point, a very small change in the viewing angle from the H point means a very large energy shift. As long as the energy perturbation due to the wave-function admixture is smaller than the spin-orbit splitting, the states on the hole octahedron are the same "super-spin-orbit scatterer" as those in the [001] direction. Abruptly at the "corner" this eigenfunction condition is broken down. The scattering rate in the (001) plane is analyzed in a similar fashion.

Finally, we see from the data of Table I as well as from the similarity of the overall shapes of the curves in Fig. 2 that the scattering rates have (within an accuracy of about 10%) a completely linear dependence on concentration. This is true both of the total rate and, except for the defect scattering, of each of the components we have derived by the analysis presented above.

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Angular Anisotropies in the Photoemission from Polycrystalline Gold*

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Measurements of the photoelectron energy distributions from gold indicate angular anisotropies of the emission even for evaporated films. In particular, relative intensities and positions of the d-band emission peaks depend on the electron emission angle. We also observe the dependence of the energy distribution on the incidence angle and polarization of the photons.

A significant part of existing photoemission data has been obtained from samples prepared by evaporation (i.e., polycrystalline specimens). Although theory[1] and recent experiments[2] indicate that angular anisotropies should exist for single-crystal materials, it has been implicitly assumed for evaporated samples either that the emission is isotropic or that the randomly arranged crystallites cause averaging of any anisotropies. In particular, analyses of such photoemission data generally have not considered possible anisotropies which could occur as a result of particular measurement conditions. We show experimental evidence here that the photoemission from the d bands of evaporated gold does depend on the emission angle of electrons as well as the incidence angle and polarization of photons. An immediate implication of these results is that proper analysis of photoemission data must consider the geometric conditions of the measurements.

The experiment consists of an ultrahigh vacuum system (1×10^{-9} Torr) which houses the sample manipulator, and a light source with monochromator. The sample was prepared by evaporating 99.999%-purity gold from a tungsten filament onto a polished molybdenum substrate. Maximum pressure during evaporation reached 4×10^{-8} Torr. X-ray analysis[3] of the sample in-

dicated that a large fraction of the crystallites were oriented with their (111) faces nearly parallel to the surface, although there was random registration between adjacent crystallites. Energy analysis of the photoemitted electrons was accomplished by a three-grid hemispherical retarding-potential analyzer (1% energy resolution above 5 eV). The analyzer and sample are mounted together on a manipulator having four independent rotary motions, which allows the incidence angle and polarization of photons and the emission angle of electrons to be treated as independent parameters. Signal detection is made with a channel electron multiplier which intercepts about 10^{-3} of the emission solid angle. Digital counting techniques are used for recording the emitted current versus the retarding potential, and numerical differentiation[4] of these data is used to determine the energy distribution curve.

Two light sources were used for this experiment. One is a standard helium discharge lamp which provides unpolarized radiation at 21.2 eV. The second light source is the National Bureau of Standards 180-MeV electron synchrotron. This source provides a polarized continuum radiation[5] (theoretically, about 90% polarized) extending to about 100 eV. A 2.2-m grazing-incidence monochromator is used to disperse either source, and the grating blaze angle limits the spectral range between 15 and 70 eV. Further details of the experimental techniques will be discussed in a separate report.[6]

Figure 1 shows the relevant parameters for the experiment. The incidence angle (ψ) is defined with respect to the sample normal; the detector position specifies the emission angle of detected electrons, and is defined by the azimuthal (φ) and polar (θ) angles. By convention, s-polarized light has its electric vector *in the plane* of the sample surface, whereas the electric vector for p-polarized light, being in the incidence plane, has components *normal to* as well as *in the plane of* the sample surface. Changes in polarization are accomplished by rotating the sample in the optical axis.

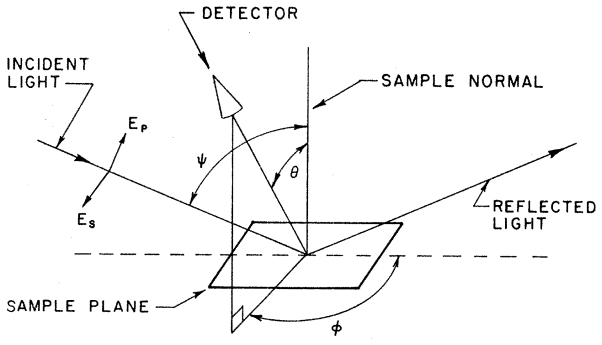

FIG. 1. Geometrical configuration of the experiment showing the various parameters.

