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THEORY OF SURFACE PLASMON EXCITATION IN LOW-ENERGY ELECTRON DIFFRACTION AND IN PHOTOEMISSION*

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A theory of inelastic scattering of electrons by surface plasma oscillation is presented for low-energy electron diffraction and photoemission. The calculations give results which lend quantitative support to the interpretations of some prominent inelastic effects as due to surface plasmon excitation in recent experiments by Lander and Morrison in low-energy electron diffraction and by Smith and Spicer in photoemission.

Excitation of surface plasmons (SP) in a degenerate semiconductor by tunneling electrons has been observed in metal-semiconductor junctions.[1] Subsequent theory[2] based on an inelastic electron-surface plasmon (el-SP) interaction model yields results that agree with experiment both in magnitude and line shape. Recently, precise measurements[3,4] with low-energy electron diffraction (LEED) of the inelastic spectra of electrons in the system W(100-Cs) [Cs evaporated on a (100) face of tungsten] have revealed SP excitation in the Cs surface layer. This process was observed to have a high scattering cross section. Moreover, the data[4] for Cs coverage up to the formation of a "duolayer" have been interpreted by MacRae et al. as providing evidence for nonmetallic character of layers of low density due to transition to a Wigner-Mott state. In this Letter we present a calculation of the el-SP scattering in LEED. The results are not only consistent with the observation of large SP excitation, but also provide a framework for re-examining the Mott-transition hypothesis. The theory is easily extended to treat el-SP scattering in photoemission processes.

We idealize the Cs adsorbed on W as a film of thickness d bounded on one side by a semi-infinite W plasma.[5] The dielectric functions are taken to be $\epsilon_W = 1-\omega_W^2/\omega^2$ for W and $\epsilon_{Cs} = 1-\omega_{Cs}^2/\omega^2$ for Cs. Here ω_W and ω_{Cs} are bulk plasma frequencies of W and Cs, respectively. The dispersion of SP with inclusion of retardation effects[6] is shown in Fig. 1. Retardation effects are unimportant in our calculation because, in the small region $Q < \omega_{Cs}/c$ of Q space where they are significant, the SP fields are small.[6] We note that the SP for the present problem is not given by either $\mathrm{Re}\,\epsilon_{Cs}(\omega) = -1$ or by formula (1) of Ref. 4, as was assumed there.[7] The high-frequency

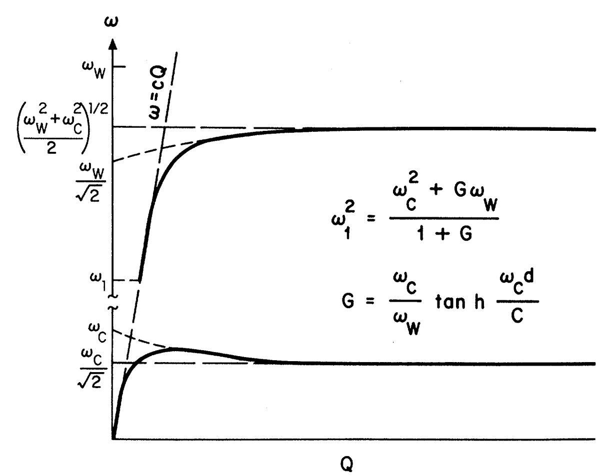

FIG. 1. Schematic dispersion relations for surface plasmon oscillations in vacuum-Cs-W interfaces. The ω_C in the legends is identical to ω_{Cs} in the text.

mode plays no role for incident electrons at 10-eV energy. The el-SP interaction can be expressed in terms of the creation and annihilation operators $c_{\vec{Q}}^\dagger$, $c_{\vec{Q}}$ of an SP excitation of wave vector $\vec{Q}$ obtained from quantization of the SP wave field.[2] Explicitly, it is

$$e\varphi(\vec{r}) = e\sum_{\vec{Q}}[\pi\omega_{\vec{Q}}/2Q\mathfrak{D}(Q)]^{1/2}\varphi_{\vec{Q}}(x)e^{i\vec{Q}\cdot\vec{r}} \times (c_{\vec{Q}}^\dagger + c_{\vec{Q}}). \tag{1}$$

