loquium on the Optical Properties and Electronic Structure of Metals and Alloys, edited by F. Abeles (North-Holland, Amsterdam, 1966), p. 164.

<sup>6</sup>N. E. Christensen and B. O. Seraphin, Phys. Rev. B

<u>4</u>, <u>3321 (1971)</u>.

<sup>7</sup>S. Methfessel, Z. Phys. <u>147</u>, 442 (1957).

<sup>8</sup>R. Y. Koyama and N. V. Smith, Phys. Rev. B  $\underline{2}$ , 3049.

## Photoemission Spectroscopy in the Presence of Adsorbate-Covered Surfaces

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A theory of the ultraviolet photoemission spectroscopy of metals with adsorbate covered surfaces yields  $\Delta j(\omega) \propto G_{aa}^{\ I}(\omega - \omega_0) - DG_{aa}^{\ R}(\omega - \omega_0)$ .  $\Delta j(\omega)$  is the excess current at the energy  $\omega$  produced by the adsorbates,  $\omega_0$  is the photon energy,  $(1/\pi)G_{aa}^{\ I}$  is the density of states at the adsorbate, and  $G_{aa}^{\ R}$  is the real part of the Green's function at the adsorbate. D is nonzero if  $\omega - \omega_0$  is degenerate with the metal energy bands, and can be large  $(D \sim 1)$  for typical experimental conditions.

Recent work by Eastman and Cashion<sup>1</sup> (EC) has demonstrated that ultraviolet photoemission spectroscop<sup>\*</sup> (UPS) can be used to determine the electronic energy levels of adsorbates on metal surfaces. As pointed out by EC, UPS has certain advantages over other methods. It is not restricted to energies within a few eV of the Fermi energy as is field emission, and it has better energy resolution and should be simpler to interpret than ion neutralization spectroscopy. Our purpose here is to present a theory of UPS in the presence of adsorbate covered surfaces.

We picture the process of photoemission as the photon excitation of an electron from the N-electron ground state  $|I\rangle$  of the metal-adsorbate-vacuum complex to an excited state  $|f\rangle$  in which it is not correlated with any other electrons.  $|f\rangle$  is the incoming wave solution.<sup>2,3</sup> The total wave function of the N-electron excited state,  $|F\rangle$ , is an antisymmetrized product of the one-electron excited state  $|f\rangle$  and a N-1 particle state. The photoemission current per unit energy at energy  $\omega$  produced by photons of energy  $\omega_0$  is

$$j(\omega) = (2\pi/\hbar) \sum_{F} |\langle F|H'|I\rangle|^2 \delta(E_F - E_I - \omega_0) \delta(\omega - \epsilon_f),$$
(1a)

$$H' = (e/mc) \sum_{l} \vec{A}_{l} \cdot \vec{P}_{l} \equiv \sum_{l} \tau_{l}, \qquad (1b)$$

where  $E_i$  and  $E_f$  are the total energies of the ground state and the excited state, respectively, and  $\epsilon_f$  is the energy associated with  $|f\rangle$ . The zero of energy is taken to be the vacuum level. Equation (1) yields

$$j(\omega) = (2\pi/\hbar) f_0(\omega - \omega_0) \operatorname{Im}\left[\sum_f \langle f | \tau G(\omega - \omega_0) \tau | f \rangle \delta(\omega - \epsilon_f)\right],$$

$$\tau = \vec{A} \cdot \vec{P},$$
(2a)

where  $G(\omega - \omega_0)$  is the Green's function of the metal plus adsorbate at energy  $\omega - \omega_0$ , and  $f_0$  is the Fermi factor.

Our treatment is confined to the case in which the interaction between adsorbates is unimportant compared to the adsorbate-metal interactions. This should be the case for many chemisorbed atoms and molecules up to one monolayer coverage. The results of EC for both CO and O on Ni are consistent with this assumption. Thus, multiple scattering from different adsorbates is neglected. The ground state of the metal-adsorbate complex is assumed to be an eigenstate of the many-body Anderson Hamiltonian

$$H = \sum_{m,\sigma} \epsilon_m n_{m\sigma} + \epsilon_a \sum_{\sigma} n_{a\sigma} + U n_a + \sum_{m,\sigma} (V_{ma} a_{m\sigma}^{\dagger} d_{\sigma} + V_{am} d_{\sigma}^{\dagger} a_{m\sigma}).$$
(3)

