Investigation of the vectorial photoelectric effect in magnesium

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The photoelectric yield from Mg has been measured in the photon range 3.8–11.6 eV using plane polarized light at different angles of incidence. The results are interpreted in terms of volume and surface photoexcitation.

In an earlier paper,[1] we had given evidence for optical excitation of the surface photoelectric effect in Al. The present investigation of Mg gives photoemission data from a much broader photon range, allowing the possibility to investigate further the sources of photoelectrons in free-electron-like metals while confirming the conclusions drawn in Ref. 1.

The investigation was undertaken at a base pressure of $>1\times10^{-10}$ Torr. During the sublimation of Mg, the chamber pressure rose to $(8-9)\times10^{-9}$ Torr. As a substrate, we used a supersmooth quartz piece which had been coated with 500-Å Au *in situ*. The sublimation rate was 15–20 Å/sec, and the film thickness was measured as 1000 Å. The conditions described produced a very specular film.

In free-electron-like metals, two separate sources of electromagnetic fields act to excite photoelectrons: First, the optical field directly associated with the incident light; second, the surface-plasmon field associated with surface plasmons created by the incident light interacting with surface roughness.[2] Both fields can excite photoelectrons in essentially two ways; either by surface photoexcitation where the surface conserves momentum,[3–5] or volume excitation where lattice potentials conserve momentum.[4] Surface photoelectric emission can only be excited if the electromagnetic field has a component of the $\vec{E}$ vector perpendicular to the surface. This is the case for the surface-plasmon field and the p-polarized (the $\vec{E}$ vector lies in the plane of incidence) optical field at an oblique angle of incidence. Experimental results presented are for s- and p-polarized-light induced photoemission using different angles-of-light incidence and photon energies well below, at, and above the surface-plasma energy. The results obtained are interpreted in terms of both surface- and volume-effect forms of photoexcitation.

Figure 1 shows the measured photoelectric yield per incident photon at normal light incidence for Mg in the photon range 4.0–11.6 eV. The spectra can conveniently be divided into three regions.

I. THRESHOLD REGION 3.8–5.5 eV

From recent calculations[5] on the surface photoeffect, we can conclude that this low-energy photon range is where the surface effect should dominate the yield for p-polarized light at oblique angles of incidence. Thus we should be able to estimate its importance in Mg by measuring the "vector" ratio $Y_p(\hbar\omega,\phi)/Y_s(\hbar\omega,\phi)$ of yield from p- and s-polarized light for photon energies near threshold[6] and comparing it with what could be expected from a pure volume theory.

Consistent with the notation of Eq. (32), Ref. 5, we have

$$\frac{Y_p(\hbar\omega,\phi)}{Y_s(\hbar\omega,\phi)}=\frac{Y_{p,\mathrm{vol}}(\hbar\omega,\phi)+Y_{p,\mathrm{surf}}(\hbar\omega,\phi)}{Y_{s,\mathrm{vol}}(\hbar\omega,\phi)}, \tag{1}$$

$$\frac{Y_p(\hbar\omega,\phi)}{Y_s(\hbar\omega,\phi)}=\frac{Y_{p,\mathrm{vol}}(\hbar\omega,\phi)}{Y_{s,\mathrm{vol}}(\hbar\omega,\phi)}\left[1+\frac{Y_{p,\mathrm{surf}}(\hbar\omega,\phi)}{Y_{p,\mathrm{vol}}(\hbar\omega,\phi)}\right], \tag{2}$$

$$\frac{Y_p(\hbar\omega,\phi)}{Y_s(\hbar\omega,\phi)}=\frac{\Delta R_p(\hbar\omega,\phi)}{\Delta R_s(\hbar\omega,\phi)}\left[1+\mathcal{V}_p(\phi)\,Y_{\mathrm{ratio}}(\hbar\omega)\right]. \tag{3}$$