$\varphi_{\vec{Q}}(x)$ is equal to $A_1(Q)e^{-Qx}$ for $x>d$, the vacuum region; $A_2(Q)e^{Qx}+A_2'(Q)e^{-Qx}$ for $d>x>0$, the Cs region; and $A_3(Q)e^{Qx}$ for $0>x$, the W region.[8] $\mathfrak{D}$ and the A's are involved functions of $\vec{Q}$ and the parameter $\eta=\omega_{\rm Cs}/\omega_{\rm W}$. However, as $\eta^2 \ll 1$ we can expand these quantities in powers of η^2. To lowest order in η^2, $A_1 \approx (e^{2Qd}-e^{-2Qd})$, $A_2 \approx (1+e^{-2Qd})$, $A_2' \approx (-1-e^{-2Qd})$, $A_3 \approx (1-e^{-4Qd})\eta^2$, and $\mathfrak{D} \approx (e^{2Qd}+1-e^{-2Qd}-e^{-4Qd})$. The el-SP interaction in the W region is smaller by a factor of η^2. The total potential of the scattering surface is the sum of the crystal potential

$$U(\vec{r}) = \sum_{\vec{R}} v_{\vec{R}}(\vec{r}-\vec{R}) = \sum_{\vec{G}} U_{\vec{G}}(x)e^{i\vec{G}\cdot\vec{r}} \tag{2}$$

and the SP potential $V(r)=e\varphi(\vec{r})$. Here $v_{\vec{R}}$ is the atomic potential at site $\vec{R}$, and the $\vec{G}$'s are the reciprocal vectors of the lattice planes. Then the scattering process is analogous to the bremsstrahlung of an electron in the field of a nucleus. As the electron is being scattered by the lattice, it emits SP's under the influence of the lattice potential.

The theory can be developed starting from the two-potential formula[9]: The T matrix for $U+V$ scattering is $T_{fi} = \langle\varphi_f|U|\chi_i^+\rangle + \langle\chi_f^-|V|\psi_i^+\rangle$. $\chi_{i,f}^\pm$ are outgoing- and incoming-wave solutions for U scattering and satisfy the Lippman-Schwinger equations

$$\chi_{i,f}^\pm = \varphi_{i,f} + \frac{1}{E-H_0 \pm i\epsilon}U\chi_{i,f}^\pm. \tag{3}$$

Similarly $\psi_i^\pm$ satisfy these for $U+V$ scattering. $\chi_{f,i}^\pm$ are the LEED wave functions[10] and are rather complicated. For the present purpose of calculating only the el-SP scattering we take $U=U_0(x)$ [the $\vec{G}=0$ component in Eq. (2)], thus ignoring diffraction. Then the eigenfunction of U_0, e.g., χ_f^- will be a product of a SP wave function φ_{n_f}, a plane wave $e^{i\vec{K}_f\cdot\vec{r}}$ for electron motion parallel to the interface, and a normal wave function $\xi_{k_{fx}}^-(x)$. The state $f \equiv \{k_{fx}, \vec{K}_f, n_f\}$ has total energy

$$E_f = \hbar^2(k_{fx}^2+K_f^2)/2m + \sum_{\vec{Q}}\hbar\omega_Q(n_{fQ}+\tfrac{1}{2}). \tag{4}$$

For a real SP emission process, the U_0 term of T_{fi} vanishes because the n_f-SP state is orthogonal to the initial 0-SP state. The remaining term $\langle\chi_f^-|V|\psi_i^+\rangle = \mathcal{T}_{fi}$ obeys the $\mathcal{T}$-matrix equation

$$\mathcal{T}_{fi} = V_{fi} + \sum_g V_{fg}\mathcal{T}_{gi}(E-E_g+i\epsilon)^{-1} = V_{fi} + \sum_g V_{fg}V_{gi}(E-E_g+i\epsilon)^{-1} + \cdots \tag{5}$$

upon iteration. The first two terms are the 1- and 2-SP processes. The intensity of electrons scattered via 1-SP emission of wave vector $\vec{Q}$ and energy $\hbar\omega_{\vec{Q}}$ to a final state f defined as the ratio (flux of electrons in state f)/(incident electron flux) is given by

$$R_f^{(1)}(\vec{Q}) = \left(\frac{m}{\hbar^2}\right)^2\int\frac{d\epsilon_{fx}}{|k_{xi}k_{xf}|}|V_{fi}|^2\delta(E_f-E_i). \tag{6}$$

