

dominant mechanisms causing a temperature-dependent resistivity between 1 to 5 °K. The calculated magnitudes of the electron-phonon scattering are too small to explain our data, and are without a mobility dependence. Their contributions to our high-mobility samples may have produced the curvature of ρ vs T , but theory predicts negligible contributions even in these cases. The anomalous scattering suggested by Kawaji³ and also localization effects¹¹ will give a temperature dependence $\sim \ln(1/T)$, which may also have contributed to this curvature. The effects of analyzing the data with such additional terms have been estimated and do not change our conclusions. Any observed effect attributed only to electron-phonon scattering should be shown to be independent of mobility.

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Classical Local-Field Effect in Reflectance from Adsorbed Overlayers

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The role of the local-field effect in differential reflectance spectroscopy is studied within a classical model for an ordered overlayer of a weakly adsorbed species on a metal substrate. Results for Ar on Al at two coverages strongly indicate the importance of the local-field effect in such optical studies.

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There has been a great deal of interest in recent years in the use of differential-reflectivity methods to study the electronic properties of adsorbed objects on a variety of substrates. In particular, experiments have been reported^{1,2} on differential reflectance spectra from rare-gas atoms adsorbed on metallic and oxide surfaces down to submonolayer coverages. In this paper we report on the first quantitative and detailed study of the

classical local-field effect in such systems, and its possible implications for the measurement of optical reflectance. Our results, showing a striking correlation with experiments, suggest that the local-field effect is indeed quite important in surface reflectance spectroscopy. Although no systematic study of the role of the local-field effect in this problem has been attempted in the past, ideas rather similar to ours have appeared

in the literature in such contexts as the coverage dependence of the adsorbate vibrational frequency,³ and the surface-enhanced Raman spectroscopy.^{4,5}

We consider an ordered overlayer of adsorbed atoms, forming a two-dimensional square lattice of lattice constant a_1 , on top of a metal substrate. Let z_0 be the separation between the adsorbed layer and the metal surface, where the metal is presumed to occupy the half-space $z > 0$. We imagine that the polarizability tensor $\vec{\alpha}(\omega)$ of an adsorbed atom is diagonal and frequency dependent, while the dielectric response of the metal is described by a local, complex function $\epsilon(\omega)$. When parallel- (or p -) polarized light of angular frequency ω is incident on the system in the x - z plane at an angle of incidence θ_i , the electric field just outside the metal surface in the absence of the adlayer is given by $\vec{E}^0 = (E_x^0, 0, E_z^0)$, and its components can be computed classically from the superposition of the incident and reflected electric fields.⁶ The external field polarizes the adsorbed atoms, which are presumed to have no permanent dipole

moment, and they in turn induce image dipoles in the substrate metal. We assume $a_1 \ll \lambda$, where λ is the wavelength of light, so that the variation of the electric field parallel to the surface can be ignored. On exposure to light, then, the adsorbed layer consists of an array of dipoles each of moment $\vec{p} = (p_x, 0, p_z)$, located at $(ia_1, ja_1, -z_0)$, where i and j are integers with $-\infty < i, j < \infty$. This choice implies that the z axis goes through one of the adatoms. In addition, there appears another array of dipoles located in the image plane, each having a dipole moment $\vec{p}_I = [(\epsilon - 1)/(\epsilon + 1)](-p_x, 0, p_z)$, with location at (ia_1, ja_1, z_0) in the quasistatic screening approximation.⁷ The approximation of using the classical theory of static screening is expected to be good for $\omega \ll \omega_p$, the plasma frequency of the substrate.

Let us denote by \vec{E}_{dip} the net dipolar field produced at an adsorbate site, say the one specified by $(0, 0, -z_0)$. After carrying out two-dimensional lattice sums of the type discussed in the literature,^{3,8-10} we find that the z component of this field may be written as^{11,12}

$$(\vec{E}_{\text{dip}})_z = (p_z/a_1^3) \{ \xi_0 + [(\epsilon - 1)/(\epsilon + 1)] \xi_I \}, \quad (1a)$$

$$\xi_0 = -9.0336, \quad (1b)$$

$$\xi_I = 16\pi^2 \sum_{i,j=0}^{\infty} (i^2 + j^2)^{1/2} \exp[-(4\pi z_0/a_1)(i^2 + j^2)^{1/2}]. \quad (1c)$$

Similarly, the tangential or x component of the net dipolar field at an adatom may be expressed as

$$(\vec{E}_{\text{dip}})_x = (p_x/a_1^3) \{ -\xi_0 + [(\epsilon - 1)/(\epsilon + 1)] \xi_I \} / 2. \quad (2)$$

