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Charge Flow and *d* Compensation in Gold Alloys*

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Measurements were made by x-ray photoelectron spectroscopy of the 4*f* level energies in Au and the 3*d* level energies in Ag with these elements in several forms: pure metals, Au-Ag alloys, $AuAl_2$, and $AuGa_2$. Only very small core-level energy shifts are seen, even though existing Mössbauer isomer-shift data for Au show that there are differences in *s* charge at Au sites such that one would anticipate substantial level shifts. These two sets of observations are interpreted within the framework of band theory to mean that when Au is alloyed with Ag, Al, or Ga, the flow of *s* charge onto Au sites is accompanied by a compensating depletion of *d* charge. The problems associated with relating chemical shifts in alloys to charge flow are considered in some detail. It is concluded that the ratio of *d* depletion to conduction electron gain is 0.6 ± 0.2 in the case of $Au_{0.5}Ag_{0.5}$, and similar behavior is encountered in other Au alloys.

Since Rowland's classic NMR investigations of Cu and Ag alloys,[1] the noble-metal alloys have generally been considered prototypes for conventional Friedel charge-screening theory.[2] In this scheme approximately free conduction electrons screen impurities, the *d* conduction bands are full, and *d* character plays little or no role in alloying effects. Unlike Cu and Ag, Au is not suitable for NMR studies, but the Mössbauer isomer shift has been used to investigate Au alloys.[3-5] These results, which are measurements of electron density at the nucleus, indicate that there is a rather substantial flow of *s*-like electron charge onto Au sites upon alloying, regardless of the atomic species of the alloy partner. In the case of the 1:1 Ag-Au alloy, for example, there is a charge gain corresponding to $\sim\frac{1}{6}$ of a 6*s* electron; in $AuAl_2$ the Au atom shows a gain in *s* density at the nucleus which corresponds to almost one 6*s* electron. This tendency, consistent with the view that Au is relatively electronegative, is sometimes justified by the observation[6] that the 6*s* level in atomic Au is lower in energy than the *s* valence electron levels of the other metallic atoms. As contrasted with the Mössbauer isomer shift, the energy shifts of core electrons depend on changes in the bulk charge around an atomic site. The investigation reported in this paper of such core-level chemical shifts in the Au-Ag alloy system and in certain Au intermetallic compounds was undertaken to determine whether the observed *s*-electron density differences indeed are reflected in the core-level energies of Au in these substances. It turns out that they are not, and competitive *d* effects dominate.

EXPERIMENTAL PROCEDURES

Core-level binding energies in the pure metals, in the alloys, and in the several intermetallic compounds were determined by measurement of the spectra of photoelectrons emitted by the samples when irradiated with Mg K_α x rays (1253.6 eV). Foils of 100% Au, of 100% Ag, and of Au-Ag alloys (atomic compositions 94.81-5.19; 50.41-49.59; 5.29-94.71) were prepared from very pure metals.[7] Weighed amounts were melted under H_2 at about 1200 °C in boats made of pure silica. Each melt, while kept in rapid motion, was quenched under H_2; the ingot was rolled; and finally the foil was annealed under H_2 for several hours. Samples of $AuAl_2$ and $AuGa_2$ were obtained from the Alloy Physics Section, National Bureau of Standards, and their preparation is described elsewhere.[8]

Metallic foils were wrapped around standard cylindrical aluminum sample holders, and powder specimens of $AuAl_2$ and $AuGa_2$ were pressed into In foil, which completely covered the holder. A strip of pure Rh foil was affixed to each sample to provide a standard monitor Rh line. Care was taken to assure that sample, monitor foil, and sample holder were in good electrical contact.

Rh was chosen as a monitor foil because it is a noble metal whose strong electron line (M_V) does not interfere with analysis of the Au N_{VII} and Ag M_V lines.

Measurements of binding energies of Au N_{VII} (4*f*), Ag M_V (3*d*), and Rh M_V (3*d*) electrons were made with a Varian IEE photoelectron spectrometer. These particular levels were chosen because they are the narrowest and most intense within the accessible energy range. A Mg anode in the x-ray source provided the $K\alpha_{1,2}$ photons, 1253.6 eV. Since the electrostatic analyzer of this spectrometer is operated to transmit electrons of a selectable fixed energy and the spectrum is scanned by application of a variable retarding potential between the electron source region and the analyzer, energy calibration depends only on the retarding potential and an additive term. The

TABLE I. Measured binding energies in eV of Au $N_{\rm VII}$ and Ag $M_{\rm V}$ lines in Au, Ag, Au-Ag alloys, $AuAl_2$, and $AuGa_2$.