The matrix element V_{fi} guarantees momentum conservation, $\vec{K}_f+\vec{Q}=\vec{K}_i$. Similarly the 2-SP contribution is

$$R_f^{(2)}(\vec{Q},\vec{Q}') = \left(\frac{m}{\hbar^2}\right)^4\int\left|\sum_{\vec{K}_g,n_g}\frac{V_{fg}V_{gi}}{|k_{xg}|}\right|^2\frac{\delta(E_f-E_i)d\epsilon_{fx}}{|4k_{xi}k_{xf}|}, \tag{7}$$

and f is derived from the initial state by the emission of two SP $\vec{Q}$ and $\vec{Q}'$. We re-emphasize that SP excitation is strongly attenuated by Landau damping (LD). These lifetime effects are extremely important and account for the broad line shapes in all SP emission processes.[2] To include damping, it is sufficient[11] to replace the δ function in $R_f^{(1)}$ by a Lorentzian whose width Γ is the SP decay width. The totality of back-scattered electrons with 1-SP emission is given via

$$R = \sum_{\vec{Q}}R_f^{(1)}(\vec{Q}) \equiv \int(dR/d\epsilon_f)d\epsilon_f. \tag{8}$$

$dR/d\epsilon_f$ defined by the identity is the quantity to be compared directly with the LEED inelastic spectrum. Evaluating the V_{fi} and summing over $\vec{Q}$, we get

$$\frac{dR}{d\epsilon_f}(\epsilon_f) = \frac{\pi^2}{2}\left(\frac{me^2}{\hbar^2}\right)\int d\vec{Q}\frac{\hbar\omega_Q}{\mathfrak{D}(Q)}\frac{\Gamma}{2\pi[(\epsilon_i-\epsilon_f-\hbar\omega_Q)^2+(\Gamma/2)^2]}\frac{1}{\hbar^2/2m|p_{xi}p_{xf}|}|\langle\xi_f^-(p_{xf},x)|\varphi_{\vec{Q}}(x)|\xi_i^+(p_{xi},x)\rangle|^2, \tag{9}$$

where

$$p_{xf} = \left(\frac{2m}{\hbar^2}\epsilon_f - k^2\right)^{1/2}.$$

The ϵ_f dependence of $(dR/d\epsilon_f)$ gives the line shape of the SP loss in LEED. It can be deduced from the ϵ_f dependence of the integrand in (9), which is mainly due to the large LD and the dispersion of the SP. $dR/d\epsilon_f$ peaks at $\epsilon_f = \epsilon_i - \omega_{\rm Cs}/\sqrt{2}$ because there is a large volume of phase space ($Q \gtrsim 1/d$) for which $\omega_Q = \omega_{\rm Cs}/\sqrt{2}$. There is a physical restriction on the size of Q because SP with wavelengths smaller than the interelectronic spacing are so strongly damped as to be nonexistent. This means that the integration over $\vec{Q}$ should be carried out only up to Q_C, a cutoff wave number. Since $\varphi_{\vec{Q}}(x)$ is negligibly small inside the W region, the details of the wave functions there are not important. For numerical calculations we have therefore adopted a model for $U(x)$ as a potential well of width d and depth $U_{\rm Cs}$ next to another well of depth $U_{\rm W}$ extended indefinitely in one direction; the form of the potential inside the W is unimportant. $U_{\rm Cs}$ ($U_{\rm W}$) is taken as the sum of the work function and The Fermi energy of Cs (W). The scattering states ξ_f^- and ξ_i^+ can be obtained analytically. We take Γ to be $\alpha(Q/k_{\rm Cs})$ due to the LD of SP and $k_{\rm Cs} = \omega_{\rm Cs}/v_{\rm F}$.[2] α determines the size of the LD and in turn the width of $dR/d\epsilon_f$. The magnitude of $dR/d\epsilon_f$ is in the main determined by Q_C. First we consider the thick Cs plasma of ten monolayers with $d \approx 30$ Å. Experiments[3,4] have shown that a large fraction of the back-scattered electrons have undergone 1- and 2-SP processes in this case. By use of Eq. (1) and a similar expression for 2-SP emission, we find the theoretical 1- and 2-SP contributions agree with experiment for a value of Q_C of 1.5×10^7 cm^{-1} (which is roughly equal to $k_{\rm Cs}$) and for a value of α of 6 (which gives $\mathrm{Im}\omega \sim \mathrm{Re}\omega$ at Q_C).[12] These values for Q_C and α are then used to determine the 1-SP contribution R for various Cs coverages. The results depicted in Fig. 2 show that R starts from zero at $d = 0$, rises rapidly for small d, and saturates as $d \to \infty$. This behavior is in agreement with the LEED experiments.[3,4,13,14]

