patterns. The intensity will decrease markedly as the transition temperature is approached because the exponent in the Debye-Waller factor becomes large (negative) as the frequency of the surface mode goes to zero.[9]

We have shown that surface-induced dynamic effective charges give rise to long-range dipole-dipole interactions which can drive the surface unstable and into a reconstructed periodic configuration. We feel that the virtue of our theory lies in its simplicity and we believe that it is applicable to all semiconductor surfaces which exhibit reconstruction.

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Surface-Effect Characteristics of Photoemission from Clean Copper-Crystal Surfaces

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With photon energies within 1.5 eV above the threshold, photoelectric yields, as measured from Cu (100) and (111) with obliquely incident light, exhibit strong deviations from the $Y \propto (\hbar\omega - \varphi)^2$ dependence found at normal incidence. A preliminary energy analysis shows the distribution of the emitted electrons to shift towards the high-energy edge when the angle of incidence changes from 0° to 60°. The results are interpreted in terms of a surface photoelectric effect.

An old controversy revolves around the question of how to separate the surface and volume contributions in the photoemission process.[1] The volume excitation arises through a coupling to the periodic potential, while the surface barrier is the momentum-conserving agent for excitations in the surface region. At photon energies far from the photoelectric threshold the volume contribution is believed to be dominant, but close to the threshold the surface effect should be important. Explicit formulas for the energy and angular distributions, and the frequency dependence of the total yield of this process have been given by Mahan,[2] who assumed a simple model for the surface of a free-electron–like metal.

We wish to report here experimental evidence from copper of an effect which, when compared with Mahan's formulas, has several features characteristic of the surface effect. Photoelectric yields were measured with varying angle of incidence of uv light within 1.5 eV above the threshold. Our present collector geometry is not ideal for energy analysis. Nevertheless, a preliminary energy analysis of the electrons emitted could be made.

The sample was a copper single crystal of high purity, and large flat faces parallel to the crystallographic planes (111) and (100) were prepared and cleaned as described in a previous publication.[3] The work functions given there were well reproduced for the (100) face, while $\varphi(111)$ stabilized at a value slightly lower in this experiment.

At constant frequency we have measured the ratio between the yield at an angle θ and that at normal incidence, using unpolarized light. By increasing the angle of incidence the photocurrent was observed to increase and pass through a maximum at about 71°. Accurate measurements were performed up to about 80°. The experimental points in Fig. 1 show the angular dependence of the yield ratio of the (111) surface for a photon energy of 5.15 eV. Measurements performed to the other side of the surface normal produced a result nearly symmetric to that of Fig. 1. Measurements on the (100) face gave the same general features with a maximum in the range 70°–73°.

The enhancement of the current at large angles has previously been observed by others[4] and named vectorial photoemission. Juenker, Waldron, and Jaccodine[5] measured rather large enhancements on polycrystalline molybdenum, and they suggested an explanation based on the classical refracting properties of a metal surface. Assuming for each electric field component a photocurrent proportional to its square, and assigning a special weight B to E_z, the electric field component normal to the surface, we may write

$$Y(\theta)/Y(0) = AS(E_x^2 + E_y^2 + BE_z^2), \qquad (1)$$

where $Y(\theta)$ is the photocurrent per incident photon at an angle of incidence θ, S is the illuminated surface area, and A is a phenomenological

