the characteristics have been noted by other investigators (*). The majority are pointed out for the first time in this work since they represent experimental information never before available.

- *1. An increase in potential across a metal/solution interface produces a decrease in the reflectivity of the metal.
- *2. Structure in the spectral representation of $\Delta R/R$ occurs at the same energy as structure in R in most cases.
- *3. The major peak structure in $\Delta R/R$ tails off to low energy.
- *4. A higher energy plateau is observed in the ER of Au.
- 5. A variable high energy dropoff is present in the ER of Ag.

6. Clean, smooth, strain free Ag displays no ER structure near 3.3 eV.
- *7. $\Delta R/R$ scales with Δq .
8. $\Delta R/R$ displays a magnitude variability that depends on the electrode bias potential.
- *9. There is no dramatic difference between the ER of a metal recorded in two quite different electrolytes.
10. The magnitude of $\Delta R/R$ increases slightly with the addition of oxygen to the solution.
- *11. The maximum in the major structure of $\Delta R/R$ versus photon energy shifts with electrode bias potential.
12. The character of the peak shift depends on the solution composition.
13. The major structure in the ER of (100) Ag is shifted to higher energy with respect to the same structure in the ER of (110) Ag.
14. The ER of (110) Ag displays an anisotropy, using normal incidence radiation, that depends on photon energy.
15. There is no anisotropy in the ER of (100) Ag.
16. There is no anisotropy in the ER of (110) Au.
17. The anisotropy in the ER of (110) Ag disappears with large negative electrode potentials.
18. The anisotropy in the ER of (110) Ag occurs to some degree at all photon energies when it is present.

19. The angular dependence of the (110) Ag ER anisotropy varies with electrode potential.
20. The angular dependence of the (110) Ag ER anisotropy is independent of modulation amplitude for small amplitudes.
21. The anisotropy goes away when an oxide layer is produced on Ag.

Comparison to the McIntyre-Aspnes Theory

As outlined in the introduction, McIntyre has explained most of the previously observed features of metallic ER with his model, developed in collaboration with Aspnes, which is based on charge modulation of the free electron dielectric function in a thin inhomogeneous layer. The location of structure in $\Delta R/R$ with this model is dependent on optical coupling between the bulk solution and the bulk metal and on the location of structure in ϵ_2^b of the bulk metal. This can explain why $\Delta R/R$ is less than zero and why peaks in $\Delta R/R$ appear near peaks in R of the bulk metal (features 1, 2, and 4). Since there is not much change in the optical properties of the bulk solutions resulting from different electrolytes, this theory also anticipates the observation of feature 9.

The comparison of the M-A theory with my data for (110) Ag, shown in Figure 23, exhibits a remarkable agreement. The symbols are taken from Figure 21 and have been scaled by the experimental $\Delta q/A$. The calculation uses Eqs. (2) and (B-5). The optical properties of bulk Ag used in this determination were measured on thin films by another investigator.⁵⁴

Figure 23. Comparison of M-A model to my experimental $AR^{-1} \Delta R/\Delta q$ taken from Figure 21 for $\Phi = -1.0$ V (SCE). Experimental parameters, $\Delta q = 4.14 \mu\text{coul}$, $A = 0.6 \text{ cm}^2$. Theoretical parameters,³² $\tau = 1.04 \times 10^{-14}$ sec, $\omega_p = 1.4 \times 10^{16} \text{ sec}^{-1}$, $N = 5.85 \times 10^{22} \text{ electrons/cm}^3$, $n_a = 1.36$.

The M-A theory should be most applicable near the potential of zero charge, PZC, since the interface region is free from complicated distortions. This is the potential where, in the absence of specific adsorption, there is no excess ionic charge on the solution side of the double layer (Appendix C). This condition is analogous to the "flat band" potential about which semiconductor ER is conducted.³

The potential of $\Phi = -1.0$ V (SCE), the experimental value in Figure 23, is very close to the accurately measured value of the PZC for (110) Ag of -1.01 V (SCE). The PZC determination is probably not generally applicable to the concentrated solutions employed in my experiment where the double layer structure is dominated by the character of the inner layer. Even though the electrolytes chosen in this work do not strongly adsorb, there quite likely was some minor contribution to the Inner Helmholtz Plane in the concentrated solutions employed. Under these conditions the PZC is expected to move to slightly more negative potentials.

An additional success of the M-A theory demonstrated by my results is the linear scaling of $\Delta R/R$ with Δq (feature 7). This reflects the combined effect of the linear approximation, LA, theory and the electron density assumption.

McIntyre invoked a surface plasmon mechanism to explain the low energy structure in Ag near 3.3 eV which I see only under unfavorable conditions (feature 6). An additional discussion of this behavior is contained in Appendix A. Surface plasmons are also the source of the low energy tailing in Au (feature 3), according to McIntyre.

The M-A theory does not address itself to effects of variations in the average electrode potential (features 8 and 11) nor to any behavior related to the crystal lattice orientation (features 13 and 21). Neither does it treat the more subtle evidence of dependence on the chemical makeup of the interface (features 5, 10, and 12).

The LA theory, which is independent of the modulation mechanism, can be expanded to include anisotropy and bias potential effects, in simple additive combination. To enable subtraction of the M-A component of the signal, however, would require knowledge of how the anisotropic mechanism depends on Δq , which is not available without a detailed theory.

McIntyre²⁸ has suggested an explanation for some of his anomalous bias potential effects which may serve as an explanation of the potential dependence of the anisotropy that I observe (feature 17). In his measurements on Au films, he saw the appearance of positive structure near 4 eV which became more pronounced as the Au was biased more positive than 1.0 V (SCE). Although McIntyre's structure may be questionable, since the potential region was approaching that where oxide formation begins, his interpretation is interesting. He suggested that the positive electrode potential region caused a reducing of the effectiveness with which the bound electrons are shielded thereby allowing their contribution to the ER to be noticeable. The anisotropy reflects the interaction of the electrons, which sense the photon probe, and the ion lattice, which displays the crystal symmetry.

The modulation of this interaction probably takes place within a shallow region of the sample surface beyond which the modulating field is screened. By biasing the electrode to a more negative potential, the electron density in the surface region increases. The modulating field is more effectively screened and may not penetrate to a depth where the electrons feel the lattice. Without the lattice, the anisotropy is absent. As the electrode potential is increased positively, the electrons are "pushed" back into the region where the lattice exists and the anisotropy appears. The fact that the angular dependence of the anisotropy changes with bias potential (feature 19) illustrates the complexity of the mechanism.

Interaction Between Photons and an Adsorbed Layer

In this section I consider some of the unexplained features of the experimental ER one might be tempted to interpret as due to optical interactions with the unmodulated solution phase adjacent to the sample. If there were ions specifically adsorbed at the IHP with an orientation reflecting the two-dimensional symmetry of the surface, anisotropy might be expected. The OHP ions, which tend to have hydration sheaths and which are much farther from the effect of the lattice, would add a higher order correction to this model.

The LA theory includes the capability of describing the effect of an unmodulated overlayer through Eq. (D-3) (Appendix D). The possibility of anisotropic contributions from such a structure in the absence of anisotropy from the metal is remote for several reasons:

- a) It is not expected that the crystal lattice effect would be strong enough to orient a solution molecule and at the same time be screened out so that surface electrons in the metal had no knowledge of the lattice symmetry.
- b) In order to explain my experimental results, the overlayer mechanism must be peculiar to Ag only. The experiment was performed with the same electrolyte (HClO_4) on both Ag and Au. One would expect the same overlayer effect to operate on each metal.
- c) There is no change in the gross polarization dependent behavior attributable to solution composition (KOH or HClO_4) on Ag. The solutions of these electrolytes have a very different make-up and consequently would be expected to have a very different IHP, if it is present at all.
- d) Even if a sub-monolayer of oxide were present, it has been shown⁴⁴ that anodic oxide films tend to be amorphous and do not grow epitaxially. My cursory investigation of the ER of Ag in the known presence of an oxide (feature 21) seems to substantiate this argument.
- e) The correction term in Eq. (D-3) is of the same order of magnitude as λ/d_o . This would be no larger than 10^{-3} . If present at all, the correction would be very small and could not produce such pronounced effects as observed in experiment.