Equation (3) assumes a single adsorbate level with wave function  $\varphi_a \equiv |a\rangle$ . Equation (5) of Penn, Go-

mer, and Cohen<sup>4</sup> for G is used in (2a) to obtain

$$\frac{\Delta j(\omega)}{j_0(\omega)} \equiv \frac{j(\omega) - j_0(\omega)}{j_0(\omega)} = (\alpha - \beta) G_{aa}^{I}(\omega - \omega_0) + \gamma G_{aa}^{R}(\omega - \omega_0),$$
(4a)

$$j_{0}(\omega) = \frac{2\pi}{\hbar} \sum_{m,f} |\langle f | \tau | m \rangle|^{2} \delta(\omega - \omega_{0} - \epsilon_{m}) \delta(\omega - \epsilon_{f}), \qquad (4b)$$

$$\alpha = \left[2f_0(\omega - \omega_0)/\hbar j_0\right] \sum_f \delta(\omega - \epsilon_f) |u_f|^2, \tag{4c}$$

$$\beta = \left[2f_0(\omega - \omega_0)/\hbar j_0\right] \sum_f \delta(\omega - \epsilon_f) |v_f|^2, \tag{4d}$$

$$\gamma = \left[2f_0(\omega - \omega_0)/\hbar y_0\right] \sum_f \delta(\omega - \epsilon_f) 2\operatorname{Re}(v_f u_f^*), \tag{4e}$$

$$u_f = \langle f | \tau | a' \rangle, \quad |a'\rangle = |a\rangle + \sum_m \frac{v_{ma}}{\omega - \omega_0 - \epsilon_m} | m \rangle, \tag{4f}$$

$$v_f = \pi \sum_m \langle f | \tau | m \rangle V_{ma} \,\delta(\omega - \omega_0 - \epsilon_m). \tag{4g}$$

 $G_{aa}{}^R$  and  $G_{aa}{}^I$  are the real and imaginary parts of the Green's function at the adsorbate.  $j_0(\omega)$  is the photoemission current in the absence of adsorbates.  $|a'\rangle$  of (4f) is the adsorbate wave function in the presence of the metal. In deriving (4) we have assumed that  $\omega = \epsilon_f$  is sufficiently large and the adsorbate coverage sufficiently low that the change in  $|f\rangle$  due to the presence of adsorbates may be neglected. Equation (4) for  $\Delta j/j_0$  treats H of Eq. (3) exactly. Should the resonant level  $\epsilon_r$  of the adsorbate lie below the bottom of the metal conduction bands,  $\epsilon_B$ , then in the energy region of primary interest,  $\omega \approx \epsilon_r + \omega_0$ ,  $j_0(\omega) = 0$ , and  $v_f = 0$ . Consequently, for  $\omega < \epsilon_B + \omega_0$ ,

$$j(\omega) = (2/\hbar) \sum_{f} \delta(\omega - \epsilon_{f}) |\langle f| \tau | a' \rangle|^{2} G_{aa}^{I}(\omega - \omega_{0}).$$
(5)

In this energy regime the imaginary part of the self-energy,  $\Sigma_a^{I}$ , associated with  $G_{aa}^{I}$ , is not due to  $V_{ma}$  but arises from metal-adsorbate electron-electron Coulomb interactions. If these are weak compared to  $V_{ma}$ , then (5) will hold approximately, with  $\Sigma_a^{I}$  determined by the Coulomb interactions. To estimate  $\alpha$ ,  $\beta$ , and  $\gamma$  of (4), the metal wave functions  $\{|m\rangle, |f\rangle\}$  are approximated in the metal,