	Au	$Au_{0.9481}$-$Ag_{0.0519}$	$Au_{0.5041}$-$Ag_{0.4959}$	$Au_{0.0529}$-$Ag_{0.9471}$	Ag	$AuAl_2$	$AuGa_2$
Au $N_{\rm VII}$	83.15[a]	83.15	83.25	83.45		84.5	84.45
Ag $M_{\rm V}$		367.0	367.25	367.60	367.45		

[a] All binding energies were normalized to a Rh $M_{\rm V}$ value of 306.6 eV. See text for discussion of this monitor.

latter, determined by the energy assigned to the monitoring standard line, includes the spectrometer work function and the analyzer parameters. Each of the lines measured happens to be one member of a well-resolved doublet imposed on a smoothly varying background, and the binding energy values were obtained with the aid of a computer analysis scheme constrained to yield doublet components having the same peak widths and the theoretical relative intensities. With the analyzer set to transmit either 30- or 50-eV electrons, widths of 1.2–1.3 eV full width at half-maximum (FWHM) were obtained for the Au, Ag, and Rh lines.

RESULTS AND DISCUSSION

In Table I are listed the measured Au $N_{\rm VII}$ and Ag $M_{\rm V}$ binding energies normalized to the energy of the Rh $M_{\rm V}$ level arbitrarily taken to be 306.6 eV. This value, obtained with a spectrometer work function of 5.0 eV, is very close to the literature value of 307.0 ± 0.3 eV.[9] The measured energy of this line in all samples varied between 306.6–306.4 eV. Energies of individual lines were reproducible to ± 0.05–0.08 eV. Since each energy value in Table I is based on the Rh $M_{\rm V}$ normalization, the error for each entry is estimated to be no more than ± 0.1 eV.

In every case, the Au $4f$ levels appear to be more deeply bound in the alloy than in the pure metal. Similar shifts occur in the optical absorption edges of the Ag-Au alloys.[10] By itself, this suggests a small net flow of charge off, *not onto*, the Au sites. Together with the isomer-shift data, the present results indicate, however, that the primary effect of alloying Au is not the motion of charge onto or off a Au site, but is instead a depletion of d and a very nearly matching increase in s (or free-electron-like) conduction electron character at a Au site. The idea that the Au d electrons play some role in alloying is not entirely new; among all the metals of the Periodic Table the ratio of the metal radius to ionic radius is smallest for Au, suggesting[11,12] that the $5d$ shell is in some sense "squeezed." Results here presented, the alloy solute Knight shift behavior[12] and the question[3] of charge compensation for the large conduction electron transfer indicated by isomer shifts all suggest d effects. What is new is the use of the electron binding energy shifts to make a quantitative estimate of Au d effects.

In studying the Au case, one is necessarily concerned with the general question of relating an electron binding energy shift in an alloy to charge transfer effects; and the Au_xAg_{1-x} alloy system may usefully be considered in this context. Au and Ag are of like valence, and their metals have essentially identical lattice constants, hence neither volume nor valence effects contribute significantly to alloy behavior. The isomer shifts are nevertheless substantial: $Au_{0.5}Ag_{0.5}$ exhibits[4] a shift of − 1 mm/sec relative to pure Au; within the uncertainties the shift varies linearly across the entire alloy range $0 \leq x \leq 1$. Currently accepted values[5,13,14] for the nuclear parameters and for the $6s$ contact charge density make a − 1 mm/sec isomer shift correspond to an increase of charge at the Au nucleus in the alloy amounting to 0.15 ± 0.05 of the contribution of a $6s$ electron in the free atom. It is more useful to calibrate the charge density in terms of conduction electron character appropriate to the Au Fermi level, ϵ_F; in these terms the − 1 mm/sec shift indicates[15] a transfer of slightly more than 0.2 units of conduction electron charge onto the Au site. The chemical shifts in Table I, however, are an order of magnitude smaller and opposite in sign to what would be expected if such charge transfer occurred without compensation. Moreover, the effects are even larger in other Au alloys. As examples, one may consider the interesting[3,8,16,17] ordered alloys $AuAl_2$, $AuIn_2$, and $AuGa_2$. For $AuAl_2$ the isomer shift (− 7 mm/sec) suggests a conduction electron increase of about 1.5 units of conduction electron charge, and again the photoemission data suggest an order-of-magnitude smaller effect of opposite sign. These estimates of quantity of charge transferred are based on the assumption that no change in character of the conduction electron wave function accompanies the conduction electron density increase. However, as we have already indicated, there is a depletion in d count; the concomitant reduction in screening of the nucleus causes the conduction electron charge c to contract, thus increasing the contact density. With complete d compensation (i.e., a $d^n c^x$ renormalized atom goes over to $d^{n-\Delta n} c^{x+\Delta n}$), atomic calculations[14] suggest that the conduction electron flow Δn, necessary to account for the isomer shifts, is two-thirds of that required without compensation. In view of this we will employ a Δn of 0.13 and