For these reasons I tend to reject the possibility of an adsorbed layer or film that has an optical effect on $\Delta R/R$ but does not perturb the metal by its presence.

Vectoral Perturbation

Several possible explanations for the symmetry properties of the single-crystal ER of metals rely on arguments centered around the symmetry properties of the face-centered cubic Brillouin zone. These ideas depend on the assumption that the electron energy states in the surface region can be represented by the band structure of the bulk, or at least that the surface electrons affected by the modulation participate to a large enough degree in interactions with bulk states, that symmetry properties of the ER signal reflect the symmetry of the bulk. This is not expected to be a good approximation for quantitative work but may clarify the understanding of the polarization dependent structure of the ER of Ag.

A formalism exists for qualitative analysis of the symmetry behavior of semiconductor ER which was developed by Bottka and Fischer⁵⁵ on a suggestion by Phillips.⁵⁶ It was originally intended for use with the Franz-Keldysh effect as a modulation mechanism but should be good for any vectoral perturbation of the joint density of states (JDOS). It is discussed in terms of the effect on ϵ_2^b for a transition between a single pair of bands. The field-perturbed result can be written by modifying Eq. (B-8).

$$\epsilon_{\mu}^b(\omega, \vec{F})_2 = A\omega^{-2} \sum_i |M_i|^2 J(\omega, \vec{F}_i) \quad (3)$$

Here, the sum i is over the symmetry equivalent (before the application of the field) regions of $\vec{k}$ -space that contribute to the transition of interest (the star of $\vec{k}$). It is assumed that there is no change in the interband matrix elements so that M_i still adequately describes the way the polarization vector of the photon samples each region i . $\vec{F}_i$, the resolution of the perturbation vector $\vec{F}$ in the local coordinate system i , has an as yet unspecified effect on the local JDOS. The orientation of $\vec{F}$ is different in each system i causing differences among the $J(\omega, \vec{F}_i)$.

Consider the f.c.c. Brillouin zone for Ag. In the energy range of interest (near 4 eV), interband transitions occur between states of Λ symmetry. This is the symmetry of a cube diagonal. There are 8 equivalent members to the unperturbed star of $\vec{k}$ (i is summed from 1 to 8). In the absence of $\vec{F}$ all $J(\omega, 0)$ are equivalent and Eq. (3) reduces to Eq. (B-8), the isotropic result. When $\vec{F}$ is present, the $J(\omega, \vec{F}_i)$ are no longer equivalent. Figure 24 shows the f.c.c. Brillouin zone and the symmetry reducing effect of a vectoral perturbation in the $[110]$ direction. The 8 previously equivalent members of the star of Λ are shown as dotted lines. Member directions terminating on the zone face (at L), shown with a double circle, are perpendicular to $\vec{F}$ (2, 4, 7, 8) while the remaining four members (1, 3, 5, 6) are oriented at 35.3° with respect to $\vec{F}$. Equation (3) now depends on photon polarization since the JDOS must remain in the sum and acts as a weight factor for M_i .

Figure 24. Brillouin zone for Ag with a vectorial perturbation, $\vec{F}$, applied in the $[110]$ direction. The eight members of the star of Λ are shown with dotted lines.

As might be expected from the general symmetry arguments presented in Chapter I, the analysis if repeated for $\vec{E}$ parallel to [111] or [100] yields an isotropic result when the photon polarization vector is restricted to lie in a plane perpendicular to $\vec{E}$.

The validity of the field-free matrix element assumption can be tested by observing the polarization ratio $\Delta R_{100}/\Delta R_{110}$ for a variety of modulation amplitudes. (See Figure 17) The demonstrated independence of this ratio for $\Phi_{AC} < 35$ mV implies that, for small modulation amplitudes, any variation in ΔR due to $\vec{E}$ occurs equally for [110] and [100] polarizations of the light. That is, the variation occurs in the JDOS, not in M_i that depends on the polarization. This provides a good explanation for feature 20.

Franz-Keldysh effect

The previous arguments describe the formalism that can explain the anisotropy in ER of metals provided a vectorial perturbation mechanism can be justified. The first guess one might explore would be to follow the quantum mechanical theory for the effect of a uniform electric field on optical transitions in a bulk crystal. The result would be similar to thoroughly researched semiconductor electric field effects, only modified by the presence of a Fermi surface. This analysis is not expected to be valid under conditions of a spatially varying field. Aspnes and Frova⁵⁷ have described a method for applying the uniform field result to an inhomogeneous system. However, their analysis assumes that at any depth the uniform field

equations apply. This requires that $\vec{F}$ be uniform over many lattice constants, a condition that clearly does not apply in metallic ER.⁵⁸

Indirect transitions

Morris and Lynch⁵⁹ demonstrated the possibility of indirect interband transitions in dilute AgIn alloys. This mechanism contributes to absorption at an energy just below the onset of direct transitions. Scattering from the In impurity atoms supplied enough momentum in that case for electrons to become excited from the p-band at the Fermi level near L_2' to the L_1 critical point. The change in wavevector (proportional to momentum change) needed to make this transition is only $0.2 \times 10^8 \text{ cm}^{-1}$, a small fraction of a reciprocal lattice vector.

If an electron could gain momentum from an interaction with the perturbing field in an electric field modulated surface region, a similar indirect interband transition may be the cause of polarization dependent structure in the ER of Ag. To estimate the magnitude of the field needed I might use the equation of motion for an electron in the presence of an electric field: $d(\hbar\vec{k})/dt = -|e|\vec{F}$. With dt of the order of an electron lifetime (10^{-14} sec) and dk equal to the needed wavevector change ($0.2 \times 10^8 \text{ cm}^{-1}$), the required field is only 14 V/cm. This is five orders of magnitude smaller than the field expected at the surface of the metal in the metal/electrolyte double layer. Even if the field were exponentially attenuated with distance into the metal, there would still be enough momentum available from

the field for indirect transitions to take place at a depth 10 times the Thomas-Fermi screening length. Certainly by this depth the bulk band structure has more meaning and field assisted indirect interband transitions might be expected.

Figure 25 shows the band structure of Ag and Au near L and the contributions to ϵ_2^b resulting from interband transitions in that region of $\vec{k}$ -space. In Ag, the p-s gap is smaller than the d-p gap. In the corresponding onset of absorption, $\hbar\omega_1$ lies at a lower photon energy than $\hbar\omega_2$. If, in the presence of an electric field, transitions were allowed from the Fermi surface to the bottom of the s-band at L_1 , then an additional contribution to ϵ_2^b would be expected below $\hbar\omega_1$. The strength of these transitions would depend on the direction of the perturbing field in the local coordinate system. This would give rise to the anisotropy producing $J(\omega, \vec{F}_i)$.

No indirect transitions are allowed at the d-p gap since the final states at L_2' are already filled.

This model does a good job of explaining the absence of anisotropy in Au (feature 16). Since the d-p gap in Au is smaller than the p-s gap, the onset of p $\rightarrow$ s transitions is swamped by the presence of strong d $\rightarrow$ p transitions. Field induced indirect transitions in Au may take place but they are unobservable.

Most recent assignments of the onset energy $\hbar\omega_2$ in Ag are about 3.87 eV (Appendix B). This is exactly the region of the greatest contribution to the anisotropy in Ag.

Figure 25. Field assisted indirect interband transitions in Ag and Au. The schematic ϵ_2^b resulting from $d \rightarrow p$ direct transitions, which start at $\hbar\omega_2$, and $p \rightarrow s$ direct transitions, which start at $\hbar\omega_1$, are also shown. Indirect transitions are masked in Au.