$\Delta R=1-R$, where R is the reflectance, and $\mathcal{V}_p(\phi)$ $Y_{\mathrm{ratio}}(\hbar\omega)$ is the ratio of the surface-to-volume effect photoemission for p-polarized light. $\mathcal{V}_p(\varphi)$ contains all effects due to angle-of-light incidence at energy $\hbar\omega$. It is defined in Eq. (30) of Ref. 5 and is a function of metal optical constants, as well as angle-of-light incidence. $Y_{\mathrm{ratio}}(\hbar\omega)$ is the characteristic ratio of the strength-of-surface photoexcitation to volume excitation. This ratio, described in Eqs. (28) and (29) of Ref. 5, is defined so as to be independent of angle-of-light incidence.

The volume photoexcitation component in Y_{ratio} $(\hbar\omega)$ was calculated for Mg assuming isotropic excitation in a three-step model, as previously described in Ref. 5 and elsewhere.[7] In this model, the volume effect is determined by Fermi level, work function, optical-absorption coefficient, and electron inelastic scattering length l_e. l_e was assumed[8] ~ 50 Å for $\hbar\omega\simeq4.2$ eV, the energy of the present calculation, and the assumed "isotropic-excitation" volume-effect model was considered

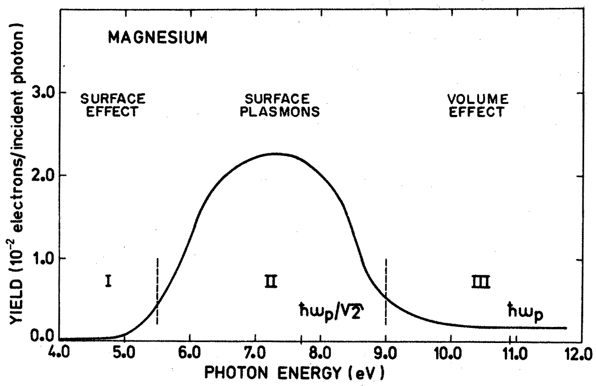

FIG. 1. Mg photoyield vs photon energy at normal light incidence. The free-electron value of the volume-plasma energy for Mg is 10.9 eV, and the corresponding surface-plasma energy is 7.7 eV.

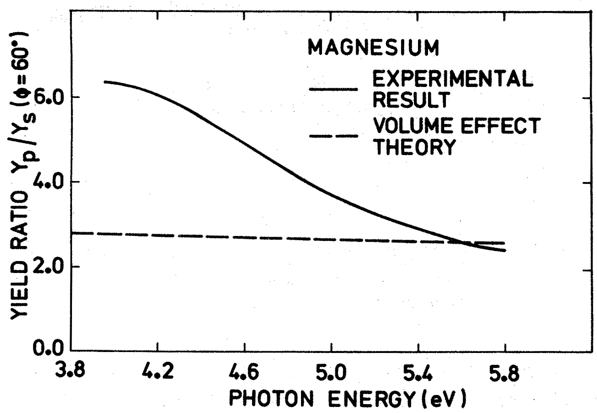

FIG. 3. "Vector ratio" of Mg photoyield from p-polarized light to photoyield from s-polarized light at 60° angle-of-light incidence vs photon energy (4.0–5.8 eV).

valid for two reasons. There is no preferred direction in the types of polycrystalline Mg films studied, and in a polyvalent metal, a number of reciprocal-lattice vectors having varying directions can take part in the volume excitation. Finally, a 4.2-eV light beam incident at 70° on Mg, refracts at an angle of only 25°, indicating very weak "directionality" effects in volume excitation at this energy, even if the assumption of isotropic excitation was not strictly valid.

The surface photoexcitation component in Y_{ratio} was calculated for Mg following the formalism developed in Ref. 5.[9] The resultant yield thus includes the strong effects of interaction with surface-polarization charge, as first described in Ref. 5. The yield was evaluated at 4.2 eV.