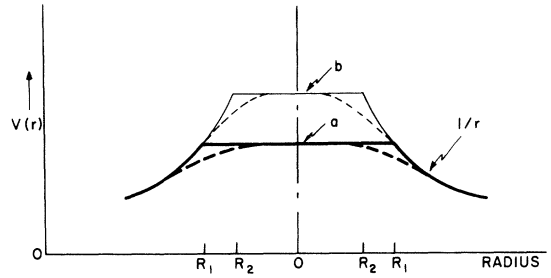

FIG. 1. Curve a: schematic Coulomb potential due to a valence electron charge concentrated in spherical shell of radius R_1. The rounded shoulder, dashed line, indicates the effect of radial extent of the charge. Curve b: same for electron compressed to radius R_2.

1.0 for $Au_{0.5}Ag_{0.5}$ and $AuAl_2$, respectively, in what follows. Although the uncertainties in these values are important for quantitative detail, they do not affect the basic conclusions of this paper.

The Coulomb potential due to a valence electron, with charge concentrated on a spherical shell of radius R_1, is indicated schematically in Fig. 1. The effect of compressing the valence electron to a radius R_2 is also shown. In actuality, valence electron charge is not concentrated in an infinitely thin spherical shell, and the rounded shoulders (shown dashed) in the plots indicate the effect of the radial extent of the valence electron charge. A core electron samples the interior plateau of the potential, while a valence electron overlaps the charge and samples the shoulder region. Core electron levels therefore tend to exhibit a common[18] and larger chemical Coulomb shift than those of valence electrons. It is useful to write the absolute chemical shift of an electron level i due to a change in conduction-band character in the form

$$\Delta\epsilon_i = \Delta[nF^0(c,i)] \quad . \tag{1}$$

In this equation n is the valence electron count and F^0 is the familiar Slater integral[19]

$$F^0(i,j) \equiv \int\int P_i(r_1)^2 (1/r_>) P_j(r_2)^2 r_1^2 dr_1 r_2^2 dr_2 \quad , \tag{2}$$

where the $P(r)$ are one-electron radial functions. The shift may involve changes in either valence electron count at the atomic site in question, or the interaction, or both. Aspherical, exchange, and correlation terms have been omitted.

Equation (1) becomes particularly useful if the F^0 terms, rather than being characteristic of free atoms, are instead appropriate to atoms[20,21] for which the $P(r)$ have been normalized to atomic volumes as they are in the alloy. It is the way in which the volume is chosen that defines how charging effects are derived for the alloy. One could choose some "standard" volume for a given atomic species; F^0 would be fixed, and Δn would represent the flow of charge into or out of that volume. The chemical shift as obtained with Eq. (1) would have to be modified by the addition of a (weaker) potential term associated with the nonzero charge outside the chosen volume, i.e.,

$$\Delta\epsilon_i \to \Delta n[F^0(c,i) - F^0_{\rm latt}] \quad . \tag{1'}$$

Alternatively, one could define the volume as that in which the site is neutral; charge flow would then be characterized by volume change and

$$\Delta\epsilon_i \to n\Delta F^0(c,i) \quad . \tag{1''}$$

There are obvious virtues and shortcomings in choices such as these; and although quantitative characterization of descriptions such as "complete screening" in alloys must depend upon a definition of the characteristic volume or other equivalent measure, such an exact definition happens not to be vital for the analysis of the Au cases discussed here.