Stress modulation

Another possible explanation for metallic ER which includes a mechanism for anisotropy is stress modulation. In a bulk crystal a uniaxial stress lowers the crystal symmetry. However, momentum is still a good quantum number to within a reciprocal lattice vector. Transitions remain vertical and the dominant effect is due to a shift of energy gaps or a change in the amplitude of matrix elements. The differential dielectric function under these conditions approximates the first derivative of the unperturbed value. Piezoreflectance of Ag films^{54,59,60} exhibits peaks of both signs, unlike the one-signed experimental ER.

If an electric field produces a piezoreflectance signal there must be a coupling between the field and a stress. This has been observed in ER of semiconducting crystals with 43m (zinc blende) symmetry.⁶¹ However, in crystals with inversion symmetry (such as the noble metals) there is no coupling between the applied field and an induced stress. If it is present in metallic ER, stress modulation would have to exploit the lower symmetry in the surface region due to the preferred direction of the surface normal, or the direct piezo-optic effect due to pressure on the crystal surface transmitted by double layer compression. Any stress modulation mechanism must explain the absence of anisotropy in the ER of Au.

Although I have insufficient information to exclude this mechanism completely, the evidence seems to make it an unlikely consideration.

Anisotropic Electron Gas

The M-A theory assumes that only the free electron component of ϵ is modulated and that the free electrons have no interaction with the lattice. Since this model explains many of the features of ER in metals it might be plausible to hypothesize a surface electron gas which causes, through planar charge density fluctuation, most of the ER effect. If this collection of electrons were placed on top of the periodic lattice of ion cores one might expect some charge density concentration over the lattice sites. To properly describe the many-body dielectric function of this gas requires a $\vec{q}$ dependent formalism. Most of the larger Fourier components would have $\vec{q}$ perpendicular to the surface due to the severe inhomogeneity in that direction. However, some non-zero component of $\vec{q}$ would lie parallel to the surface to describe the effect of inhomogeneity due to electron concentration over the ion cores. On a (110) surface one would expect an anisotropic dielectric tensor reflecting the lack of symmetry in the plane. Surface inhomogeneities, such as bumps and steps in the lattice, could be included by considering their contribution to the $\vec{q}$ vector parallel to the surface.

The detailed formalism for this phenomenon does not exist so no additional discussion is warranted. However, it remains an interesting possibility for theoretical investigation.

Surface States

One other possibility exists which can be invoked to explain virtually every feature of the experimental ER results. This is the existence of electron states, either intrinsic or in combination with solution constituents, which are localized in the surface region and which have a different character than the bulk states.

Metallic surface states

Intuitively one might expect localized states as an intrinsic result of the lower symmetry in the surface region, even in the absence of perturbing field effects. Several theoretical works exist on the calculation of surface energy bands for metals.^{39,62,63}

Periodicity parallel to the surface is retained so that wave functions are Bloch-like in that plane. However, due to the loss of periodicity perpendicular to the surface, the wave functions are molecular-like in that direction. No calculations exist for low symmetry surfaces of noble metals so no discussion of the expected transitions or their anisotropy can be conducted.

Such surface states were suggested as a cause of ER in Au as early as 1970 by Cahan et al.¹² (see Chapter I). However with the introduction and partial success of the M-A model and because of the lack of other independent work on surface states, the idea was more or less forgotten.

Interphase surface states

These states would exist because of a complicated interaction between the electrolyte and the metal. McIntyre¹¹ has suggested that if chemisorbed species are able to alter ϵ^b in the interphase region, either through strong interaction with d-electrons in the surface atoms of the metal or by introduction of new transfer absorption processes, they would produce effects on the ER that might vary non-linearly with potential bias. These extrinsic surface states, he suggested, are expected to add a higher order correction to the M-A theory and may be responsible for the peak shift phenomenon. McIntyre²⁸ elaborated on this idea with the proposal that virtual bound states are created by the adsorbate-metal interaction which reflects the properties of the metal. Such virtual states have been observed in photoemission.⁶⁴

More recently, Bennett and Penn⁶⁵ have advanced a theory for the calculation of the optical properties of an adsorbate atom, using a Green's function technique. The formalism is rather complicated and is presented with no comparison to experiment.

Experimental electrochemical spectroscopy evidence indicates that sub-monolayer films have measurable effects on the optical properties of the substrate. Kolb et al.⁶⁶ have shown that Tl, Cu, and Pb adsorbed on Au produce reflectance changes that, to first order, closely approximate the ER of clean Au. Takamura et al.⁴⁵ observed Au in the presence of 10^{-3} M Pb^{2+} and identified four different

adsorption states with a combination of electrochemical and optical techniques. The first adsorption state produced a reflectance change that resembles clean Au ER. This effect has also been observed by McIntyre and Kolb⁶⁷ and Takamura et al.¹³ in reflectance measurements of thin oxide layers on Au. It appears as though the identity of the adatom plays a secondary role.

Using this picture, "clean" metal ER would be caused by a complex interaction between an adsorbed species and the metal which could be approximated to first order by a two dimensionally uniform electric field. The interaction would be present with water dipoles, hydrated ions, adsorbed cations, and sub-monolayer films, which would all, at low coverage, affect the metal in the same way. Changes in the electric potential difference between the metal and the solution would modify the character of these interphase surface states and would cause the observed changes in optical interactions.

The interphase surface state model could, in principle, explain most of the experimental details of metallic ER. The energy location, sign, and shape of $\Delta R/R$ would simply reflect the character of these states (features 1, 3-6, 9, 10). The fact that the structure appears where the optical properties of the substrate are rapidly changing (feature 2) could be explained by a combined effect of multiphase optics and the metallic character of the states. Changes in electron density in the surface region induced by changes in potential would modify the surface state occupation and would be manifested thru the dependence of $\Delta R/R$ on Δq (feature 7). As the potential barrier

imposed by the metal/solution potential difference is modified, the energy structure of the states would change. This would cause peak shifting (features 11, 12) as well as other bias potential dependent features (8, 13, 18-20). Since the interphase surface states would reflect the optical properties of the substrate, they would have the symmetry of the two dimensional single crystal surface region. On low symmetry planes one would expect anisotropy with normal incidence photon interactions (features 14, 15). The absence of anisotropy under negative bias conditions on Ag (feature 17) as well as its absence with heavy oxide coverage (feature 21) suggests that the interaction of the surface states with the lattice symmetry would be easily broken. The absence of anisotropy on single crystals of Au (feature 16) is not easily explained with this model. It may indicate that these states would have quite different character on Au and Ag.

Although interphase surface states can be invoked to explain metallic ER, there is danger in using them as the universal cause. In the absence of theoretical guidelines one can easily point to nonexistent theories as the source of poorly understood phenomena. This is a strong temptation, but any conclusions based on incomplete ideas should always be considered hypothetical.

CHAPTER V. CONCLUSION

The results of this research have demonstrated beyond doubt that the electroreflectance on the (110) surface of Ag involves a modulation of electron states that possess the crystal surface symmetry. The most plausible interpretation, excluding such exotic mechanisms as intrinsic surface states or an anisotropic electron gas, involves a combined effect of a McIntyre-Aspnes-like charge modulation, which is responsible for the gross details, and field assisted indirect interband transitions which add an anisotropic contribution. These indirect transitions, from the Fermi surface near L to L_1 , are suppressed by cathodic polarization (less than -0.9 V SCE) as the electron density in the surface region more effectively screens the modulating field, and by overlapping direct transitions (as in Au) which mask the observation of their effect. These ideas qualitatively explain the majority of the features of metallic ER listed in Chapter IV (features 1, 2, 4, 7-9, 14-17, 19, 20). Surface conditions, as discussed in Appendix A, explain features 5, 6, and 13, while extrinsic chemical interactions are most successfully invoked to interpret the second order effects represented by features 3, 10-12, 18, and 21.