The calculated "vector ratio" $Y_p(\hbar\omega, \phi)/Y_s(\hbar\omega, \phi)$, described in Eq. (3), is shown plotted for Mg from 0 to 60° and 4.2-eV excitation in Fig. 2. Both the pure-volume-effect component $\Delta R_p/\Delta R_s$ and the included surface-effect factor $\mathcal{V}_p(\varphi)\, Y_{\text{ratio}}(\hbar\omega)$ are shown in this plot and compared with the experimental result. It is a distinct advantage of measuring and calculating the "vector ratio" that the pure-volume-effect component $\Delta R_p/\Delta R_s$ is very insensitive to uncertainties in metal optical constants[10–12] and can be unambigously determined. Thus the large deviation in the experimentally determined Y_p/Y_s from calculated $\Delta R_p/\Delta R_s$ of Fig. 2 clearly shows the inability of the isotropic volume theory to explain the experimental data.

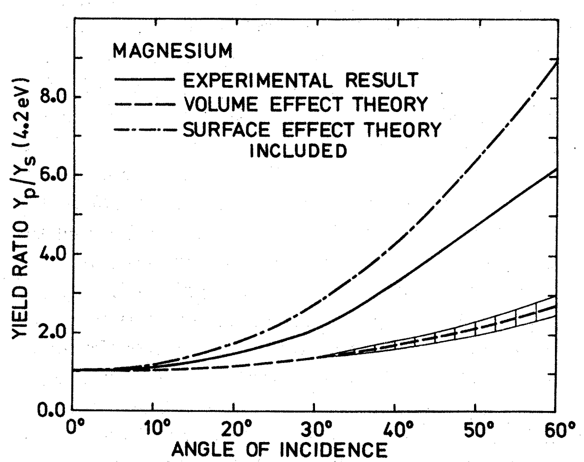

FIG. 2. "Vector ratio" of Mg photoyield near threshold (4.2 eV) for p-polarized light to photoyield from s-polarized light as a function of angle-of-light incidence. The cross-hatched region bracketing the volume calculation indicates the range of that calculation resulting from ±20% variations in ϵ_1 and ϵ_2.

Very good agreement is obtained between experimental results and the calculation which includes the surface effect when one considers the first-principles nature of this calculation. Figure 3 shows $Y_p(\hbar\omega, 60°)/Y_s(\hbar\omega, 60°)$ for the photon range 4.0–5.8 eV and supports the prediction in Ref. 5 of an increasing "vector" ratio as one gets closer to threshold. Quantitative comparisons are made difficult at the high-energy end of the photon range by electrons excited by the surface-plasmon fields.

II. SURFACE-PLASMON REGION 5.5-9.0 eV ($\hbar\omega_p/\sqrt{2} \approx 7.7$ eV)

The great increase in the photoelectric yield around the surface-plasma energy in the free-electron-like metals has been extensively discussed in the literature[13–16] and will not be reviewed here. Our interest in this region will be to determine if the photoyield induced by decaying surface plasmons exhibits any strong dependence on the polarization of the incident light. Since the plasmons are created by the incident light through interaction with the roughness of the surface, any strong polarization dependence in the yield should indicate that p- and s-polarized light probe different rough-