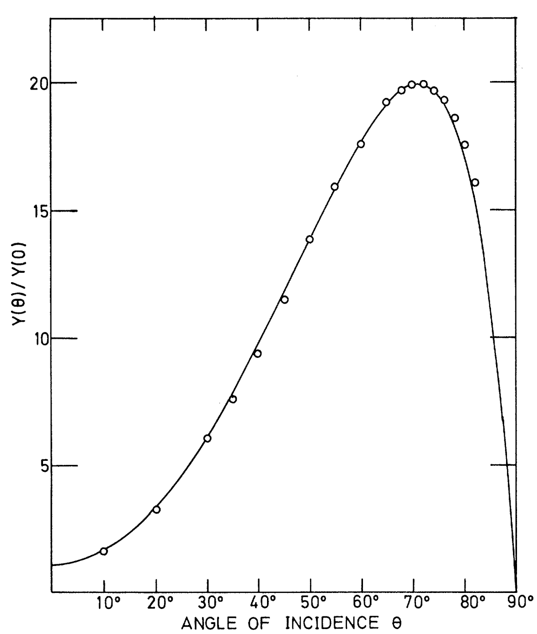

FIG. 1. The yield ratio as measured with unpolarized light and a photon energy of $\hbar\omega = 5.15$ eV on a Cu (111) surface (circles). The solid curve has been calculated from the phenomenological theory of Ref. 2.

constant. Treating the surface as a sharp boundary between vacuum and a medium of dielectric constant $\epsilon = (n+ik)^2$, one can calculate the field components as functions of the angle θ. With $\epsilon = (1.4 + i1.7)^2$, as obtained from the measurements of Ehrenreich and Philipp,[6] we have computed the total yield ratio $Y(\theta)/Y(0)$ based on Eq. (1). The result is compared with experiment in Fig. 1. B has been chosen to normalize the theoretical curve to the measured value at 60°. The theoretical prediction of a maximum in the yield ratio, which Juenker, Waldron, and Jaccodine were not able to observe in their measurements on molybdenum, is here verified experimentally on copper.

As discussed by Juenker, Waldron, and Jaccodine, this phenomenological theory does not distinguish between a surface and a volume effect. Since

$$(E_z^2)_{\text{vacuum}} = (n^2 + k^2)^2 (E_z^2)_{\text{metal}} \qquad (2)$$

one can equally well use the field value inside or outside the optical discontinuity by choosing suitable values of the constant $B_{v,m}$ (v for vacuum, m for metal). The vectorial effect exists even for $B_v = 1$, but the fit in Fig. 1 was made by the choice $B_v \simeq 8$ or $B_m \simeq 188$.

In further contrast to the work of Juenker, Waldron, and Jaccodine, we observed a highly frequency-dependent B, i.e., the enhancement $Y(\theta)/Y(0)$ changed rather rapidly with the frequency of the light. This means that the yield of the current emitted by light at oblique incidence must have a frequency dependence different from that at normal incidence. We then measured the yields for the (111) and (100) surfaces at 70° incidence. The results are shown in Fig. 2 together with the yield from (111) at normal incidence. The latter is well described by the usual quadratic function $Y(\omega) = \alpha(\hbar\omega - \varphi)^2$, where α is a constant.

The difference in frequency dependence suggests the possibility that most of the extra electrons emitted by light of oblique incidence are due to a separate excitation process. If a volume effect were to be essential in an explanation of this, we should find close correlations with the band structure. Now, for copper at our energies there are no final states with momentum in the [100] direction while there is a high density of states with momentum in the [111] direction.[7] In view of this essential difference, the close similarity observed between the (100) and (111) faces seems to rule out any important con-

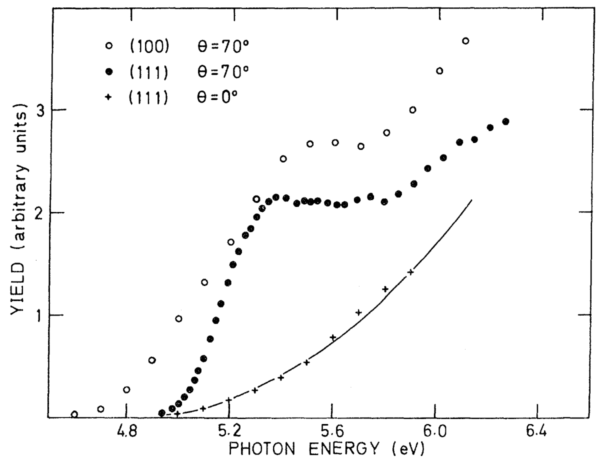

FIG. 2. Experimental photoelectric yields versus photon energy (point symbols). The solid line is the best fit by a $Y \propto (\hbar\omega - \varphi)^2$ dependence to the yield at normal incidence.