The Au site shift involves *d* band as well as *s* conduction-band terms, i.e.,

$$\Delta\epsilon_i = \Delta[n_d F^0(d,i)] + \Delta[n_c F^0(c,i)] - [\Delta n_d + \Delta n_c]F^0_{\rm latt} \quad . \tag{3}$$

It must be noted that $\Delta\epsilon$ of Eq. (3) is the shift of an electron level with respect to vacuum for an isolated sample, whereas the photoemission experiment measures the position of a core level in a sample whose Fermi level is made equal to that of the spectrometer (the work function is that of the spectrometer). Thus, any shift in the Fermi level, $\Delta\epsilon_F$, from one isolated sample to another is included in the photoemission measurement, i.e.,

$$\Delta\epsilon_i' = -\Delta\epsilon_F + \Delta n_d F^0(d,i) + \Delta n_c F^0(c,i) - [\Delta n_d + \Delta n_c]F^0_{\rm latt} \quad , \tag{4}$$

as specialized for the case of no change in atomic volume [after Eq. (1′)].

We calculate for Au values[21] of the integrals

$$F^0(c,4f) \sim 13.5 \text{ eV} \quad , \qquad F^0(5d,4f) \sim 22 \text{ eV} \quad ,$$

with the functions normalized to the Wigner-Seitz cell characteristic of Au (or Ag) metal. Estimates of $F^0_{\rm latt}$, typically as much as 5 eV for the case at hand, depend upon the assumed location outside the cell of the displaced charge. One sees immediately that the Δn_c values derived from isomer-shift measurements imply large conduction electron contributions to $\Delta\epsilon$. In most cases these are too large to be sustained in a metal and they must be cancelled by a compensating term. Without compensation, the Au $5d$ bands in $AuAl_2$ would lie almost entirely above the vacuum zero.

Applying Eq. (4) to the Au $\Delta\epsilon'$, we note that there remain two undetermined parameters $\Delta\epsilon_F$ and Δn_d. We will make crude estimates of $\Delta\epsilon_F$ in order to ascertain the behavior of Δn_d. Between pure Au and pure Ag the absolute position of ϵ_F probably varies by less than 1 eV,[22] and there is some question as to which lies lower. Let us assume a $\Delta\epsilon_F$ of ± 0.3 eV for $Au_{0.5}Ag_{0.5}$; one then obtains the ratio

$$\Delta n_d/\Delta n_c \equiv X_{c\text{-}d} = -0.6 \pm 0.2 \ ,$$

depending on the choice of $\Delta\epsilon_F$ and of F^0_{latt}. Although the ratio X is sensitive to the parameters employed, it appears that the Δn_c inferred from the isomer shift is substantially compensated by $5d$ electron depletion. The compensation increases, i.e., $X \to -1$, when the Fermi level of Au lies above that of Ag, as argued by Levin and Ehrenreich.[10]

In the case of $AuAl_2$ the situation is at one time more clear-cut and more complicated. The complications arise from the question of atomic volume change. The case is nevertheless simpler because, as in most Au alloys, Δn_c is substantially larger than in the Ag-Au system, and in first approximation one can omit from Eq. (4) all terms but those involving Δn_c and Δn_d. Neglecting volume effects, one has, in the limit of large Δn_c and small chemical shift,

$$X_{c\text{-}d} \approx \left(\frac{F^0(c, 4f) - F^0_{\text{latt}}}{F^0(5d, 4f) - F^0_{\text{latt}}}\right) \approx -0.5 \text{ to } -0.6 \ . \tag{5}$$

The volume associated with a $AuAl_2$ molecule in the crystal is approximately 7% greater than the volume of the three atoms in their pure metals. This volume change is perhaps best accounted for by adding to the right-hand side of Eq. (4):

$$n_d \, \Delta F^0(5d, 4f) + n_c \, \Delta F^0(c, 4f) \ , \tag{6}$$

where the ΔF^0's arise from the changes in the volumes to which the electron orbitals are normalized. For a 7% increase in the Au site volume, the terms (6) show a lowering of the $4f$ energy equal to approximately half the measured $\Delta\epsilon'$ given in Table I. Volume effects thus make significant contributions to the observed chemical shift, but they do not greatly affect estimates of charge compensation.

