

described elsewhere.

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Direct Optical Excitation of the Surface Photoelectric Effect

S. A. Flodström

Department of Physics and Measurement Technology, Linköping University, Linköping, Sweden

and

J. G. Endriz

RCA Laboratories, David Sarnoff Research Center, Princeton, New Jersey 08540

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Measurements on Al of the ratio of the photoyields by p - and s -polarized light, Y_p/Y_s , and the absolute yield for p -polarized light Y_p , at different angles of light incidence and at energies near photoemissive threshold, give results which are in excellent agreement with the strength of the surface photoelectric effect implied in recent calculations.

We present in this paper what we believe to be the first experimental evidence which unambiguously shows the direct optical excitation of the surface photoelectric effect.^{1,2} Excitation of the effect in surface-plasmon decay has recently been reported and explained.³ In contrast, no firm data have previously been presented for direct optical excitation of the effect although the literature of attempts to do so spans three decades.^{1,4,5} This apparent paradox between observation of the surface effect in surface plasmon decay and failure to observe it in direct optical excitation has been in large measure cleared up in a recent theoretical description of the surface photoelectric effect, which stresses the heretofore unappreciated strong frequency dependence in the effect while pointing out the importance which surface roughness can have in any experimental studies.⁶

Briefly stated, the theoretical treatment⁶ points out that the surface effect is strongest near threshold frequencies in nearly free-electron metals, becoming weaker at higher energies, and almost totally suppressed near the volume plasma energy. Because surface plasmons can exist near these threshold energies and are easily excited through slight surface roughness, the

decay of these plasmons introduces strong surface photoexcitation which can severely perturb any photoyield measurements. It is thus suggested that any attempts at direct optical observation of the surface effect be carried out near threshold energies on very smooth samples of metals for which the surface plasma energy is energetically removed from the photoemission threshold (e.g., polyvalent metals).

Aluminum, the metal chosen for the present studies, is almost unique among nearly free-electron metals in having a surface plasma energy (10.5 eV) well removed from its threshold energy (4.1 eV), and in being amenable to smooth-surface preparation.^{3,7} By contrast, most of the previous experimental attempts at observing optical excitation of the surface effect were carried out on the alkali metals at energies for which the surface effect would be expected to be weak, or obscured by spurious coupling to surface plasmons. It is particularly difficult to obtain extremely smooth samples of the alkali metals.

The Al films described in this paper were prepared by evaporation of 1000-Å films in 1 min at pressures of 2×10^{-8} Torr, followed by measurement at 1×10^{-10} Torr. Surface rough-

ness was monitored by observing the normal incidence photoyield in a manner implied in Ref. 3. It is estimated that the films prepared had an rms height variation of under 15 Å. While smooth surfaces were critical in obtaining suitable results in the present study, a detailed description of the procedures followed in obtaining such surfaces will not be pursued in this Letter since the subject is extensively discussed in Refs. 3 and 7. Attempts to detect optical excitation of the surface effect were restricted to the energy range 4.1 eV (threshold) to 6.0 eV, well removed from the strong coupling to surface plasmons which can occur at 10.5 eV.

As was first pointed out by Mitchell,¹ the surface photoelectric effect can only be excited by *p*-polarized light, that is, light with its electric field vector \vec{E} in its plane of incidence, and necessarily only to oblique angles of incidence.⁸ Thus many previous experiments have attempted to detect the surface effect by measuring deviations in the ratio of photoyield from *p*-polarized light to photoyield from *s*-polarized light from what one would expect in a volume-effect theory of photoemission. This so-called "vector ratio" measurement of Y_p/Y_s has the advantage that theoretical calculations of this quantity within the isotropic volume-effect theory⁹ depend only upon the relative reflectance values for the two light polarizations,

$$\frac{Y_{p,\text{vol}}(\hbar\omega, \varphi)}{Y_{s,\text{vol}}(\hbar\omega, \varphi)} = \frac{1 - R_p(\hbar\omega, \varphi)}{1 - R_s(\hbar\omega, \varphi)} \equiv \frac{\Delta R_p}{\Delta R_s},$$

being independent of the details of the excitation and escape mechanisms of the electrons within the metal. Furthermore, the uncertainty in $\Delta R_p/\Delta R_s$ is significantly less than the uncertainty in ΔR_p or ΔR_s individually, so that the theoretical value of the "vector ratio" within the isotropic volume-effect theory can be very accurately determined. This point is made explicitly in the plot of $Y_p/Y_s(5.4 \text{ eV})$ for Al, calculated in the volume theory, and shown in Fig. 1. The cross-hatched area shows the minimal error introduced in the calculated ratio by varying the optical constants used by $\pm 20\%$.

The experimentally determined vector ratio $Y_p/Y_s(5.4 \text{ eV})$ is also shown in Fig. 1 as a mean of data points representing two different 1000-Å films having slightly different, but extremely low, surface roughness. (The round data points are from the film having the lowest surface roughness.) The deviation of this curve from the vol-

