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Photoemission Studies of Silver with Low-Energy (3 to 5 eV), Obliquely Incident Light

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By use of the photoemission-into-electrolyte technique, the photoyields of silver have been measured for p- and s-polarized light in the energy range 3 to 5 eV with a wide range of incident angles. Pronounced structure, providing striking evidence for the validity of the nonlocal theory of the surface photoeffect, is obtained.

Vacuum photoemission experiments are limited to photon energies above the work function. The usual scheme for reducing the low-energy limit is to overlay the surface with cesium, the reduction of the work function resulting from the high polarizability of the cesium atoms. However, the extent to which the resulting photoemission is distorted by the cesium and thus no longer representative of the metal is unknown. An alternative is to study photoemission into an electrolyte[1]; the reduction of the work function occurs through the presence of an electrical double layer at the metal-electrolyte interface. The possibility that the electrolyte will affect the photocurrents sufficiently that they will be of limited utility for drawing conclusions about the metal must be faced. There is now evidence that such is not the case,[2] and we will present strong evidence to substantiate this view below. Indeed, the principal purpose of this note is to point up the effectiveness of this technique in solid-state investigations.

The low-energy limit on vacuum photoemission is unfortunate for silver. The occurrence of the sharply defined plasmon for energies above about 3.8 eV and suppression of the plasmon effects at about 4.0 eV due to transitions from the d bands take place below the work function. We have studied the photoemission into an electrolyte in the energy range from 3 to 5 eV. To include the possibility of observing manifestations of the surface photoeffect,[3-5] we have used polarized light with the apparatus of Ref. 2. The samples were thick (2500 Å) single-crystal films with (111) surfaces prepared by evaporation onto mica.

What would we then expect for the photoyields resulting from photons of energy $\hbar\omega$ incident at angle θ in the electrolyte? The simplest theoretical expressions for the yields, Y_p and Y_s, for p- and s-polarized light result from the isotropic-volume-excitation model.[6] In this case the yields for p and s light are given by

$$Y_{p,s}=A_{p,s}[\alpha\xi/(1+\alpha\xi)]P/2, \quad (1)$$

where α is the optical absorption coefficient, ξ the electron escape length (taken here for simplicity to be a function of ω), A_p (A_s) the absorptance for p (s) light, and P a function describing the escape of excited electrons through the surface.

The use of this model cannot be justified for the low energies of interest here. However, we can easily modify the expression for the p yield to improve significantly the physical content. Since the surface is (111), the normal passes through the L point of reciprocal space, in the neighborhood of which the threshold for interband transitions occurs at $\hbar\omega \sim 3.8$ eV.[7] This threshold involves transitions from the Fermi surface. Since the work function here is about 3 eV, those electrons excited at that L point associated with the surface will have energy and momentum sufficient to contribute to the photocurrent. Thus, it is the electric field component

normal to the surface which is primarily responsible for the photocurrent. With the surface normal the z direction and the light incident in the x-z plane, we can extract from Eq. (1) the part associated with excitations in the z direction by multiplying by $G(\theta,\omega)=|E_z|^2/(|E_z|^2+|E_x|^2)=\epsilon_0\sin^2\theta/(\epsilon_0\sin^2\theta+|\epsilon-\epsilon_0\sin^2\theta|)$, where E_x and E_z are the usual local electric field components within the photoemitter of dielectric constant $\epsilon=\epsilon_1+i\epsilon_2$ and ϵ_0 is the optical dielectric constant of water. $Y_p^z=GY_p$ should then represent the yield far better than Y_p. The quantity $S_p=A_pG\alpha$ is shown in Fig. 1 for silver in water.[8] (We assume throughout that $\alpha\xi\lesssim 1$, the normal situation.) The refractive peak associated with the zero in ϵ_1 at $\hbar\omega=3.78$ eV appears. Also in Fig. 1 is a sketch of the joint density of states for conduction-band transitions near L.[7] The association of the strong increase in S_p with the onset of these transitions appears reasonable. To attempt here a more detailed association of band effects with the anticipated yield involves a number of complications. For example, transitions from the d bands to the Fermi surface set in at about 4.0 eV. Such transitions cannot contribute directly to the photoyield but will increase the optical absorptance, suggesting that the expected yield should be reduced for $\hbar\omega>4.0$ eV. An additional effect tends to compensate for this drop. As the energy increases, the yield from scattered electrons and from higher-order direct effects due to the electric field component parallel to the surface will increase. The former effect will also contribute to the yield a low-energy tail below $\hbar\omega=3.8$ eV, perhaps not unlike that of S_p. Since the yield is $Y_p^z\cong S_p\xi P$, and ξP, which probably increases slowly as ω increases and includes a cutoff of the yield at the work function (~3 eV), should not have dramatic effects, we conclude that the shape of the p yield should be roughly like S_p.