To estimate  $\alpha$ ,  $\beta$ , and  $\gamma$  of (4), the metal wave functions  $\{|m\rangle, |f\rangle\}$  are approximated in the metal, z < 0, by  $\{|\vec{k}_m, l\rangle, |\vec{k}_f, n\rangle\}$ , the Bloch wave functions in the absence of a surface. The scattering of an electron in the state  $|f\rangle$  is described in a phenomenological manner by multiplying  $|k_f n\rangle$  by  $\epsilon^{\lambda z}$ , where  $l = \lambda^{-1}$  is the electron mean free path.<sup>5</sup> For *l* much greater than the metal lattice spacing, these approximations give

$$|\langle f|\tau|m\rangle|^2 \simeq (l/2L) \,\delta_{\vec{k}_f,\vec{k}_m}^{+} |\langle \vec{k}_f, n|\tau|\vec{k}_f, l\rangle|^2 \tag{6}$$

in agreement with Mahan.<sup>5</sup> L is the length of the metal in the z direction. Equation (6) is consistent with the usual "three-step" picture of photoemission in which the wave functions entering (4b) are replaced by infinite-crystal wave functions, and the matrix element is multiplied by an escape probability.<sup>6</sup> In this approximation  $j_0$  is given by the direct-transition model.

In a similar manner an approximate expression for  $\beta$  of (4a) is obtained:

$$\beta \simeq \frac{1}{2} L N_{S} \Big[ \sum_{knl} \delta(\omega - \epsilon_{k,n}) \delta(\omega - \omega_{0} - \epsilon_{k,l}) \big| \langle \vec{\mathbf{k}}n | \tau | \vec{\mathbf{k}}l \rangle |^{2} | V_{kl,a} |^{2} | \nabla_{k_{z}} \epsilon_{kl} |^{-1} \Big] \\ \times \Big[ \sum_{knl} \delta(\omega - \epsilon_{k,n}) \delta(\omega - \omega_{0} - \epsilon_{k,l}) \big| \langle \vec{\mathbf{k}}n | \tau | \vec{\mathbf{k}}l \rangle |^{2} \Big]^{-1} \\ \equiv \frac{1}{2} L N_{S} \langle | V_{kl,a} |^{2} | \nabla_{k_{z}} \epsilon_{kl} |^{-1} \rangle_{0} = \frac{1}{2} a_{0} c_{S} \langle N_{a} | V_{kl,a} |^{2} | \nabla_{k_{z}} \epsilon_{kl} |^{-1} \rangle_{0},$$

$$(7)$$

where  $\langle \rangle_0$  denotes an average as defined by (7);  $N_s$  is the number of adsorbate atoms;  $a_0 = (V/N_a)^{1/3}$ , with V the volume of the metal and  $N_a$  the number of atoms in the metal; and  $c_s$  is the ratio of the number of adsorbate atoms to the number of metal surface atoms. Similarly,  $\gamma$  and  $\alpha$  of (4a) are given approximately by

$$\gamma \simeq 2 \frac{a_0}{l} c_s \left\langle \frac{N_a |\langle a'| \tau |kn\rangle|^2}{|\langle kl| \tau |kn\rangle|} V_{kl,a} \right\rangle_0, \tag{8a}$$

$$\alpha \simeq \frac{2}{\pi} \frac{a_0}{l} c_s \rho_m (\omega - \omega_0)^{-1} B \left\langle \frac{N_a |\langle a'| \tau |kn \rangle|^2}{|\langle kl| \tau |kn \rangle|^2} \right\rangle_0, \tag{8b}$$

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(9)

where  $\rho_m$  is the metal density of states per atom. *B* of (8b) is defined by

$$N_a^{-1}\sum_{kn}\delta(\omega-\epsilon_{kn})|\langle a'|\tau|kn\rangle|^2\sum_{kn}\delta(\omega-\omega_0-\epsilon_{kl})=B\sum_{knl}\delta(\omega-\epsilon_{kn})\delta(\omega-\omega_0-\epsilon_{kl})|\langle a'|\tau|kn\rangle|^2.$$

If  $\alpha - \beta \gg \gamma$ , then  $\Delta j/j_0 \sim G_{aa}^{I}(\omega - \omega_0)$  and UPS would provide a direct measure of  $G_{aa}^{I}$ , the density of adsorbate states. From (4c)-(4e), this obtains only if  $v_f/u_f$  is small, i.e., if  $\gamma/\alpha \ll 1$ . EC find a resonant level of CO adsorbed on Ni at  $\epsilon_r \simeq 8$  eV below the Ni Fermi energy. For Ni,  $\epsilon_B = 6.5$  eV below the Fermi energy. Equations (8) and (5) give for  $\epsilon_r < \epsilon_B$ 