Perhaps the most significant contribution of this work was the experimental demonstration that single crystal metallic electroreflectance can be carefully controlled and is an extremely sensitive

probe of the energy structure of the interface region. Clearly more study is required and should be directed along the following lines.

1. A more thorough measurement of the ER of single crystal noble metals other than Ag should be conducted to positively verify the unique anisotropic behavior using Ag.
2. A "dry" technique should be developed to permit simultaneous intense electric field application and optical observation on the surface of metals. This would allow the field effect to be studied without interference from a solution and over a wide temperature range.
3. Other materials that could be easily studied with the electrolyte technique include Pd, Cd, In, and Zn as well as Ni.
4. The calculation of surface energy bands for low symmetry planes of the noble metals should test the intrinsic surface state mechanism.
5. A theoretical effort should be undertaken to calculate the effect of an intense, extremely localized electric field on the bound state energy structure of a metal surface.
6. A quantum mechanical theory for optical interaction with a perturbed surface that includes microscopic inhomogeneities should be performed to provide theoretical support for surface symmetry experiments.

APPENDIX A. ANOMALOUS RESULTS

Two types of spectra that look quite different from the reproducible ER on Ag appeared under identifiable conditions and can be labeled as anomalous. They are reported here for the sake of completeness and to illustrate the importance of proper surface preparation.

Surface Film

On electropolished samples, even though they looked very clean, it was necessary to subject the surface to an in situ cathodic hydrogen reduction treatment that removed a contaminating byproduct layer. This was also found necessary in differential capacitance⁴⁹ and electron diffraction⁴² studies of electropolished single crystals of Ag. Without the reduction of this contamination, distinctly different ER and capacitance behavior was observed.

The anomalous ER is shown in Figure A1. With $\hat{e} \parallel [110]$, a negative peak was seen at 3.93 eV which is shifted only 0.03 eV from where it appeared on clean samples. However, with an increasing component of $\hat{e}$ along $[100]$, $\Delta R/R$ became dominated by a positive peak that appeared at almost exactly the same energy as the negative peak on clean samples. When the anomalous $\Delta R/R$ was present, the double layer capacitance exhibited a hysteresis with potential and looked nothing like published data.⁵⁰

This behavior could be eliminated, and the contamination removed, by biasing the sample to $\Phi < -1.2$ V (SCE), where the atomic hydrogen was just beginning to evolve, for about 30 minutes. After this

Figure A1. Anomalous ER on (110) Ag due to a contaminating film left from electropolishing. The inset shows the orientation of the light polarization with respect to the crystal. 1 M KOH; $\Phi_{DC} = -0.2$ V (SCE); $\Phi_{AC} = 35$ mV rms at 1 kHz.

treatment, the C_{dl} took on the appearance of the published data and the normal ER, characteristic of clean single crystal Ag, returned. Trace remnants of coverage may be the cause of the variability in the high energy dropoff above 4 eV in Ag (feature 5, Chapter IV). Such contamination, if present would have been below the detection capability of the electrochemical monitors.

A detailed study of this phenomenon was not made because it was considered as a contamination to the experiment. However, it exhibits interesting features of its own that warrant a more thorough treatment. The most intriguing feature is how the modulated reflectivity changed character so drastically when the plane of polarization at normal incidence was rotated. Controlled stripping voltammetry analysis should be performed to identify the extent of coverage. It might also be possible to study the chemical makeup of the surface by such techniques, or with some high vacuum method like LEED (provided the film would stand the vacuum).

Surface Distortion

Most of my carefully prepared Ag surface had ER that did not display any pronounced structure in the region 3.2 to 3.5 eV. This is in contrast to other work on Ag ER.^{7,9,10,15,16} McIntyre²⁸ reported that, in his oblique incidence ER on films of Ag, structure at 3.25 eV was very sample dependent and attributed this to the generation of surface plasmons (Appendix B). My normal incidence ER on smooth, unstrained Ag show no such low energy structure. However, on some samples it was observed (note the slight tendency in Figure 14).

In the example shown in Figure A2 the low energy structure was particularly pronounced. This sample was hastily treated with the etch-polish procedure and was left with observable scratches. There was a dramatic polarization dependence in the low energy structure and the anisotropy of the high energy peak was reduced.

I attribute the appearance of the low energy structure to surface strain. Other investigators^{7,15,17} using unpolarized light on mechanically polished bulk silver, to which no strain relief technique was applied, all show a rise at about 3.2 eV followed by a dip near 3.4 eV. The unannealed thin film data at oblique incidence^{9,10} also display this feature. It is well known that thin films exhibit a high degree of strain before annealing.

The preferential orientation may be due to preferentially aligned distortion. Electron diffraction studies⁴² on mechanically polished (1000 Å alumina) single crystals of Ag showed that there was a pronounced orientation of deformation with the [100] direction parallel to the scratches.

From this evidence it is clear that metallic ER is a very sensitive probe of the surface structure and with the proper interpretation can be used to advantage in crystallographic surface studies.

Figure A2. Anomalous ER on (110) Ag due to surface imperfection for three orientations of the light polarization vector $\hat{e}$. 1 M KOH; etch-polished surface; $\Phi_{DC} = -0.3$ V (SCE); $\Phi_{AC} = 35$ mV rms at 1 kHz.

APPENDIX B. ELECTRONIC AND OPTICAL PROPERTIES OF THE NOBLE METALS

Band Structure

The single particle electronic band structures (allowed electron energy as a function of electron momentum $\hbar\vec{k}$) of the noble metals Cu, Ag, and Au are very similar. Their real space lattice is face-centered cubic and the reciprocal space unit cell, the Brillouin zone, is the truncated octahedron. The band structures are characterized by the broad sp-band which crosses and hybridizes with the narrow d-bands. The major differences among the noble metal band structures are the position of the d-band with respect to the sp-band, the width of the d-band, and the location of the Fermi level.

Silver

Christensen has calculated the augmented plane wave bands⁶⁸ as well as the relativistic augmented plane wave bands⁶⁹ for Ag which are shown in Figure B1. The major changes in the RAPW result is the addition of spin-orbit splitting and the shift of gap energies. In considerations of electron transitions from filled states below the Fermi level to unoccupied states above the Fermi level using energy changes of less than 5 eV, attention is drawn to the region around L. The bands of interest in discussions of the optical properties are indicated in the relativistic notation as L_{6+5+} , L_4^- , and L_4^+ . The non-relativistic notation for these bands is actually better known and will be used in this work. The notation relations are summarized in Table B1.

Figure B1. RAPW band structure for Ag.⁶⁹ 1 ryd = 13.6 eV.

Table B1. Equivalent notation for the bands near L

Atomic	APW	RAPW
s	L_1	L_4^+
p	L_2'	L_4^-
d	L_3	$L_6^+ + 5^+$

The calculated p-s gap is very sensitive to the choice of crystal potential. In addition, the APW result for this gap in silver is 4.34 eV while the RAPW result, which should be more rigorously correct, is 3.48 eV. The higher energy, however, is more in line with experiment.

Gold

Christensen and Seraphin⁷⁰ have calculated the RAPW bands for Au. The form of the bands is similar to those of Ag so there is no point in reproducing them here. For the sake of this work the notable changes in going from Ag to Au are the changes in gap energies at L. The calculated d-p gap is at 1.37 eV compared to 3.82 in Ag. The s-p gap is calculated to be 3.74 eV compared to 3.48 eV in Ag. Experiments are used to adjust these assignments, however indications are that the s-p interband energy is smaller than the d-p gap in Ag, while the situation is reversed in Au.