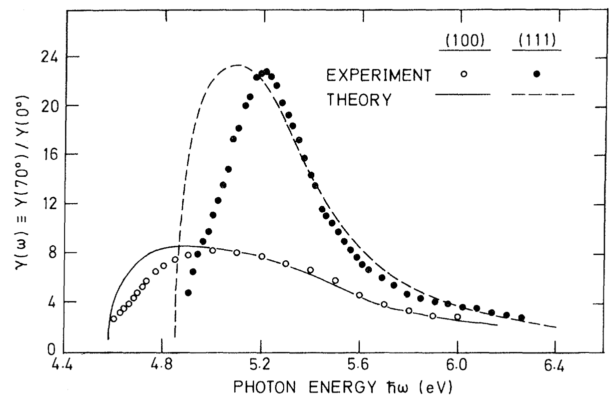

FIG. 3. The measured ratio $Y(70°)/Y(0°)$ versus photon energy for the (100) and (111) surfaces. The solid and dashed curves show the best fits obtained with the theoretical frequency dependence of the surface effect.

tribution from a volume effect. In the theory of the surface effect the photocurrent is proportional to $(\hat{\epsilon}\cdot\hat{z})^2$ where $\hat{\epsilon}$ is the polarization vector and $\hat{z}$ the surface normal. Accordingly, the surface effect should depend upon the variation of E_z, but not upon E_x or E_y for an ideal surface. Since our results show E_z to be more efficient than E_x and E_y by at least 1 order of magnitude, a natural hypothesis is that this is due to the surface effect becoming important at oblique angles of incidence. Therefore, at $\theta = 70°$ we attempt to separate the yield into two contributions:

$$Y_{70°}(\omega) = \beta(\hbar\omega - \varphi)^2 + Y_{s\,70°}(\omega), \qquad (3)$$

where β is a constant, not necessarily equal to α, and $Y_{s\,70°}(\omega)$ is the surface contribution at $\theta = 70°$. In our measurements we cannot separate out $Y_{s\,70°}(\omega)$ since we do not know the value of β, but in order to contrast the two terms with respect to their frequency dependence, we have instead plotted the ratio

$$\gamma(\omega) \equiv \frac{Y_{70°}(\omega)}{Y_{0°}(\omega)} = \frac{\beta}{\alpha} + \frac{Y_{s\,70°}(\omega)}{\alpha(\hbar\omega - \varphi)^2} \qquad (4)$$

for both surfaces. In Fig. 3 these measured values of $\gamma(\omega)$ are compared with the solid curves as calculated with $\alpha = \beta$, and taking the frequency dependence of $Y_{s\,70°}(\omega)$ to be that of Mahan's theory. Near threshold the theory predicts a $(\hbar\omega - \varphi)^{5/2}$ dependence of the surface yield. This differs from the observed third-power dependence shown by the linear increase of the $\gamma(\omega)$ curves, but on the high-frequency side of the maxima, the measured values of $\gamma(\omega)$ are well described by the theory for a suitable choice of a parameter V_0. This parameter is defined as the energy difference between the vacuum level and the bottom of the Fermi sea. The fits in Fig. 3 were obtained by choosing the rather low values of $V_0(111) = 5.3$ eV and $V_0(100) = 5.4$ eV. If taken literally, these values mean that the extra electrons emerge from a layer within the surface region where the depth of the Fermi sea is rather well defined and equal to about 0.45 and 0.80 eV for the respective surfaces. Obviously the depth of the Fermi sea changes smoothly from zero to its interior value in the surface region. But since the gradient of the surface barrier, $\partial V/\partial z$, is large in this region, as required in order to give sufficient strength to the transition matrix element, the surface electrons have to be emitted from an extremely narrow layer parallel to the surface. Now, E_z^2 changes by a factor $1/(n^2+k^2)^2$ over the optical discontinuity, which is in fact no real discontinuity, but a layer of finite thickness. For copper, the factor $1/(n^2+k^2)^2$ is about $\frac{1}{23}$, and it might well be that the simultaneous changes in light intensity, surface barrier gradient $\partial V/\partial z$, and electron density at the surface combine in such a way that electrons originating in a narrow layer emerge with a rather well-defined energy.