For s light, the electric field is parallel to the surface, and the character of the yield is more subtle. We expect a small yield associated with second-order direct transitions starting at the edge at 3.8 eV[7], and increasing roughly like the density of states of Fig. 1. This yield should be superimposed upon a background yield of scattered electrons extending to lower energy. $S_s=A_s\alpha$, which appears in Eq. (1), is shown in Fig. 1 and includes just these features; the shape of this curve should roughly represent the s yield. Taking P to be independent of polarization, the shape of the yield ratio Y_p^z/Y_s is shown in Fig. 1.

Experimental results for the p and s yields are shown in Fig. 2. These results correspond reasonably well to those suggested by the simple

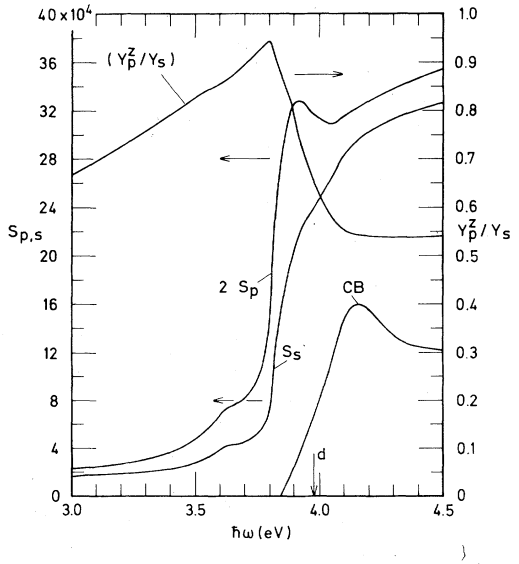

FIG. 1. Anticipated frequency dependence of the p yield S_p, the s yield S_s, and the yield ratio Y_p^z/Y_s. CB is a sketch of the joint density of states for direct transitions from the conduction band in the vicinity of the L point; the threshold for transitions from the d band is denoted d.

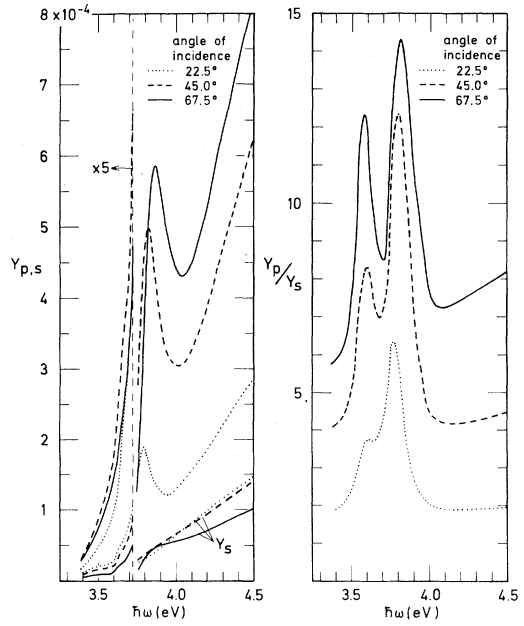

FIG. 2. The experimental results for the p yield Y_p, the s yield Y_s, and the yield ratio Y_p/Y_s. The work function is 3.2 eV.