Optical Properties⁷¹

Light acts as a probe of the electronic energy structure of a solid. By observing the photon-electron interaction, much has been learned about fundamental properties of matter. The electric field of the incident light, $\vec{E}(\vec{r}, t) \propto \exp(-i\omega t)$, induces a displacement $\vec{D}(\vec{r}, t)$ which is tensorially related to the electric field by a dielectric tensor. The Fourier transforms of these quantities are connected through the relation $D_\mu(\vec{q}, \omega) = \sum_\nu \epsilon_{\mu\nu}(\vec{q}, \omega) E_\nu(\vec{q}, \omega)$. $\epsilon_{\mu\nu}(\vec{q}, \omega)$ describes the optical properties of the medium and has the same symmetry properties as the real space lattice. The tensorial form can be simplified with two assumptions: 1) In systems of at least orthorhombic symmetry, the dielectric tensor is diagonal. 2) If the spatial dependence of the fields is neglected and the dipole approximation made, then we have the $\vec{q} = 0$ limit of the more general result.⁷² The simplified result is

$$D_\mu(\omega) = \epsilon_\mu(\omega) E_\mu(\omega) \quad (\text{B-1})$$

In general the displacement is out of phase with the field so the dielectric tensor is complex.

$$\epsilon = \epsilon_1 + i\epsilon_2 \quad (\text{B-2})$$

Energy absorption in the medium is proportional to the imaginary part of the dielectric tensor and can be easily connected to quantum mechanical energy eigenstate transition formalism. The experimentally

measured ratio of reflected to incident light intensity (R) is a complicated function of both ϵ_1 and ϵ_2 (see Appendix D). Fortunately, causality imposes an interdependence between ϵ_1 and ϵ_2 of the form

$$\epsilon(\omega)_1 = 1 + (2/\pi) P \int_0^{\infty} \omega' d\omega' \epsilon(\omega')_2 (\omega'^2 - \omega^2)^{-1} . \quad (B-3)$$

Therefore it is possible to calculate ϵ_2 from quantum mechanics and then use B-3 to get ϵ_1 .

Discussion of photon-electron interactions will be centered around two basic phenomena: 1) Single particle excitations involve the absorption of a quantum of energy from the incident photon and the resulting transition of one electron from an initial state to a higher energy final state. 2) Collective excitations are due to the incomplete screening of the long range coulomb interaction between electrons. These are manifested as a coherent oscillation of charge.

Single particle excitations

The dielectric tensor that describes the medium's response to a photon probe by individual electron transitions can be split into two terms, the free and bound electron contributions.

$$\epsilon = \epsilon^b + \epsilon^f \quad (B-4)$$

Free electron effects These excitations involve the transition of an electron from an occupied state to an empty state in the same band. For this to take place with momentum conservation, some

scattering mechanism must be involved. Prime examples are lattice vibrations and impurity atoms. This is a phenomenon of an electron gas which is to first order independent of the lattice symmetry. It is therefore expected to behave isotropically and enters as an additive contribution to the diagonal of the dielectric tensor. Its functional dependence on photon energy $\hbar\omega$ is

$$\epsilon^f(\omega) = 1 - \omega_p^2 (\omega^2 + i\omega\tau^{-1})^{-1} \quad (\text{B-5})$$

where τ is a relaxation time that characterizes the scattering mechanism and ω_p^2 is $4\pi N e^2 m^{-1}$, called the plasma frequency. (N is the electron density with m and $-|e|$ the electron mass and charge.)

Bound electron effects This category covers what are commonly called interband transitions. They result when a quantum of energy, $\hbar\omega$, is absorbed and an electron makes a transition between energy states that have the same momentum $\hbar\vec{k}$ but are in different bands. Such excitations are called direct since they involve no additional momentum change outside of that supplied by the reciprocal lattice vectors. Quantum mechanics predicts the functional dependence of the imaginary part of the bound dielectric tensor, which depends on crystal symmetry. The interband energy difference is a function of $\vec{k}$ and can be expressed as $\hbar\omega_{n'n}(\vec{k})$. The result¹ depends on a sum over possible initial states n and final states n' .

$$\epsilon_{\mu}^b(\omega)_2 = A\omega^{-2} \sum_{n'n} \frac{1}{4} \pi^{-3} \int_{\text{BZ}} d^3k |M|^2 \delta(\omega_{n'n}(\vec{k}) - \omega) \theta_{n'n}(\vec{k}) \quad (\text{B-6})$$

where

$$A = 4\pi^2 e^2 \hbar^{-1} m^{-2}$$

$$M = \hat{e}_\mu \cdot \vec{P}_{n'n}(\vec{k}) \quad (B-7)$$

$\hat{e}_\mu$ is a unit vector parallel to the photon field

$\vec{P}_{n'n}(\vec{k})$ is the interband momentum matrix element

$0_{n'n}(\vec{k})$ is the probability n' is empty and n is filled as defined by the Fermi surface .

For transitions localized in reciprocal space $\vec{P}_{n'n}(\vec{k})$ is a slowly varying function of $\vec{k}$ in that region. Under this assumption, due to the symmetry of the Brillouin zone, the integral can be separated into a sum of symmetry equivalent local integrals; i. Each local integral is taken over the restricted region in $\vec{k}$ -space where transitions occur. For high symmetry points the sum is over the star of $\vec{k}$.⁷³ The simplified result is

$$\epsilon_\mu^b(\omega)_2 = A\omega^{-2} \sum_{n'n} \sum_i |M_i|^2 J_{n'n}(\omega) \quad (B-8)$$

where

$$J_{n'n}(\omega) = \frac{1}{4} \pi^{-3} \int_{loc} d^3k \delta(\omega_{n'n} - \omega) 0_{n'n} \quad (B-9)$$

is the interband joint density of states (JDOS). In unperturbed cubic crystals, such as the noble metals, the JDOS is identical for each symmetry equivalent region i . M_i depends on the orientation of the photon field (polarization of the light) in each local system. For cubic crystals, when summed over i , the orientational dependence cancels out. The resulting $\epsilon_{\mu}^b(\omega)_2$ is isotropic (independent of μ).

The JDOS, which contains the energy structure of $\epsilon_{\mu}^b(\omega)_2$, can be re-expressed as a $\vec{k}$ -space surface integral ($\int d^2k$) over the constant interband energy difference surface (CEDS) given by $\hbar\omega_{n'n} = \hbar\omega$. The result is

$$J_{n'n}(\omega) = \frac{1}{4}\pi^{-3} \int d^2k \, O_{n'n} |\vec{\nabla}_{\vec{k}} \omega_{n'n}|^{-1} . \quad (B-10)$$

The source of structure in the JDOS can be identified from Eq. (B-10). The most obvious causes are extrema in the interband energy difference $\hbar\omega_{n'n}$. This makes optical interactions a sensitive test of critical point energy gaps. A more subtle cause of structure can be traced to the occupation factor $O_{n'n}$. The JDOS is basically the weighted area of the CEDS. The Fermi surface defines how much of this area should count. As $\hbar\omega$ changes, the CEDS varies. If the Fermi surface has a shape similar to the CEDS for some photon energy range, then while that range of energies is being scanned, the effective CEDS area changes rapidly. This causes a rapid alteration in the JDOS and therefore in the interband dielectric tensor $\epsilon_{\mu}^b(\omega)$. It is this occupation factor mechanism that is the source of the interband onset structure in the noble metal optical properties.

Collective excitations

Included in this category are bulk charge fluctuation effects (plasmons) and surface charge oscillations (surface plasmons). Bulk plasmons, since they represent a periodic bulk charge concentration, cannot be excited with the transverse fields present in light. Because of the equivalence of the transverse and the longitudinal dielectric functions in the $\vec{q} = 0$ limit, the conditions for bulk plasmon excitations to exist, if a longitudinal probe were available, can still be determined. This phenomenon is not of obvious concern to metallic ER. The surface plasmons, however, can exist in a variety of modes. With the aid of surface roughness caused by imperfect planar topography some of these modes can radiate and thus can be excited by light. The conditions for excitation of a surface plasmon can be estimated from an elementary study of the electromagnetic boundary conditions at a solid surface. At an interface between a substrate (s) and an ambient medium (a, here assumed to be non-absorbing) the result is that there must be a photon field component normal to the surface with

$$-\epsilon_{s1} = \epsilon_a, \text{ and } \epsilon_{s2} = \text{small} . \quad (\text{D-11})$$

If a simple free electron model with $\tau = \infty$ (Eq. (B-5)) is used for ϵ_{s1} , the surface plasmon energy requirement is

$$\hbar\omega = \hbar\omega_p(\epsilon_a + 1)^{-1/2} \quad (\text{B-12})$$

At a vacuum interface $\hbar\omega = \hbar\omega_p(2)^{-1/2}$. In a more dense ambient medium the surface plasmon is shifted to lower energy.