$$\gamma/\alpha \approx \sigma [\Gamma(\overline{\omega})/\Gamma_0(\epsilon_r)]^{1/2} [j(\epsilon_r + \omega_0)/j_0(\overline{\omega} + \omega_0)]^{-1/2},$$

where  $\sigma = 2c_s a_0/lB$ , and  $\overline{\omega}$  is an energy greater than  $\epsilon_B$  but less than the bottom of the Ni *d* bands. In this region EC find that  $j_0(\overline{\omega} + \omega_0)$  is essentially independent of  $\overline{\omega}$ ;  $\Gamma_0(\epsilon_r)$  is the width of the resonant peak at  $\epsilon_r$ , and  $\Gamma(\overline{\omega}) \approx \pi N_a \langle V_{kl,a} \rangle_0^2 \rho_m(\overline{\omega})$ . Equation (9) is valid for  $(\overline{\omega} - \epsilon_r)/\omega_0 \ll 1$ . For  $\epsilon_r$  $> \epsilon_B$ , Eqs. (8) and (4a) give  $\gamma/\alpha \approx \sigma [\Delta j(\epsilon_r + \omega_0)/j_0(\epsilon_r + \omega_0)]^{-1/2}$ .

Our theory holds for large  $\hbar \omega_0$  and low adsorbate coverage. For  $\hbar \omega_0 = 40.8 \text{ eV}$  and  $c_s \simeq \frac{1}{2}$ , EC find  $j(\epsilon_r + \omega_0)/j_0(\overline{\omega} + \omega_0) \sim \frac{1}{8}$  for CO on Ni. EC estimate  $a_0/l \sim \frac{1}{4}$ . We take B = 1 and we guess that  $\Gamma/\Gamma_0 = 2$ . These values yield  $\gamma/\alpha \sim 2$ . This result must be regarded as a rough estimate because of the approximations used to obtain it; nevertheless, we feel it is significant and demonstrates that, for energies  $\omega > \epsilon_B + \omega_0$ , one *cannot* assume a priori that UPS simply measures the density of adsorbate states.  $G_{aa}^{R}$  may contribute to  $\Delta j/j_0$ . An analysis of field emission in the presence of adsorbates led to the conclusion that for field emission  $G_{aa}^{R}$  does not contribute to  $\Delta j/j_0.^4$  The physical reason is that in field emission the relative contributions of  $G_{aa}^{R}$  and  $G_{aa}^{I}$ to the current depend on the ratio of tunneling probabilities: metal-vacuum tunneling to adsor-



FIG. 1.  $\Delta j(\omega)/j_0(\omega)$  as given by Eq. (10) of the text. *D*, as defined in (10), is the strength of the antiresonance. bate-vacuum tunneling.

The effect of  $G_{aa}^{R}$  on  $\Delta j/j_{0}$  is shown in Fig. 1. If  $G_{aa}(\omega) = (\omega - \epsilon_{r} - i\Gamma)^{-1}$ , then (4a) gives

$$\Delta j/j_0 \propto (1 - D\widetilde{\omega})/(\widetilde{\omega}^2 + 1), \tag{10}$$

where  $D = |\gamma/(\alpha - \beta)|$  and  $\tilde{\omega} = (\omega - \epsilon_{\gamma})/\Gamma$ . For D = 0,  $\Delta j/j_0$  is a Lorentzian of width 1 centered at  $\tilde{\omega} = 0$ . As D increases, the peak shifts to lower energies and the line shape becomes antisymmetric. The curve in Fig. 2 shows the experimental results of EC for  $\Delta j$ . We expect  $\Delta j \propto G_{aa}^{\ I}(\omega)$  for  $\omega - \omega_0 < \epsilon_B$  and  $\Delta j \propto G_{aa}^{\ I}(\omega) - DG_{aa}^{\ R}(\omega)$  for  $\omega - \omega_0 < \epsilon_B$  and  $\Delta j \propto G_{aa}^{\ I}(\omega) - DG_{aa}^{\ R}(\omega)$  for  $\omega - \omega_0 < \epsilon_B$ . The antiresonant behavior in  $\Delta j$  observed by EC is characteristic of a contribution from  $G_{aa}^{\ R}$ ; there is an additional negative contribution to  $\Delta j$  caused by the extra scattering from adsorbates. For  $\omega - \omega_0 < \epsilon_B$ ,  $\Delta j$  is quite symmetric as expected; EC also observed an additional resonant peak at 10.7 eV below the Fermi energy, which is fairly symmetric.