The total electric field felt by the adsorbed atom situated at $(0, 0, -z_0)$ is the superposition of the external field and the dipolar field. We must, therefore, have the self-consistency condition

$$\vec{p} = \vec{\alpha}(\omega) \cdot (\vec{E}^0 + \vec{E}_{\text{dip}}) \quad (3)$$

for the induced dipole moment of the adatom. Let us introduce the following notations for simplicity: $\vec{P} = \vec{p}/a_1^3$, and $\Gamma_i(\omega) = \alpha_i(\omega)/a_1^3$ where $i = x, y$, or z . Then Eq. (3) leads, after a modest amount of algebra, to the results

$$P_x = \Gamma_x E_x^0 / \{ 1 + (\Gamma_x/2) [\xi_0 - ((\epsilon - 1)/(\epsilon + 1)) \xi_I] \}, \quad (4a)$$

$$P_z = \Gamma_z E_z^0 / \{ 1 - \Gamma_z [\xi_0 + ((\epsilon - 1)/(\epsilon + 1)) \xi_I] \}. \quad (4b)$$

Equations (4) may be used to define the macroscopic electric field in the adsorbed layer, and hence its effective dielectric constant, by regarding it as a uniform layer of thickness d ($d \sim 2z_0$). The continuity of the normal component of the displacement field and the tangential component of the electric field allows us to identify E_z^0 and E_x^0 with the macroscopic fields D_z and E_x in the film. Then, noting that the volume per adatom is $a_1^2 d$, we find that the adsorbed layer can be characterized by an anisotropic dielectric tensor with components (suppressing the frequency dependence)

$$\epsilon_x = \frac{1 + (\Gamma_x/2) \{ 8\pi(a_1/d) + \xi_0 - [(\epsilon - 1)/(\epsilon + 1)] \xi_I \}}{1 + (\Gamma_x/2) \{ \xi_0 - [(\epsilon - 1)/(\epsilon + 1)] \xi_I \}}, \quad (5a)$$

$$\epsilon_z^{-1} = \frac{1 - \Gamma_z \{ 4\pi(a_1/d) + \xi_0 + [(\epsilon - 1)/(\epsilon + 1)] \xi_I \}}{1 - \Gamma_z \{ \xi_0 + [(\epsilon - 1)/(\epsilon + 1)] \xi_I \}}. \quad (5b)$$

These dielectric response functions can be used to compute the change of reflectance of p -polarized light from a metal surface when covered with a uniform film of an optically anisotropic substance.^{13,14} Adapting the result of Eq. (5.6) of Ref. 14 to our case, we find that the differential reflectance upon adsorption is

$$\left(\frac{\Delta R_p}{R_p}\right)_a = 4\left(\frac{\omega}{c}\right)d \cos\theta_i \text{Im} \left\{ \frac{(\epsilon - \sin^2\theta_i)(\epsilon_x - 1) + \epsilon^2 \sin^2\theta_i(\epsilon_z^{-1} - 1)}{(1 - \epsilon)(\sin^2\theta_i - \epsilon \cos^2\theta_i)} \right\}. \quad (6)$$

We have evaluated the differential reflectance of Eq. (6) for the adsorption of rare-gas atoms such as Ar and Kr on a number of simple metals for several values of the lattice parameter a_1 or, equivalently, the coverage θ . The input parameters in the calculation, apart from a_1 , are the thickness d of the adsorbed layer, its distance z_0 from the surface, the complex dielectric constant $\epsilon(\omega)$ of the substrate, and the dimensionless polarizabilities $\Gamma_x(\omega)$ and $\Gamma_z(\omega)$. The angle of incidence θ_i also has to be specified. For simplicity in our calculations, we take the polarizability of the adatoms to be uniform, i.e., $\Gamma_x = \Gamma_z$, although a more complicated form poses no special difficulty. When the polarizability is expressed in terms of oscillator strengths in the usual manner,¹⁵ we have ($\Gamma_x = \Gamma_z = \Gamma$)

$$\Gamma(\omega) = \left(\frac{e^2}{\hbar a_0}\right)^2 \left(\frac{a_0}{a_1}\right)^3 \sum_{\nu} \frac{f_{\nu}}{\omega_{\nu}^2 - \omega^2 - i\gamma_{\nu}\omega}, \quad (7)$$

where $a_0 = \hbar^2/me^2$ is the Bohr radius, and the sum over ν goes over to an integral when $\hbar\omega_{\nu}$ exceeds the ionization energy. Figure 1 shows the differential reflectance of p -polarized light incident on argon-covered aluminum at $\theta_i = \pi/4$ for two values of a_1 , viz. $a_1 = 4$ and 8 \AA . The former value corresponds approximately to a monolayer coverage as suggested by experiments on the physisorption of Ar on graphite¹⁶; the latter value is roughly representative of $\theta \cong 25\%$. We take $z_0 = 2 \text{ \AA}$ and $d = 4 \text{ \AA}$ in our calculations. The dielectric constant of Al is taken from a Kramers-Kronig analysis¹⁷ of the experimental reflectance data. For the polarizability of the adatom we use free-atom properties, e.g., the oscillator strengths for single-electron transitions as given by Cooper¹⁸ and excitation and ionization energies obtained experimentally.^{19,20} The spin-orbit splitting of the $3p$ level is ignored and therefore Eq. (7) is multiplied by 6 to account for the electron occupancy of this level. We consider discrete transitions of the type $3p - ns$ ($4 \leq n \leq 6$) and $3p - nd$ ($3 \leq n \leq 6$) for which oscillator strengths are tabulated.¹⁸ In addition continuum transitions of both $3p - s$ and $3p - d$ types are considered in computing $\Gamma(\omega)$. Finally we choose $\hbar\gamma_{\nu} = 0.5 \text{ eV}$ for the discrete transitions to account for the sub-

strate-induced broadening of the adsorbate levels in an approximate manner. Smaller values of γ_{ν} narrow down and enhance the peaks of Fig. 1 without altering our conclusions in any significant way. In the continuum region we set $\gamma_{\nu} = 0^+$.