Experimental Applications

Silver

The bands near L, the dark region in Figure B1, which are responsible for the interband optical properties of Ag near 4 eV are shown in Figure B2. The assignment of gap energies and effective masses is due to Rosei et al.,³⁴ and is based on experimental thermomodulation at low temperatures. $\vec{k}_\perp$ is perpendicular to Λ , the 3-fold rotational symmetry axis, and $\vec{k}_\parallel$ is parallel to that axis. The onset of p $\rightarrow$ s transitions, 3.87 eV, occurs before the onset of d $\rightarrow$ p transitions, 4.03 eV. The results of this assignment as well as a representative selection of other experimental assignments can be summarized in tabular form.

Table B2. Assignment of interband onset energies (eV) in silver

Reference	Method	$\hbar\omega_1$	$\hbar\omega_2$	$\hbar\omega_c$
74	piezomodulation	3.8		4.1
75	alloys	3.88	4.4	4.1
76	optical properties	3.86		
54	piezomodulation	3.98	3.92	4.25
32	thermal variation	3.87		4.11
34	thermomodulation	3.87	4.03	4.16
77	fit to data of Ref. 74	3.87		4.2

Figure B2. Band structure of Ag near L showing the three bands responsible for optical structure near 4 eV. $\parallel$ and $\perp$ refer to orientation with respect to the rotational symmetry axis Λ . The effective mass is a measure of the inverse curvature of the band. Assignments are due to Rosei et al.³⁴

the $d \rightarrow p$ transition causes a more dramatic structure than the $p \rightarrow s$ transition.^{34,78} Recently experimental support for Christensen's calculated $\hbar\omega_c (L_2^I - L_1)$ has been offered⁷⁹ by an assignment of 3.33 eV based on dilute alloys of Cd, Mg, and Sn. This interpretation depends on an extrapolation which may become quite tenuous at low concentrations due to the possibility of indirect transitions. It has also been suggested³² that the onset edge is not confined to a small region around L and that extended regions of $\vec{k}$ space contribute. This would make the constant matrix element approximation invalid.

At the Ag/vacuum interface the surface plasmon energy occurs at 3.64 eV.⁸⁰ This was demonstrated on rough thin films. The surface plasmon was subdued on smoother films.

Gold

The onset of interband transitions in Au occurs first from the $d \rightarrow p$ gap and has been located near 2.5 eV.^{32,81,82} However RAPW calculations of Christensen and Seraphin⁷⁰ for the CEDS and the Fermi surface indicate that there is a coincidence of the two at 2.38 eV over a large region of $\vec{k}$ -space. This would make the localized transition interpretation invalid.

The absorption edge tails to lower energy than expected from thermal broadening of the Fermi surface. This has been identified^{32,83} as being due to low energy interband transitions at X which begin at about 1.7 eV. These transitions are very weak however and are manifested as a small correction to the major structure near L.

The higher energy transitions, $p \rightarrow s$, are more in doubt. Some idea of the experimental uncertainty can be appreciated by studying the following table.

Table B3. Assignment of $\hbar\omega_c$ ($L_2^I - L_1$) in gold

Reference	Method	Assignment (eV)
83	piezomodulation	3.55
84	photoemission	4.00
85	thermomodulation	3.60
32	thermal variation	4.20
77	data fit of Ref. 83	4.57

The position of this critical point affects the onset energy $\hbar\omega_1$ which can be located near 3.56 eV.^{77,32} Other interpretations⁶⁰ of structure in piezomodulation at 3.6 eV assign this feature to transitions at X. However, due to small matrix elements for this transition it is not expected to contribute strongly.

Surface plasmons have been observed at 2.7 eV^{81,86} on roughened films and were subdued on flat films under the same conditions.

APPENDIX C. ELECTROCHEMISTRY

The Solution Side of the Double Layer^{87,88}

The so-called double layer occurs when phases containing charged particles, permanent dipoles, or induced dipoles meet to form an interface. Macroscopically the assembly appears like a dipole sheet. Microscopically the structure of the double layer may be quite complex. This section deals with the double layer at the interface between a metal and an aqueous electrolytic solution with the emphasis on the solution contribution.

Figure C1 depicts a hypothetical double layer. The metal regions are discussed in Chapter 1. In the solution, characteristic regions are indicated by their approximate locations. The distances depend on the makeup of the solution so the figure should be considered schematic only.

Inner Helmholtz plane (IHP)

This is designated as the location of electrical centers of specifically adsorbed ions. The term specific implies that forces other than pure electrostatic attraction maintain the adatom/substrate bond. These ions are in intimate contact with the metal surface so the location of the IHP is approximately the radius of a bare ion, less than 2 Å. Even in the presence of heavy specific adsorption, the overwhelming portion of the metal surface is still covered with water dipoles. The highest observed specific adsorption coverage is less than 20 percent.⁴⁰ The adsorbed species tend to be anions,⁸⁹ large cations,

Figure C1. Schematic representation of the hypothetical structure of the metal/solution double layer showing the approximate extent of various characteristic regions.

and organic molecules. Easily adsorbed ions tend not to have primary hydration sheaths. The ionic tendency for specific adsorption is summarized in the following table.

Table C1. Specific adsorption tendency (increasing downward)⁹⁰

Anions	Cations ^a
F^- , $H_2PO_4^-$	Li^+
OH^-	Na^+
Cl^- , NO_3^- , ClO_4^- , IO_3^- , BrO_3^-	K^+
Br^-	Rb^+
SCN^-	Cs^+
I^-	Tl^+

^aThere is no equivalence between the cations and anions of this table. Only the vertical order is significant.

Organic adsorption is most favorable when the water dipoles, which cover the majority of the metal, are attracted weakly to the electrode. This occurs when the metal charge is a minimum.

Outer Helmholtz plane (OHP)

This is the distance of closest approach (electrical centers) of hydrated ions. These tend to be cations. The distance is approximately the radius of a solvated ion. The OHP to IHP length is less than about 5 Å. The OHP and the IHP comprise what is frequently

called the inner layer. In many electrochemical approximations it is treated as a single sheet of charge located at some mean distance from the electrode.

Diffuse layer

The excess charge on the electrode (including the metal plus inner layer adsorbed ions) is compensated by an ionic atmosphere or diffuse layer composed of ions with concentration excesses or deficiencies with respect to their bulk values, and which are held in equilibrium by an interplay of coulombic and thermal forces. A concentration profile can be estimated from the Poisson-Boltzmann equation. This is the essence of the Gouy-Chapman theory of the double layer which is characterized by the Debye length, L_D . This parameter, which is independent of the makeup of the electrode, is measured from the OHP into the solution. It is the distance within which the concentration excess drops to e^{-1} of its value at the OHP and is given by

$$L_D \approx 3.3 \times 10^{-8} |z|^{-1} c^{-1/2} \quad (\text{cm}) \quad (\text{C-1})$$

where z is the ionic charge and c is the bulk ionic concentration in moles/liter. For concentrated solutions where c is near unity, L_D approaches the size of an unsolvated ion. This says that the diffuse layer in concentrated solutions is absent. The bulk concentration

is maintained up to the OHP where all the excess charge is located. An estimate of the electric field at the OHP can be made using the formalism of the Gouy-Chapman theory.

$$F \approx 1.5 \times 10^5 q \quad (\text{V/cm}) \quad (\text{C-2})$$

where q , in $\mu\text{coul/cm}$, is the integrated surface charge from the OHP out into the solution. For an integrated surface charge of only 20 $\mu\text{coul/cm}$ the electric fields are of the order of 3×10^6 V/cm! This can be established with a metal-solution potential difference of less than one volt.