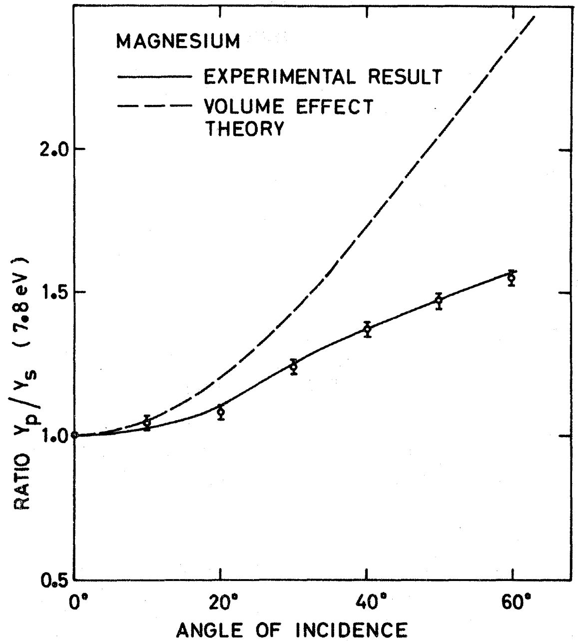

FIG. 4. "Vector ratio" of Mg at surface-plasma energy (7.8 eV) from p-polarized light to photoyield from s-polarized light as a function of angle-of-light incidence. Error bars indicate the experimental uncertainty.

ness spectra. If such polarization dependence existed, it might also influence our results in the threshold region and cause misinterpretation of the data in the low-energy region. Figure 4 shows $Y_p(7.8\text{ eV}, \phi)/Y_s(7.8\text{ eV}, \phi)$ for angles-of-light incidence up to 60°. We can see that dependence on

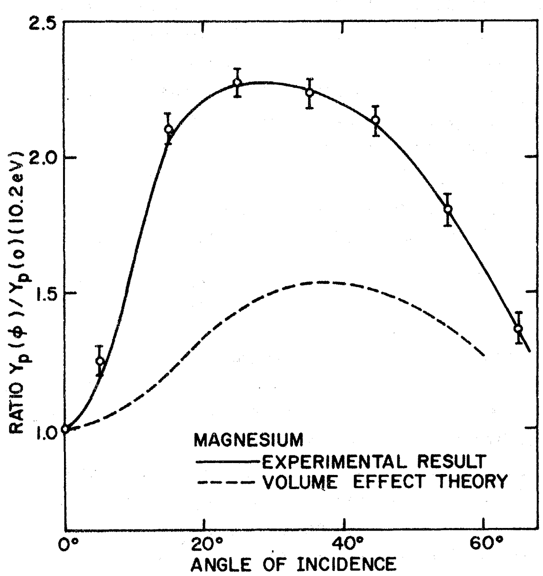

FIG. 5. Photoyield vs angle-of-light incidence for an excitation energy of 10.2 eV. Shown are the ratio of photoyield at a given angle-of-light incidence to photoyield at normal incidence for p-polarized light.

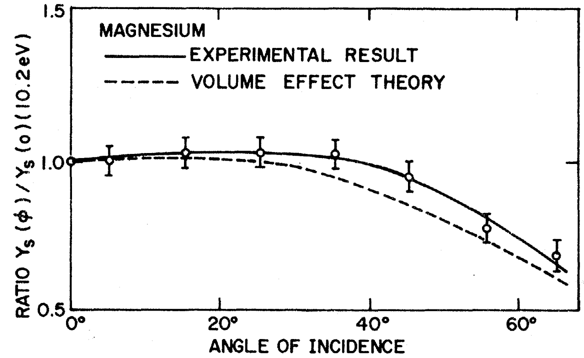

FIG. 6. Photoyield vs angle-of-light incidence for an excitation energy of 10.2 eV. Shown are the ratio of photoyield at a given angle-of-light incidence to photoyield at normal incidence for s-polarized light.

light polarization is minor in this region. Thus the only way photoelectrons from the decay of surface plasmons should influence low-energy measurements would be to hide strong "vector" effects in the yield. "Vector" effects in the low-energy region in free-electron metals is then somewhat a function of the ability to produce smooth films and to choose metals where the surface-plasma energy is well removed from threshold.[17]

It has been previously noted,[5,18] and should be reemphasized at this point, that the low vector ratio near the surface-plasmon energy does not indicate that surface-effect photoemission has been suppressed. To the contrary, surface-plasmon decay has been shown to provide the strongest form of surface-effect excitation.[18] It is only the "vector ratio" which has been suppressed by the effects of surface roughness coupling to plasmons. The actual photoyield in region II is more strongly a surface effect than in any of the three regions studied.