As an example of anisotropy due to the emission angle, we show in Fig. 2 a series of energy

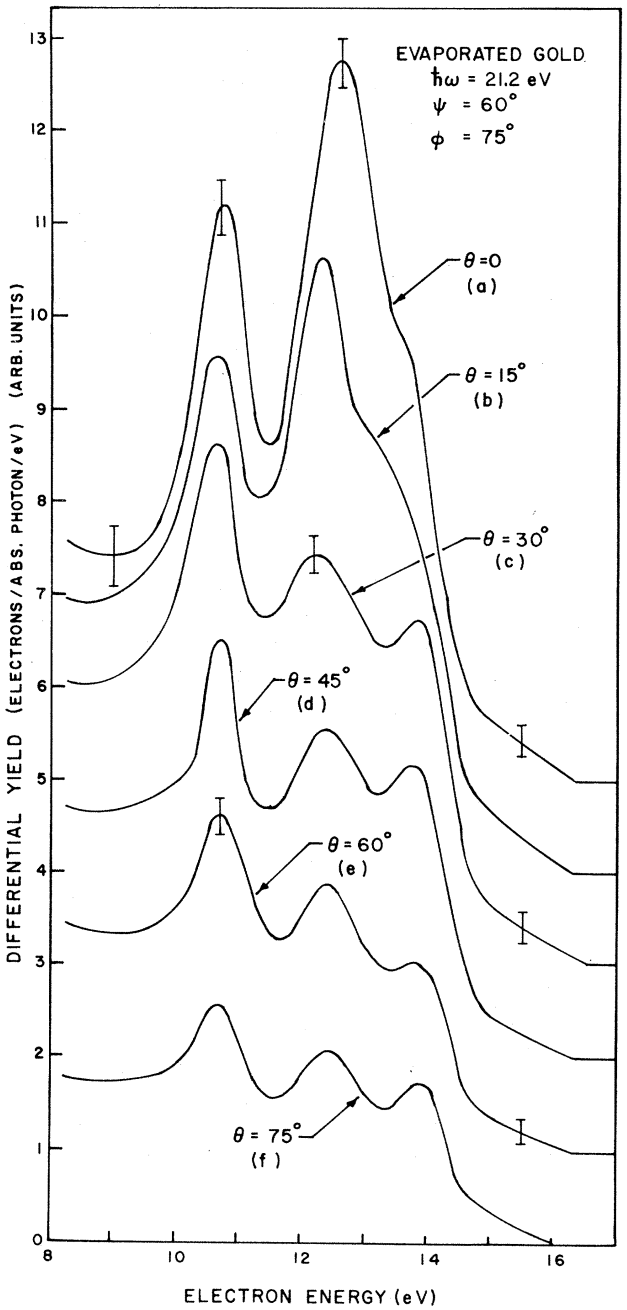

FIG. 2. Photoemission energy distributions showing anisotropy due to polar emission angle. The vertical bars denote the statistical uncertainty of the plotted curve (see text).

distributions[7] measured at $\hbar\omega = 21.2$ eV where the incidence angle is fixed at 60°, with the detector polar angle varied from the sample normal to 75° (azimuth fixed at 75°). For normally emitted electrons ($\theta = 0$), the emission is seen to comprise two primary groups originating from d-band states in gold. At 15°, there is a discernible narrowing of the leading peak accompanied by a shift to lower energy ($\Delta E \approx 0.3 \pm 0.1$ eV). At 30°, the leading peak has split into two distinct groups of smaller intensity. The three individual structures then retain their identities as high as 75°. Although the absolute yield was not measured, the energy distributions of Fig. 2 are normalized to reflect the relative yield. The low-energy group near 10.5 eV is seen to decrease monotonically with increasing polar angle. The strength of the 12.5-eV peak decreases dramatically, upon splitting, between 15° and 30°. Within the measured accuracy of the relative yield, the background of emitted secondaries appears to remain independent of the polar emission angle to about 60°; beyond this, there is a general reduction of the yield which reaches zero at grazing emission. It is also evident from Fig. 2 that the yield decreases monotonically with increasing polar angle. The general behavior of the energy distribution with polar angle (i.e., two peaks splitting to three) displayed in Fig. 2 was also observed at other incidence angles. However, there were specific differences in the degree of modulation of the peak strengths. The vertical bars indicate the statistical uncertainty ($\sqrt{N}$) of the smooth curve which was drawn through the data points. In the region of the d bands, the signal-to-noise ratio is sufficient to delineate the structure, although, in the region of the Fermi energy, the signal-to-noise ratio (approximately 1:1) does not allow a clear identification of the s-p bands or the Fermi edge as reported by others.[8,9]

Previous measurements of photoemission from gold at 21.2 eV[8,9] generally resemble the energy distribution of curve c in Fig. 2. The authors of Ref. 8 used an incidence angle near 45° with a cylindrical deflection analyzer sampling some solid angle of those electrons emitted at approximately 45° from the sample surface.[10] Therefore, they sample electrons which are emitted away from the normal, and their results are consistent with the present observations. The authors of Ref. 9 used a more standard retarding analyzer with a cylindrical collector. In this case, all electrons are energy analyzed (except those that escape through the light entrance aperture); they therefore measure a "spatial-average" energy distribution. This is also consistent with present observations since it was found here that, except for a 30° cone about the sample normal, the energy distributions generally have the three features shown in curve c of Fig. 2.