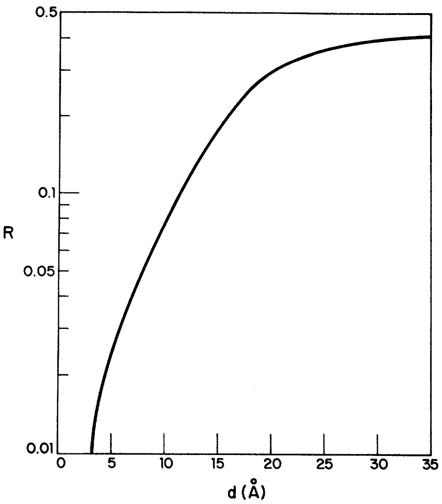

FIG. 2. Total back-scattered electrons with 1-SP emission as a function of d. See text for definitions.

The method presented can be applied to SP excitation in photoemission if we adopt Berglund and Spicer's model[15] for the process. Thus the photoexcited electron can emit SP's on traveling to and escaping across the surface. The contribution to the energy distribution curve due to SP emission can be calculated in the same way as in LEED, except that new sets of scattering states ξ_f^- and ξ_i^+ have to be used and d has to be taken to be infinite. Numerical calculations for Cs at photon energy ~10 eV with the same Q_C and α as determined previously in LEED predicts that photoelectrons which have suffered 1-SP inelastic scattering constitute a sizable fraction ($\sim\frac{1}{2}$) of the primary and show a broad peak at $\omega_{\rm Cs}/\sqrt{2}$ whose width is ~2 eV. This result has verified that the excitation of SP can contribute significantly to photoemission processes, as was first pointed out by Calcott and MacRae[16] and recently observed in the alkali metals by Smith and Spicer.[17]

Finally, we re-examine the hypothesis of the occurence of a Mott transition in the intermediate second layer with (2×2) structure.[4] For the SP mode under consideration the fields are negligibly small for $Q \ll 1/d$. Consequently, the SP of present interest exist as well-defined collective oscillations only for $1/d < Q < Q_C$. As the Cs coverage diminishes, $1/d$ increases and Q_C decreases. It is obvious that for coverages such that $1/d \gtrsim Q_C$ the SP cease to exist at all. Now, if the (2×2) layer has a composition such that for the corresponding electron density n, $Q_C \lesssim 1/d$ and if, in the hexagonal array, the electron density n_0 gives a Q_C substantially greater than $1/d$, then the present theory explains quite well the absence of SP losses in the intermediate (2×2) structure. On the other hand, if n is comparable with n_0, then, since the dependence of Q_C on n is very weak and d is independent of n for this coverage, we expect SP loss at the completion of the (2×2) structure to be of comparable magnitude to that when the hexagonal array is completely formed. In this case, an alternative explanation is called for and the Mott-transition hypothesis remains as a possibility. The problem can be settled by further experiments to clarify the nature of the (2×2) layer.

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SURFACE-PLASMON–ONE-ELECTRON DECAY AND ITS OBSERVATION IN PHOTOEMISSION*

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Evidence for the decay of surface plasmons into one-electron excitations has been obtained in photoemission measurements from a slightly roughened surface of aluminum. A simple theory has been developed which explains the resultant photoyield in terms of both the drop in reflectance resulting from roughness-aided plasmon coupling, and the relative penetration depth of the fields associated with these excited plasmons.

Optical excitations of volume plasma oscillations have long been observed. Ives and Briggs[1] first noted anomalies in the photoemission of metals near the volume plasma frequency, and Steinman[2] has since shown that these anomalies may be interpreted as the decay of volume plasmons into one-electron excitations. This plasmon-electron coupling occurs through the macroscopic Coulombic fields associated with the optically excited volume plasmons.

Surface plasma oscillations were first noted by Ritchie,[3] while Stern and Ferrell[4] later described the macroscopic Coulombic fields associated with these oscillations. The existence of such oscillating macroscopic fields implies that a surface-plasmon–one-electron coupling should occur which is analogous to the volume-plasmon–one-electron decay mechanism described above. The analogy breaks down in one respect, however. Optically excited volume plasmons are coherently excited, and their associated fields screen the excitation field to yield a unique optical-field decay length. Surface plasma oscillations, on the other hand, are most easily optically excited through the intermediary of momentum-conserving charge inhomogeneities such as surface roughness.[5] These surface excitations are not coherent with the incident optical field, and are characterized by macroscopic-field decay lengths which are independent of the