III. VOLUME-EXCITATION REGION 9.0-11.6 eV ($\hbar\omega_p \approx 10.5$ eV)

This photon range is well above the surface-plasma energy and nonradiative surface plasmons cannot be created nor do they exist. Including broadening effects relaxes the previous statement, but at a photon energy of 10.2 eV, which is well above the surface-plasma energy, the influence from photoelectrons excited by decaying plasmons should be small. It is also a photon range where calculations[5] show that the surface effect is of minor importance. Thus photoemission should be well described by an isotropic volume model, and an analysis similar to the one presented by Arakawa *et al.*[19] should apply. In our case, we have plotted $Y_p(\phi)/Y_p(0)$ and $Y_s(\phi)/Y_s(0)$ for a photon energy of 10.2 eV in Figs. 5 and 6 for angle-of-light incidence up to 60°. Also calculated and plotted in

Figs. 5 and 6 are the expressions

$$Y_p(\phi)/Y_p(0) = \alpha(\phi)\,\Delta R_p(\phi)/\alpha(0)\,\Delta R_p(0)$$

and

$$Y_s(\phi)/Y_s(0) = \alpha(\phi)\,\Delta R_s(\phi)/\alpha(0)\,\Delta R_s(0),$$

derived from the volume theory, assuming that $\alpha l_e \ll 1$, where l_e is the excited-electron inelastic scattering length. A comparison of the experimental data with volume-effect calculations indicates increases in yield with angle for p-polarized light which are substantially greater than predicted by the volume theory. This discrepancy may be within the uncertainties of the volume-effect calculation, or it may simply reflect the slight-surface-effect component remaining even at energies somewhat above the surface-plasmon energy. At any rate, the increase in yield for p-polarized light is seen to be far less than occurs in the low-energy spectral range where the surface effect is extremely strong. Yield for s-polarized light is in excellent agreement with the volume-effect calculation. This is particularly so when one notes that the slight discrepancy which does exist can easily be explained by the "effective" p-polarized excitation, which results from s-polarized light on slightly but unavoidably roughened surfaces.

Summarizing the results of our photoyield measurements on Mg, we conclude that the photoexcitation process may be conveniently broken down and described in three distinct spectral regions. In region I, excitation energies are near threshold and well below the surface-plasmon energy. Surface-plasmon excitation is almost nonexistent, but the surface photoelectric effect is extremely strong for p-polarized light at high angles of incidence. These factors result in a large observed "vector ratio" of yields from p- and s-polarized light, a ratio not explainable in the conventional isotropic excitation volume-effect theory. Observation of this large ratio and the surface-photoelectric effect is similar to that previously observed in aluminum[20] and can be expected to be seen near threshold in any nearly-free-electron metal for which reasonably smooth surfaces can be experimentally attained.

At the higher excitation energies just below and near the surface-plasmon energy, roughness-aided coupling to surface plasmons occurs in what is referred to as region II. This plasmon-excitation region is the region of strongest surface-effect photoemission, but roughness-induced coupling to plasmons is seen experimentally to be not especially dependent on light polarization; so the vector ratio is strongly suppressed in this region.

Above the surface-plasmon energy and near the volume-plasmon energy, coupling to nonradiative surface plasmons is almost nonexistent, and the surface-photoelectric effect is quite weak, even for p-polarized light at high angles of incidence. Volume-effect photoexcitation thus should dominate this region III, and the polarization and angular dependence of the photoyield should reflect this excitation mechanism. Observations of photoyield vs angles for both s- and p-polarized light are, in fact, in reasonable agreement with the volume theory in this spectral range, although the p-polarized light-induced yield increases at high angle are somewhat higher than expected. Studies are continuing, aimed at resolving this discrepancy and aimed at extending our polarized-light-yield studies to energies above $\hbar\omega_p$, an energy region for which recent calculations[21] show the possibility of greatly enhanced photoyield.

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