Charge compensation may be a more complicated phenomenon than that allowed by the model which is the basis for Eq. (4) and Δn_c: d bands and a simple orthogonalized plane-wave conduction band of rather set orbital character for each particular crystal momentum and energy. One might, for example, consider replacing the conduction- and d-band terms of Eq. (4) by "s"- and "p"-band terms and asserting that the main effect of alloying is to enchance s and deplete p count. This would imply almost complete charge compensation since the s and p radii are approximately the same; hence

$$F^0(s, 4f) \approx F^0(p, 4f) \ , \qquad X_{s\text{-}p} \approx -1 \ .$$

From a theoretical point of view it would seem that s-p compensation cannot be the dominant effect in an alloy such as $AuAl_2$. Current band theory predicts an electron count for Au of $5d^{10-x}\,c^{1-x}$ $(0.2 \lesssim x \lesssim 0.4)$. Much of the conduction electron character lies deep below ϵ_F and, while there is a substantial fraction of p character in the states near ϵ_F, we do not believe that there is sufficient p character available to account for the charge compensation.

We have so far limited attention to the $\Delta\epsilon'$ associated with Au sites. Some data exist for the other sites as well. It is of interest to examine the data for Ag in the Au-Ag alloy system in the light of Eq. (4). Charge neutrality in the 0.5-0.5 alloy implies that

$$\Delta n_d^{\text{Ag}} + \Delta n_c^{\text{Ag}} = -\Delta n_d^{\text{Au}} - \Delta n_c^{\text{Au}} \ , \tag{7}$$

and, if we assume that ϵ_F in the alloy lies halfway between that in pure Ag and pure Au, we have

$$(\Delta\epsilon_F)_{\text{Ag}} = -(\Delta\epsilon_F)_{\text{Au}} \ . \tag{8}$$

Substituting (7) and (8) into Eq. (4), one obtains

$$\Delta n_d^{\text{Ag}} = \frac{\Delta\epsilon'_{\text{Ag}} + (\Delta\epsilon_F)_{\text{Au}} + (\Delta n_d^{\text{Au}} + \Delta n_c^{\text{Au}})[F^0(c, 3d) - F^0_{\text{latt}}]}{F^0(4d, 3d) - F^0(c, 3d)} \ . \tag{9}$$

The numerical uncertainties encountered in the Au site estimates accumulate for the Ag. Using the calculated[21]

$$F^0(4d, 3d) = 25 \text{ eV} \quad \text{and} \quad F^0(c, 3d) = 13 \text{ eV} \ ,$$

we obtain

$$\Delta n_c^{\text{Ag}} = -0.12 \text{ to } -0.13$$

and

$$\Delta n_d^{\text{Ag}} = +0.04 \text{ to } +0.08$$

over the range of $X_{c\text{-}d}$ at the Au site from -0.4 to -0.8. Because of accumulation of numerical uncertainties, these results should be taken less seriously than those for Au, although the value for Δn_c^{Ag} appears to be quite stable and

$$\Delta n_c^{\text{Ag}} \approx -\Delta n_c^{\text{Au}} \ .$$

This latter near equality, instead of representing a real physical effect, may well be a numerical accident resulting from the choice of parameter values in the Au and Ag solutions. The Δn_d^{Ag} value is even more uncertain, but it is near the high limit of what may be reasonably expected. The upper edge of Ag $4d$ bands lies ≈ 4 eV below ϵ_F. Due to s-d hybridization there is in the occupied bands an amount of d character equivalent to ≈ 9.9 d electrons. This implies that

$$\Delta n_d^{\text{Ag}} \lesssim +0.1$$

and probably means that Δn_d^{Ag} can only be a fraction of 0.1. No similar problem is encountered for Au, where one is dealing with d depletion and where the squeezed d levels lie much closer to ϵ_F.

We have discussed d-electron compensation and charge flow on or off Au sites in the context of current band theory for the noble metals and find the results reasonable. We should note that there exists another model of these metals, due to Pauling, Engels, and Brewer,[23] according to which the electron count is $d^{8.5}\,c^{2.5}$. This model also allows the compensation we find. Accuracy limitations of the data and, more importantly, uncertainties in the parameters of equations such as (4) make any real test of the models impossible. One's choice of model must rest on other evidence.