Electrodes and Potentials

Electrodes

In this discussion I will consider the hypothetical electrochemical cell consisting of a left electrode (L) and a right electrode (R). The notation for the cell will be (L)/(R). The electric potential difference (PD) across the cell is defined as the potential of the right electrode minus the potential of the left electrode, $R - L$.

Two major categories of electrodes exist: 1) Polarizable electrodes are those which can assume any potential within some allowable range without the transfer of charge across the interface. 2) Non-polarizable electrodes maintain a constant potential regardless of how much charge transfer is occurring at the interface. Neither of these ideal cases exist in reality but there are good approximations.

In studies of electrode processes it is desirable to work with a cell that consists of one polarizable electrode and one non-polarizable electrode. When PD changes are imposed across the cell, the changes are concentrated at the polarizable electrode since, by definition, the other electrode maintains a constant potential. In this way one can study the polarizable electrode alone. This avoids the problem in electrochemistry associated with the inherent presence of two double layers, one at each electrode, in any cell.

Electrode potentials

There has recently⁹¹ been some controversy and misunderstanding among electrochemists over the correct relation of experimentally measured PD's to the actual metal/solution PD. In this discussion the potential of an electrode in solution is defined in terms of standard electrochemical experimental technique. This insures reproducibility and uniformity of my results when compared to the body of electrochemical literature.

An experimental cell consists of three electrodes. The sample electrode, a reference electrode, and a counter electrode. The reference electrode is some conventional non-polarizable electrode. Its ability to maintain a constant potential depends on the ease with which it can pass charge across the interface. Two commonly used reference electrodes are the normal hydrogen electrode (NHE), which achieves charge transfer through the reaction $2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$, and the calomel electrode (most commonly saturated, SCE), which achieves charge

transfer by the reaction $2\text{Hg} + 2\text{Cl}^- \leftrightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$. To ensure that the current capacity of the reference electrode is not overloaded, an electronic buffer is included to limit the demand. The counter electrode is some inert material (Pt) which merely serves to deliver current to the sample/solution interface.

The experimentally measured PD is that of the cell, (reference electrode) / (sample electrode). By standard electrochemical convention, the potential, Φ_{NHE} , of a sample electrode is defined to be the experimentally measured PD of the cell, (NHE)/(sample). The NHE is arbitrarily assigned a potential of zero. When other reference electrodes are used the electrode potential can be defined with respect to them. For instance, Φ_{SCE} is the PD of the cell (SCE)/(sample). The saturated calomel electrode is more convenient to use and was employed in this experiment. All electrode potentials reported in this work are with respect to the saturated calomel electrode. The experimentally measured PD of the cell (NHE)/(SCE) is roughly 0.24 V. The relation between the PD's of two cells with different references is

$$\Phi_{\text{SCE}} = \Phi_{\text{NHE}} - 0.24 \text{ V} \quad . \quad (\text{C-3})$$

It should be remembered that this is an experimentally defined, arbitrary means of reproducibly controlling a polarizable electrode potential and not a numerical representation of the true PD across the metal/solution interface.

Differential Capacitance

The double layer, as a macroscopic dipole layer, behaves electrically like a capacitor. Microscopically, the differential capacitance, which relates an increment in electrode potential to an increment in electrode charge, reflects the total effect of the configuration and constitution of individual components of the double layer. As such, the differential capacitance, C_{dl} , is very sensitive to structure and contamination of the interface region. There is a wide variation in experimentally reported C_{dl} which testifies to this sensitivity. Absolute purity of the system as well as a smooth sample electrode are prerequisites for reproducibility. The vast majority of double layer studies have been performed on Hg since it represents a smooth, renewable surface.

An equivalent circuit consisting of two impedances in parallel serves as a useful approximation of the double layer for analysis of the effect of rapid potential changes. The capacitive impedance decreases with driving frequency, f . The faradaic impedance (see next section), due to chemical reactions at the interface, is quite large. At higher frequencies, the AC charge flow is dominated by the capacitive impedance. Under these conditions a simple relation exists between the AC current, I_{AC} , and the AC potential, Φ_{AC} .

$$C_{dl} = I_{AC} (2\pi f \Phi_{AC} A)^{-1} \quad (C-4)$$

In this equation, A is the exposed electrode area which is microscopically available to the charging process.

The Gouy-Chapman model of the electrolyte predicts that, in the absence of specific adsorption, when the sum of anion and cation charge in the double layer is zero C_{dl} is minimized. This will occur for a given system at a characteristic electrode potential, the potential of zero charge (PZC). The PD across the interface is not zero here due to surface contributions which are not included in the analysis of ionic distributions. This minimum behavior is observed in experiments in dilute solutions where Gouy-Chapman ideas hold. The following table lists the PZC's determined by the minimum in C_{dl} for single crystal noble metals.

Table C2. Potentials of zero charge for the noble metals⁹²

Material	Crystal face	PZC (volts vs SCE)
Au	110	-0.14
Ag	110	-1.01
Ag	100	-0.91
Ag	111	-0.70

Note how the PZC is shifted to more positive values as the packing density on the crystal face increases. There is a great deal of controversy concerning these assignments but the reported values in Table C2 represent the most reliable experimental information. An

extension to concentrated solutions is probably not strictly valid. It is known that the PZC shifts to more negative values in the presence of specific adsorption

Charge Transfer⁹³

A polarizable interface acts like a capacitor in that it prohibits the transfer of charge across the boundary. After charging conditions have been established there is no net current flow through a cell with such a sample electrode. If current is present after charging it reflects charge motion with adsorption processes or the presence of a chemical reaction (faradaic current). If electrons are supplied to the solution from the electrode there is a cathodic current. When electrons are supplied to the electrode from the solution an anodic current results. There is an energy barrier at a polarizable electrode that prohibits these mechanisms. The barrier can be manipulated through changes in the electrode potential to inhibit or promote the tendency toward charge transfer processes. When the variation promotes activity, the transfer proceeds at a rate determined by Φ and the concentration of reactants. As the energy barrier is approached and surpassed in a potential scan, the current first increases. With reactant depletion near the electrode the current eventually decreases causing a peak in the $I(\Phi)$ curve. With faradaic reactions the same behavior is observed if reaction products build up, however if a steady state can be achieved, the current will level off.

Charge transfer currents invariably accompany the formation of an adsorbed or reaction product film, contamination of the solution, or decomposition of the sample. In double layer studies such as ER it is essential to avoid the conditions which promote charge transfer. By monitoring the $I(\Phi)$ behavior of the electrode, voltammetry, the polarizable potential range can be identified and electroactive impurities detected.

In the absence of impurities the ideally polarizable region is limited on the negative end by the beginning of hydrogen evolution as electrolysis of water starts. The reaction rate depends on the concentration of H^+ in solution which is reflected in the pH. Acids have a high H^+ concentration, usually in the form H_3O^+ , and a low pH while the reverse condition applies to bases. An approximate relation for the hydrogen evolution reaction is given by the potential $\Phi_h|_{SCE}$ where the reaction results in a current density of about $10 \mu A/cm^2$.

$$\Phi_h|_{SCE} \approx -(\Phi' + 0.06 \text{ pH} + 0.24) \text{ in volts} \quad (C-5)$$

The so-called hydrogen overpotential, Φ' , is different for each metal. For silver it is 0.2 V while for gold it is zero. Using C-5, $\Phi_h|_{SCE}$ estimates in 1 M H_2SO_4 are -0.5 V for Ag and -0.3 V for Au, while in 1 M KOH the results are -1.3 V for Ag and -1.1 V for Au.