The antiresonant contribution to  $\Delta j$  arises from



FIG. 2. Experimental  $\Delta j(\omega)$  as measured by EC for Ni(100) plus 0.6 layers of CO. Photon energy, 40.8 eV.

a degeneracy (or near degeneracy) between the unperturbed adsorbate level  $\epsilon_a$  and the continuum of metal states  $\epsilon_m$ . It is a general phenomenon; for example, antiresonances appear in inelastic electron-atom scattering and in atomic ultraviolet light adsorbtion. There, the interference arises from a degeneracy of a discreet two-electron excited atomic state with the continuum of single ionized atomic states. The strength of the antiresonance is directly related to the coupling between the discreet and continuum states, i.e.,  $V_{m,a}$  in the case of photoemission.

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<sup>1</sup>D. E. Eastman and J. K. Cashion, Phys. Rev. Lett. <u>27</u>, 1520 (1971).

<sup>2</sup>G. Breit and H. A. Bethe, Phys. Rev. <u>93</u>, 888 (1954).
 <sup>3</sup>I. Adawi, Phys. Rev. 134, A788 (1964).

<sup>4</sup>D. Penn, R. Gomer, and M. H. Cohen, Phys. Rev. Lett. 27, 26 (1971).

<sup>5</sup>G. D. Mahan, Phys. Rev. B 2, 4334 (1970).

<sup>6</sup>Attributing a momentum dependence to  $\lambda$  in  $e^{\lambda z}$  would have the effect of multiplying  $j_0$  by a factor of the form  $(1-P_c/P)$ , in agreement with C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030 (1964).

## Magneto-optical Study of Hole-Optical Phonon Coupling in InSb

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The interactions of bound holes with TO and LO phonons in InSb have been observed in magneto-optical experiments. Theoretical estimates of the hole-phonon coupling strengths have been obtained.

Magneto-optical studies of polarons have yielded valuable information concerning the resonant electron-optical-phonon interaction in semiconductors.<sup>1</sup> The interaction typically is manifested as a splitting and broadening of a transition such as cyclotron resonance, when the electron excitation and optical-phonon energies are comparable. Previous studies of this type have been restricted to electron excitations in a number of n-type polar semiconductors. In the present work, resonant bound-hole-optical-phonon coupling in *b*-type InSb is reported. Interactions with both TO and LO phonons have been observed. The observations serve to illustrate several significant differences between the interactions of holes and of electrons with optical phonons.

Before presenting the experimental results it will be useful to discuss briefly two factors which differentiate hole coupling from electron coupling to optical phonons. Firstly, because of symmetry considerations,<sup>2</sup> the interaction of electrons with TO phonons is expected to vanish, whereas hole– TO-phonon coupling is allowed, as confirmed by optical<sup>1,3</sup> and tunneling<sup>4</sup> experiments. Secondly, in contrast to the case for electrons in materials previously studied, free holes occupy states in both light- and heavy-mass bands. This leads to a multiplicity of initial states for magneto-optical transitions, thus tremendously complicating the study of free-hole polaron effects. It is therefore desirable to perform experiments on bound holes which possess a unique state. Another consequence of the valence-band structure is that in the presence of a magnetic field, acceptor excited states exist in association both with the lowlying heavy-hole Landau levels, and with the more widely spaced light-hole levels. In subsequent discussions, the terms "low mass" and "high mass" will be used to distinguish between these two types of acceptor excited states. Transitions involving low-mass excited states in InSb and Ge were previously investigated in some detail.<sup>5, 6</sup>

In the present experiments, the first few acceptor excitations to low-mass excited states have been studied in a spectral region encompassing the optical-phonon energies in InSb. Above a few kilo-oersteds the energies of these acceptor excitations vary approximately linearly with magnetic field. Structure in the absorption spectra due to hole-phonon coupling would first be expected when the transition energies approach the optical-phonon energies. However, this spectral region is inaccessible because of strong lattice absorption and reflection. At higher field strengths, the energy separations of the lowmass and high-mass excited states are comparable to the optical-phonon energies. It is this field region in which structure in the acceptor excitation spectra has been observed and studied.

InSb samples used in these experiments were