Shown in Fig. 3 are two energy distributions a, b measured at $\hbar\omega = 35$ eV using synchrotron radiation[11] where all parameters, except the polarization, are kept fixed. The light is incident at 45° with the detector at the 90° azimuth and 30° polar position. The relative yields of Fig. 3 were normalized to reflect the yield per absorbed photon using the optical data of Canfield, Hass, and Hunter.[12] The emitted primaries are seen to consist of two groups. They generally resemble the d-band emission doublet observed by other experimenters[13,14] for photon energies above 25 eV; however, we note some subtle manifestations due to the polarized light. The data indicate that with excitation by s-polarized light, emission from the leading high-energy group is stronger than that from the lower-energy group.[15] With p light incident, there is a reversal of the relative intensities. The leading peak decreases in intensity while the low-energy peak increases. A similar effect is observed at other polar emission angles.

Variation of the incidence angle parameter has its strongest effect on the yield of emitted pri-

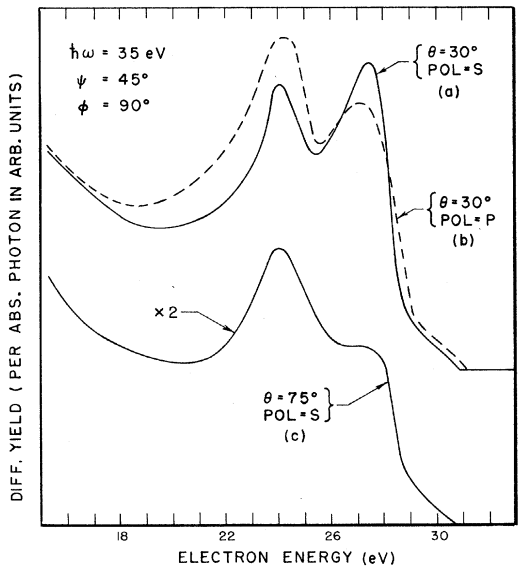

FIG. 3. Energy distributions a, b showing the effect of light polarization on the emission intensities of the d-band doublet, and c the effect of emission angle on the leading peak.

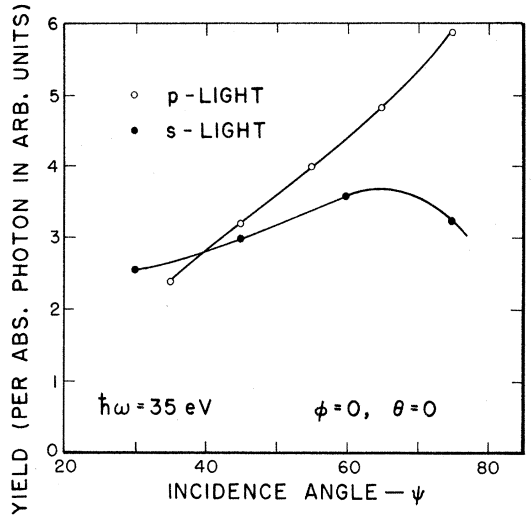

FIG. 4. Yield of normally emitted primaries as a function of incidence angle and polarization.

maries. For these measurements, the detector is positioned along the sample normal and the incidence angle of photons is varied for each of the two polarizations. The energy distributions are similar to those of Fig. 3. Figure 4 shows the yield per absorbed photon of normally emitted primaries (the primary yield is defined here as the integral of all electrons between 15 and 35 eV). For incidence angles between 30° and 75°, the normal yield increases monotonically for *p* light. For *s* light, the increase is less dramatic and shows a maximum near 65°. Since the curves of Fig. 4 have been normalized to the absorbed flux, the differences in the yield reflect differences in the excitation probabilities for the two polarizations.

These experimental results from evaporated gold give evidence that photoemission energy distributions and primary yields do depend on geometrical and physical parameters which are generally not considered. It is not clear how the preferred orientation of the polycrystalline sample influenced these results. However, it is clear that the emission spectra depend on the incidence angle and polarization of photons, and the the emission angle of electrons. With very few exceptions,[1,16] past calculations[17] have not considered these effects. Therefore, future calculations of photoemitted electron energy distributions must necessarily include a consideration of the refraction of electrons at the surface due to the transverse momenta of particular final states in conjunction with the usual conservation rules applied to the optical excitation.

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