The prominent features of Fig. 1 for $a_1 = 4 \text{ \AA}$, in the energy range $\hbar\omega \lesssim 14 \text{ eV}$, are seen to be the two peaks around 11.5 and 13.6 eV. They arise from $3p - 4s$ and $3p - 3d$ atomic transitions, respectively, but are considerably shifted in energy from the atomic values because of local-field effects. A third feature, the shoulder around 10.8 eV, is a surface plasmon effect. It is clear from Eq. (6) that peaks in differential reflectance will correspond mostly to peaks in the imaginary parts of ϵ_x and ϵ_z^{-1} . We find in fact from our calculations that the main peaks in Fig. 1 arise from peaks in $\epsilon_x(\omega)$ of Eq. (5a). They can thus be identified with classical polarization modes (or excitons, in quantum-mechanical terms), of the coupled adsorbate-substrate sys-

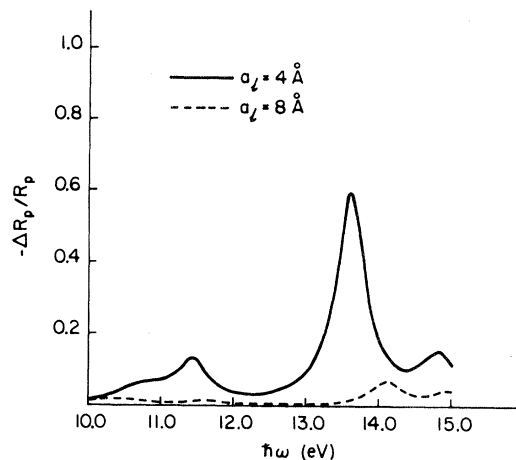


FIG. 1. The calculated differential reflectance of p -polarized light incident on argon-covered aluminum at an angle of 45° as a function of the photon energy. Argon atoms are presumed to form a two-dimensional square lattice on the substrate, and results are shown corresponding to lattice spacings of 4 \AA (full line) and 8 \AA (dashed line). Other parameters of the model calculation are $d = 4 \text{ \AA}$, $z_0 = 2 \text{ \AA}$, and $\hbar\gamma_{\nu} = 0.5 \text{ eV}$. (See the text for definitions.)

tem parallel to the surface of the system. The structures are also expected to appear in the differential reflectance spectra using *s*-polarized light. As a function of the angle of incidence θ_i , the peaks do not move in energy but their intensity decreases monotonically as θ_i increases. The 13.6-eV peak, for example, changes from 0.71 to 0.43 as θ_i is varied from 15° to 75° . Two things apparently happen at dilute coverage as shown in Fig. 1 by the curve for $a_1 = 8 \text{ \AA}$. The peak at 11.5 eV moves slightly to higher energies but is essentially suppressed at lower coverage. The other peak at 13.6 eV now moves considerably further to the right, coming much closer to the atomic transition energy, and it is still observable although significantly reduced in strength. The movement of the peak position with coverage is clearly a local-field effect, which modifies both Γ_i and ξ_I of Eqs. (8) and thereby alters the structures of $\epsilon_x(\omega)$ and $\epsilon_z^{-1}(\omega)$ in ω . The fact that the higher-energy peak always appears stronger and moves more rapidly with coverage can be understood in terms of the oscillator strengths—the *f* value for $3p \rightarrow 3d$ transition being almost 4 times that for $3p \rightarrow 4s$ transition.¹⁸ Both features of our calculations, viz. the suppression of the low-energy peak and the blueshifting of the higher energy peak as the coverage is reduced, are remarkably similar to what has been observed experimentally^{1,2} with heavier rare-gas atoms adsorbed on various metal substrates. In fact our calculations for differential reflectance with Kr on Al, using a less accurate form of the atomic polarizability, give results that are qualitatively similar to those shown in Fig. 1. The classical model discussed here cannot, of course, be taken literally if a serious attempt is made at data interpretation. Quantum-mechanical effects that must be considered include the proper dynamical response of a semi-infinite metal with nonlocality,^{21,22} and the proper specification of the localization of the metal surface.²³ In addition the polarizability of an adatom will probably be different from that of a free atom.²⁴ Nevertheless, we feel that we have shown conclusively in this paper that the local-field effect is important in optical properties of adsorbate systems, and it should be properly accounted for when explaining differential-reflectivity data.

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