There are uncertainties associated with the F^0 integrals which should be considered. As a start, one should replace free-atom F^0 values by their renormalized atom counterparts: Free-atom valence electron estimates of $F^0(c,\ \textit{core})$ grossly underestimate the chemical shift associated with flow of conduction electron charge into or out of an atomic site in alloying. More important than the omission of exchange in Eqs. (4) and (9) is the fact that the F^0 *integrals* should be replaced by *effective* F^0 *parameters* to take into account correlation, interatomic relaxation, and screening which accompany charge flow. These factors are physically similar to those producing the effective d-d Coulomb interaction in transition metals. Since, in the measurements here described, the Coulomb effects are being sampled by electrons in the interior of the ion, we may anticipate that these F^0 integrals are better approximations to the effective parameters than are the $F^0\,(d,d)$ cited above.

The results discussed here shed little light on the behavior of d charge compensation as one goes from Cu to Ag to Au. Ag compensation effects, almost equal to those for Au, were obtained from Eq. (9). We believe this is perhaps not real, but instead an accident due to choice of parameters. This interesting question and its implications for Friedel theory as applied to the noble metals require further experiment.

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Au $4f$ levels, but no analysis of these is presented.

[18] The s and p core electrons of the same principal quantum number n as the valence d electrons should exhibit chemical shifts different from those of smaller n value. The latter lie inside the potential plateaus (Fig. 1) of both the valence d and conduction electrons, whereas the former overlap the shoulder of the d potential. Unfortunately, the $5s$ line of Au and the $4p$ line of Ag, which were examined experimentally in the Au-Ag system, were so broad that no meaningful shift differences, relative to the $4f$ and $3d$, were observable.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 12 15 DECEMBER 1971

Study of Aluminum Films. I. Optical Studies of Reflectance Drops and Surface Oscillations on Controlled-Roughness Films*

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Ultrahigh-vacuum near-normal-incidence ultraviolet reflectance measurements on aluminum films of known rms surface roughness have confirmed recent theories of roughness-aided coupling to surface plasmons in free-electron-like metals and of roughness-induced light scattering. The notable success of these theories allowed the separation of experimentally observed reflectance drops into surface-plasmon-induced and scattered-light-induced components. These confirmed theories were combined with reflectance measurements to yield the surface-roughness spectra of the films studied over a spatial-frequency (wave-number) range of $\leq 1.4\times10^{-2}$ Å^{-1}. This is believed to be the first example of the use of both surface-plasmon-induced and scattered-light-induced reflectance effects for the determination of the surface-roughness spectra.

I. INTRODUCTION

Considerable theoretical[1-3] and experimental interest has developed concerning the optical[4,5] and photoemission[6] properties of roughened metallic surfaces. Optical studies have emphasized the measurement of surface-plasmon effects on rough surfaces, somewhat to the exclusion of equally significant and less understood roughness-induced scattered-light effects. Early studies by Jasperson and Schnatterly[4] confirmed the roughness-dependent coupling to surface plasmons in silver, and Stanford, Bennett, Bennett, Ashley, and Arakawa[4] showed this coupling on films of known (measured) rms surface-height variations. More recent studies by Feuerbacher and Steinman[5] substantiated the importance of roughness-aided coupling to surface plasmons in the nearly free-electron-like metal aluminum, but, unfortunately, no attempt was made to estimate the roughness of the Al films.

Preliminary roughness-dependent photoyield effects were first reported by Endriz and Spicer who attempted to describe them as resulting from the volume photoemission effect associated with the decay of surface plasmons. Here and in the succeeding paper[7] (referred to as Paper II) we report on current optical and photoemission studies of ultrahigh-vacuum-evaporated Al films of known rms roughness, which were designed to present a more definitive description of the processes involved. In analyzing these photoemission effects, it was found that the interpretation relied strongly upon a thorough understanding of roughness-dependent optical effects, particularly the less well understood scattered-light effects. Although optical effects of surface-plasmon coupling have been extensively studied, only the recent theoretical developments of Hunderi and Beaglehole,[8] Berreman,[9] and Ritchie[10] have furthered the understanding of scattered-light effects.

Because most of the existing theory of roughness-aided coupling to surface plasmons is applicable to nearly free-electron metals such as Al, it was believed that the roughness-dependent studies reported in this paper would provide confirmation of scattered-light theories and also the first opportunity to compare near-normal-incidence reflectance measurements of known roughness films to theories of surface-plasmon excitation. The investigation of Al also allows the examination of the importance of surface roughness in ultraviolet reflectance studies of polyvalent nearly free-electron metals.