The energy analyses of the electrons are just at a preliminary stage, since we have used the retarding field technique in a planar geometry. If the theory of Mahan[6] applies to our observations with such low values of V_0, the energy distribution of electrons due to the surface effect

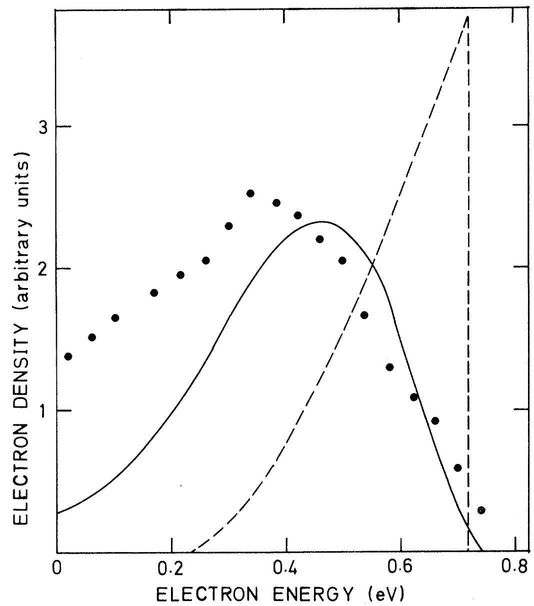

FIG. 4. Energy distribution of electrons (circles) emitted from the (111) face of Cu and measured with a plane collector. The photon energy was $\hbar\omega = 5.52$ eV, and the angle of incidence of the light 60°. The solid curve is the distorted distribution calculated for the planar geometry when the undistorted distribution of the surface effect (dashed curve) is assumed.

should be shaped like the dashed curve in Fig. 4. The distortion of this original distribution as caused by the nonideal geometry has been calculated with a disk-shaped model of the plane collector. In Fig. 4 this distorted theoretical curve is shown together with the experimental results of the energy analysis on the (111) face with $\theta = 60°$. The peak of the experimental curve does not coincide exactly with the theoretical one, but a shift in the original theoretical distribution of only 0.1 eV to lower energies will remove this discrepancy. Thus, the undistorted distribution behind the measured one must undoubtedly be peaked near maximum energy. By varying the photon energy, the distorted, theoretical curve, as well as the peak position of the measured distribution, move nearly in proportion to the increment in photon energy. This proportionality is shown for $\theta = 60°$ in Table I. In contrast, the electrons emitted by light of normal incidence

TABLE I. Observed shifts ΔE in the peak positions of distorted energy distributions similar to the one in Fig. 4 for increments $\Delta\hbar\omega$ in the photon energy $\hbar\omega$.

$\hbar\omega$ (eV)	$\Delta\hbar\omega$ (eV)	ΔE (eV)
5.32		
	0.10	0.10
5.42		
	0.10	0.09
5.52		
	0.09	0.08
5.61		
	0.19	0.18
5.80		

were found to have an energy distribution, in planar geometry, with a broad maximum within the range 0.1–0.2 eV. No significant shifts in the peak positions of these curves were found when the photon energy was varied.

Energy analysis of the electrons from the (100) face has not been performed, but proper high-resolution analysis of the energy distributions from both surfaces are now in progress.

In part we have based our argument for a surface effect on the similarity in behavior between the (100) and (111) faces. Concentrating for a moment on the quantitative difference, we note that its explanation may possibly be found in the different surface charge distributions which are related to the anisotropy of the work functions. However, as such differences may offer an opportunity to separate out volume effects, a more detailed experimental investigation is planned. Also the influence of a varying surface condition will be studied.

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