On the positive end, the polarizable limit is imposed by the formation of surface compounds involving oxygen as the OH^- in solution

breaks down. The reaction rate is higher in more basic solutions. Film formation may or may not be reversible.

Silver in basic solutions acquires a film of Ag_2O which begins forming at +0.1 V (SCE).⁹⁴ There is some evidence⁹⁵ that AgOH may form first at a potential slightly less positive than +0.1 V. The oxide is in a weakly bound state. It can be reduced by hydrogen⁹⁶ or decomposed by photochemical means. Gold is harder to oxidize with stable Au_2O_3 forming at +1.1 V (SCE).

Electropolishing⁹⁷

A special kind of faradaic reaction of interest to optical studies in general and ER in particular is the anodic dissolution of the sample so as to leave the surface smooth and shiny. The reaction occurs under proper conditions when the controlling energy barrier for decomposition is surpassed. Electropolishing is almost a black art in many laboratories that depend on it for sample preparation. To the field of electrochemistry it is no different from any other charge transfer process. The important variable to control is the electrode potential. The cell current will flow in response to proper manipulation of the energy barrier. Fortunately this procedure, which requires sophisticated equipment, is not required for the routine electropolishing of many common materials (i.e. Cu, Au). Sufficient control can be maintained without a non-polarizable reference electrode simply by monitoring the current. In more delicate systems such as Ag, proper potential control is required.

In Figure C2 the behavior typical to many metals is illustrated. Notice that the potential axis is plotted with increasingly negative values to the right. This obscure tradition is rooted in electrochemistry so I make no attempt to reverse it here. The zero of the graph is in the upper right hand corner. Increasing anodic current is downward.

Curve ABCDE is the normal active-passive behavior followed by many metals and alloys. In region AB, anodic dissolution of the metal occurs, however atoms tend to leave preferentially from dislocations and kinks resulting in an etched surface. As an oxide or other passivation layer is formed, the metal is covered and dissolution stops, region CD. At still more positive potentials, electrolysis begins and oxygen is evolved, region DE.

Curve ABFGE is characteristic of an electropolishing system. For potentials more positive than B, the metal continues to dissolve at an appreciable rate due to random, non-crystallographic dissolution. The current in region FG is independent of electrode potential. A viscous layer of reaction products forms soon after B that controls dissolution. This condition is desirable for maximum efficiency in producing a microscopically smooth surface.

The viscous layer may not dissolve when the sample is rinsed off. Anodically polished metals usually carry a compact solid film that is often of substantial thickness and protective value, a fact not fully appreciated by many investigators. Electron diffraction studies of electropolished single crystals of Ag⁴² display a contamination that

Figure C2. The electrode current versus potential characteristics of an active-passive metal and an electropolishing metal (dotted). The characteristic regions are described in the text. The origin of this curve is the upper right-hand corner.

is not present on chemically etched samples. Electropolishing remains, however, the best way to prepare strain free, microscopically smooth surfaces provided suitable elimination of the viscous layer is accounted for.

APPENDIX D. LINEAR APPROXIMATION THEORY FOR STRATIFIED MEDIA

The reflectance (ratio of reflected to incident light intensity) of a multiphase assembly is a complicated function of the optical properties of each phase. When considering modulation experiments where the thickness and/or the optical parameters associated with one or more phases is changing, the analysis can become quite difficult. Under certain simplifying assumptions and employing a formalism outlined by Aspnes,⁹⁸ concise expressions are obtained. This will be called the linear approximation theory (LA theory).

The quantity of experimental interest is the relative change in reflectance due to a change in the modulation parameter. This is expressed as $\Delta R/R$, where $\Delta R = R' - R$. Each separate phase, j , can be optically specified by its thickness, d_j , and its complex dielectric function, ϵ_j , or complex index of refraction, $n_j = \epsilon_j^{1/2}$. Normal incidence is assumed here so the tensorial properties of the individual phases are decoupled (orthorhombic or higher symmetry). For isotropic media an uncomplicated extension can be made to describe oblique incident phenomena.⁹⁹ Figure D1 illustrates the conditions of definition for R' and R in three simple cases of interest to ER. In each subfigure the ambient medium, from which the incident light originates, is on the right, and the substrate or bulk sample is on the left.

Figure D1. Schematic representation of stratified media configurations used in the LA theory to compute $\Delta R = R' - R$, the change in reflectivity. 1) thickness modulation, 2) thickness modulation with an inert overlayer, 3) spatially varying modulation. "a" is the ambient, "s" is the substrate.

Case 1: Thickness Modulation

This is the basic example upon which more elaborate treatments expand. The modulated condition involves an intermediate layer, ℓ , of thickness d . The temporal variation of the photon field goes like $e^{-i\omega t}$ where $\hbar\omega$ is the photon energy. With c as the speed of light in vacuum, the LA theory applies in this case when $|n_\ell \omega d/c| \ll 1$. It should be applicable when the thickness is much less than the optical wavelength, $\lambda = 2\pi c/\omega$.

$$\Delta R/R = -(\omega/c)d \operatorname{Im}[(\epsilon_\ell - \epsilon_s)n_a^{-1}D^{-1}] \quad (D-1)$$

In D-1, the parameter D describes the effect of overlayers on top of the modulated stratum. In this case there are no overlayers besides the ambient, and $D = D_1$ where,

$$D_1 = \frac{1}{4} \epsilon_a^{-1} (\epsilon_a - \epsilon_s) \quad (D-2)$$

For partial coverage the thickness assumes the value which is the thickness of a uniform layer with an equivalent optical effect to the actual inhomogeneous coverage.

The LA theory requires that the optical properties of these very thin layers be describable in terms of bulk optical functions. Clearly the severe non-uniformity requires a non-local theory for a completely rigorous treatment.

Case 2: Thickness Modulation With Overlayer

If an unmodulated overlayer of thickness d_o and dielectric function ϵ_o is added to case 1, the situation is only moderately more complicated. The result in Eq. (D-1) still holds, as it does for any number of overlayers, only now $D = D_2$ where

$$D_2 = D_1 [1 - i2(\omega/c)d_o[(\epsilon_o - \epsilon_a)/(\epsilon_s - \epsilon_a)]] \quad (D-3)$$

The LA theory is valid in the case if $d_o/\lambda \ll 1$ and as long as the correction to D_1 is small.

Case 3: Spatially Varying Dielectric Function

This case covers the situation where the modulation is manifested by the presence of a non-uniform intermediate layer which decays to the bulk substrate. Assume that the dielectric function of the substrate can be represented in functional form as $\epsilon_s(z)$, with the surface at $z = 0$. Provided the majority of the perturbation from the bulk substrate value, $\epsilon_s = \epsilon_s(\infty)$, occurs within a distance d , Eq. (D-1) holds with $(\epsilon_\ell - \epsilon_s)$ replaced by $\langle \Delta\epsilon_s \rangle$ where

$$\langle \Delta\epsilon_s \rangle \equiv d^{-1} \int_0^d dz (\epsilon_s(z) - \epsilon_s) \quad (D-4)$$

The LA theory applies when $\epsilon_s(z) \approx \epsilon_s$ and $\exp(in_s(z)z\omega/c) \approx 1$. This should be good for $d/\lambda \ll 1$.

If $\epsilon_s(z)$ has an exponential dropoff with z , then $\langle \Delta\epsilon_s \rangle = \epsilon_s(z=0) - \epsilon_s$.

General

Note that for separate additive contributions to the intermediate layer optical properties (i.e. $\epsilon_{\ell} = \epsilon_{\ell}^{\prime} + \epsilon_{\ell}^{\prime\prime}$), $\Delta R/R$ is additive

Other cases must be treated with more complicated and less easily understood formalism. Dignam et al.¹⁰⁰ have presented expressions for the optical effect of a uniaxial film with the optic axis oriented perpendicular to the surface. McIntyre²⁸ has reviewed the usefulness of optical probes of the electrochemical interface, denoted by the general term electrochemical modulation spectroscopy.

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