arguments above. However, there is structure for frequencies below 3.8 eV. Plotting Y_p/Y_s gives the results shown in Fig. 2; the expected peak at $\hbar\omega \sim 3.8$ eV drops off very sharply on the low-energy side and is accompanied, for the larger angles of incidence, by a peak of comparable size at $\hbar\omega \sim 3.6$ eV. Could this lower-energy peak be due to surface plasmons? In vacuum, the surface plasmon energy for silver is $\hbar\omega_{sp}{}^{vac} = 3.64$ eV. In the electrolyte, this frequency is reduced to $\hbar\omega_{sp}{}^{H_2O} = 3.49$ eV, well below the low-energy peak. Surface plasmons couple effectively to light, s and p polarized, via surface roughness, even on surfaces which are only slightly rough.[5] In the frequency region of the surface plasmon, yield ratios tend to be small, $Y_p/Y_s \lesssim 2$.[5] It is possible here that for $\hbar\omega < 3.6$ eV, the surface plasmon, by contributing relatively more strongly to the small s yield, reduces a yield ratio which would remain high for other reasons if surface-plasmon effects could be eliminated. We will return to this point below.

Another possibility which can be ruled out as the source of the 3.6-eV peak in Y_p/Y_s is a surface state.[9] To establish this, we prepared two samples simultaneously, evaporated onto one a monolayer of gold, and then measured Y_p and Y_s for both. If the low-energy structure is due to a surface state, we would expect the monolayer to obliterate it. The result is that the monolayer affects the p yield only near the peak (where it drops by ~25%) and increases the s yield by a factor of about 2. Although the ratio Y_p/Y_s is now considerably smaller, the peaks at $\hbar\omega \sim 3.8$ and 3.6 eV remain.

The results in Fig. 2 can be understood by use of the nonlocal theory of the surface photoeffect.[3-5] To employ this theory, we need a longitudinal dielectric function $\epsilon_l(q,\omega)$. (It is sufficiently accurate to use the optical value for the transverse dielectric function.) An approximate expression, based upon experimental data, has been obtained.[10] The basic idea is that the dielectric function can be written as $\epsilon_l(q,\omega) = \epsilon_d(\omega) + \epsilon_{l,M}(q,\omega)$, where the local function ϵ_d represents the effects of the rather flat, low-lying d bands, and $\epsilon_{l,M}$, the free-electron function of Mermin,[11] describes the properties of the s electrons. In $\epsilon_{l,M}$, parameters such as the Fermi velocity and the effective mass are obtained from a combination of band calculations and experiment and $\epsilon_l(0,\omega)$ is obtained from optical data. The resulting expression describes the plasmon properties very well.[10]

We calculated, with the procedure of Ref. 3, the nonlocal p yields (actually $2Y_p{}^z/P$ so that the escape function is not included), shown with their local counterparts in Fig. 3.[12] For reasons discussed above, we included only the yield contribution associated with E_z. Below the peak, the nonlocal curves drop off far more rapidly than the local. This is apparent in Fig. 3 where the ratios $Y_p{}^z/Y_s$ are shown. The nonlocal curves do have the structure of the experimental results with the exception of the low-energy drop. Thus we can identify the physical effects involved.

The 3.8-eV peak in $Y_p{}^z/Y_s$ involves both refraction and plasmon excitation. Plasmons can contribute to the yield only insofar as they decay into single-particle excitations. Near the L point interband excitations occur having the right energy and momentum to permit such decay.[7] Thus plasmons moving in the [111] direction (as they are here) should contribute to the yield. The gold-monolayer results suggest that plasmon effects are important as it is difficult to imagine a monolayer affecting the essentially macroscopic refraction behavior to the extent observed.