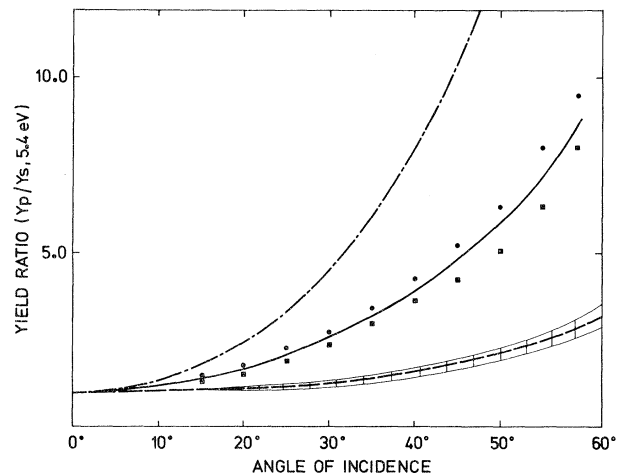


FIG. 1. "Vector ratio" of Al photoyield near threshold (5.4 eV) from *p*-polarized light to photoyield from *s*-polarized light as a function of angle of light incidence. Solid curve, mean representation of the square and round experimental data points; dashed curve, from an isotropic volume-photoeffect theory; dot-dashed curve, from the addition of a surface-effect term to the theory as described in Ref. 6. Cross-hatched region bracketing the volume-effect calculation, range of that calculation resulting from $\pm 20\%$ variations in ϵ_1 and ϵ_2 . Square data points, data from an Al film found to be slightly rougher than the film represented by round data points.

ume-effect curve is shown to be both large and well outside of the error range of the isotropic volume-effect calculation. The experimental data and the volume-effect curve are both "ratio" curves and are not what could be considered first-principles calculations. By contrast, the plot in Fig. 1, which includes the surface as well as the volume effect, includes the first-principles calculation of the surface effect in Al reported in Ref. 6. In fact, that plot scales directly from the volume-effect curve in Fig. 1 by the factor $1 + \nu_p(\varphi, 5.4 \text{ eV})Y_{\text{ratio}}(5.4 \text{ eV})$ defined in Ref. 6. In view of the first-principles nature of the surface-effect calculation, it is not surprising that some disagreement exists with experiment. Failure of the volume-effect calculation, on the other hand, cannot be easily explained, and the curves of Fig. 1 must be viewed as giving strong evidence for a direct optical excitation of the surface photoelectric effect.

In "phrasing" the experimental data in terms of a vector ratio in Fig. 1, we have allowed comparison of experimental data with an expression for the isotropic volume-effect theory which is virtually without uncertainty, thus forcing the recognition of the failure of the isotropic volume-

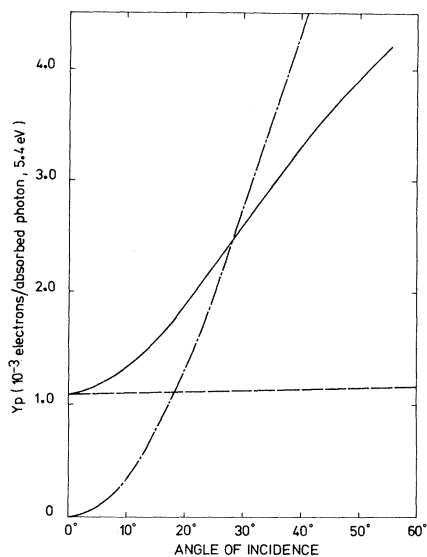


FIG. 2. p -polarized-light photoyield per absorbed photon near threshold (5.4 eV) obtained from experiment (solid curve). Also shown, calculated photoyield per absorbed photon in a volume-effect theory (dashed curve) and in the surface-effect theory of Ref. 6 (dot-dashed curve).

effect theory. The data can easily be phrased in a form which, while not as incontrovertible in its conclusions, is more easily understood and appreciated. Thus we see in Fig. 2 plots of p -polarized-light-induced photoyield in electrons per *absorbed* photon as a function of angle of incidence at 5.4 eV on Al. The surface-effect curve was taken from the calculations of Ref. 6 (the curve is specifically given by the expression $\mathcal{S}_p(\varphi, 5.4 \text{ eV}) Y_{\text{CH:forward}}(h\omega)$ defined in Ref. 6. The isotropic volume-effect curve in Fig. 2 is notable in its almost total lack of variation, 0° to 60° . This is significant because it has a straightforward physical interpretation, and because the curve differs dramatically in *shape* as well as in magnitude from the experimental curve. Physically, yield in the volume effect varies versus angle of incidence because the amount of light absorbed changes [change in $\Delta R_p(\varphi)$], or because the optical penetration depth into the metal changes (change in the optical absorption coefficient α). If the yield is normalized to the number of absorbed photons, it changes only with

changes in α . And if the electrons excited within the metal have a relatively large inelastic scattering length or escape depth ($l_e = 30 \text{ \AA}$ was assumed, consistent with Kanter¹⁰), then the normalized yield is relatively insensitive even to α . Such is the case for the volume-effect yield calculated and plotted in Fig. 2. The need to invoke the surface effect is apparent at a glance in comparing the steeply rising experimental curve of Fig. 2 [obtained by dividing experimental data by the known reflectance change, $\Delta R_p(\varphi, 5.4 \text{ eV})$] with the rising surface-effect and flat volume-effect curves.

The 5.4-eV results shown in Figs. 1 and 2 are typical of results obtained over the entire threshold region studied, 4.1–6.0 eV, and are in strong agreement with recent predictions (Ref. 6) that the surface effect should be easily observed near threshold in certain nearly free-electron metals. These results serve not only to offer the first unambiguous evidence for direct optical excitation of the surface photoelectric effect, but also to point out the danger in interpreting photoemission as an isotropic volume excitation process in all energy ranges for all types of experiments. It should be noted that there exist materials and energy ranges where the excitation of electrons through interaction with the surface, e.g., the surface photoeffect, is of great importance. A more extensive report on experimental data from different materials will be published elsewhere.

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