Below the large peak, the sharp drop in the nonlocal $Y_p{}^z/Y_s$ ratio is due to the fact that ϵ_1 is approximately 0 but negative; that is, we are below the plasmon edge. When this occurs the normal component of the electric field in the sur-

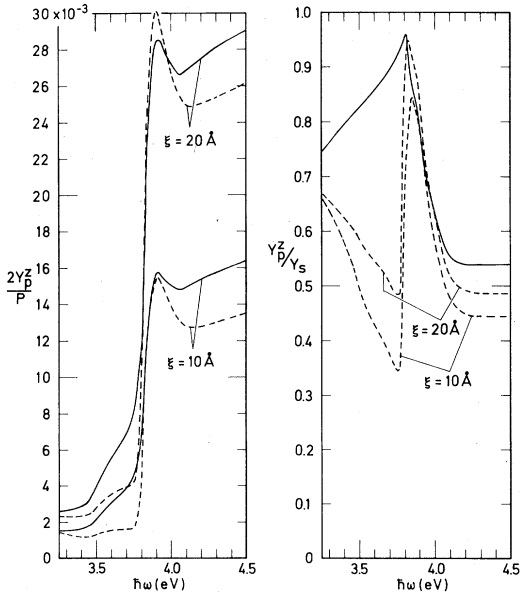

FIG. 3. Calculated values of $2Y_p{}^z/P$ and the yield ratio $Y_p{}^z/Y_s$ for $\theta = 67.5°$: full lines, local; dashed lines, nonlocal. Y_s is calculated locally.

face region is small because of a cancelation between the transverse and longitudinal fields.[3-5] As a result, the p yield is reduced considerably below the local value as is clear in Fig. 3. This region of small field extends in about 24 Å for $\hbar\omega = 3.78$ eV but decreases sharply as ω decreases. With decreasing ω then, the p yield tends to increase again with the result that $Y_p{}^z/Y_s$ increases. The increase is associated physically with intraband transitions with the momentum transfer, supplied by the longitudinal field, perpendicular to the surface. In the experimental results, this increase extends only to 3.6 eV; in the calculation the increase continues to lower energies. This result suggests that the single-particle intraband effects do act to keep the yield ratio high and it is surface plasmons, not in the calculation, which cause the sharp drop at 3.6 eV. There remains the possibility that the proper joint density of states for intraband transitions has significant structure in this energy range.

We conclude with some comments concerning the efficacy of studying solids by use of the photoemission-into-electrolytes technique. The high values of Y_p/Y_s obtained in our experiments are striking evidence that the electrolyte does not modify the surface character to any appreciable extent. An additional point in this connection is the sharpness of the structure obtained here, as is the fact that the effects of a monolayer on the surface were so apparent.

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Nonlinear Optical Excitation of the Relaxed Vibronic States of the F Center in KCl†

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We have conducted the first experiment on two-photon excitation of the F center and obtain new and conclusive information about the structure of the relaxed excited states, the strength of electron-phonon interaction, and the amount of vibronic mixing of $|2s\rangle$ and $|2p\rangle$ states, allowing the exact solution of the dynamic problem. A new resonance arising from an additional vibronic mixing ($3s$-$3p$) has been found. The values of the $2s$-$2p$ splitting and of the fluorescence lifetime from $|2p'\rangle$ have been measured for the first time.

We report the first investigation on the relaxed excited states (RES) of the F center in an alkali-halide crystal by a two-photon excitation technique.[1] The structure of the F^* center (F center in RES) in KCl is of particular interest because of the rather complex processes that are found to take place during the crystal relaxation. The experiments of Chiarotti and Grassano,[2] Kuhnert,[3] and Bogan and Fichten[4] have shown evidence that in KCl the $2s$ state, which in absorption lies 0.1 eV above the $2p$ state, crosses the $2p$ state during crystal relaxation and ends up lower in energy.[5] This model is consistent with Bogan and Fichten's assumption that the RES structure consists of nearly degenerate states $|2s'\rangle$ and $|2p'\rangle$ which result from an admixture of the $2s$ and $2p$ states, with $|2s'\rangle$ lower in energy. The exact nature and the strength of the mixing as well as the