THE VECTORIAL PHOTOELECTRIC EFFECT IN THIN FILMS OF ALKALI METALS

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Abstract

It is assumed that the photoelectric effect exhibited by thin films of alkali metals on specular platinum surfaces is proportional at any wave-length to the electric intensity just above the platinum. This electric intensity is found, using the optical constants of platinum, by computing the intensities of the wave patterns formed by the interference of the reflected and incident beams. These computations are made for various angles of incidence and for light polarized in and at right angles to the plane of incidence. The intensities thus found exhibit very large ratios of value for the two planes of polarization, in striking agreement with the characteristics of the vectorial photoelectric effect. The changes of amplitude of the perpendicular electric vector on entering the alkali metal film, as computed from the optical constants of the alkali metal, account for the experimentally found low values of the emission ratios at long, and their high values, at short wave-lengths.

When polarized light falls at high angles on specular alkali metal surfaces there are markedly different photoelectric effects, depending on whether the electric vector is parallel to the plane of incidence (symbolized usually by $\|$) or perpendicular thereto (symbolized by $\perp$). One difference is the occurrence of the "selective" effect, or the appearance of a maximum of emission in one spectral region for $\|$ light, less marked or possibly absent in $\perp$ light. Another difference is one of magnitude, the photo-emission for $\|$ light is greater than that for $\perp$ light, *in a ratio much greater than would be predicted from the optical absorbing powers of the metal for the two conditions.*[1] These two phenomena usually go hand in hand, but for purposes of differentiation the second is sometimes called the "vectorial" effect.

The vectorial photoelectric effect is exhibited in a marked degree by the extremely thin films (circa one atom deep) of alkali metals which spontaneously deposit on clean polished platinum surfaces in highly evacuated cells having large exposed surfaces of the alkali metal. "Angle curves" for such a thin film of potassium on platinum are shown in Fig. 1, reproduced from an earlier paper.[2] In Fig. 2 are shown the absorbing power curves, plotted against angle of incidence, for both platinum and potassium, for blue light of approximately the same wave-length as that used in the experiments recorded in Fig. 1. It is to be noted, first, that the photoelectric emission curves have roughly the same shape as the absorbing power curves; thus the $\perp$ curves show in each case a slow decline in value as the angle of incidence is increased, while the $\|$ curves show first an increase and then a decrease, with a maxi-

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[1] The occurrence of this discrepancy was adopted by Pohl and Pringsheim as a criterion for the existence of the "selective" effect.

[2] "Photoelectric Properties of Thin Films of Alkali Metals," Astrophys. J. **LX**, 4 (1924).

mum at 60° to 80°. But there is this characteristic difference, that while the ratio at 60° incidence does not exceed about 2 in the case of the absorbing powers, the ratio of photoelectric emissions rises as high as 20:1. (We have since obtained considerably larger values with carefully polished surfaces of pure noncrystalline platinum, as shown *infra.*) Now no physically possible values of the optical constants N and K_0 will give a ratio of absorbing power

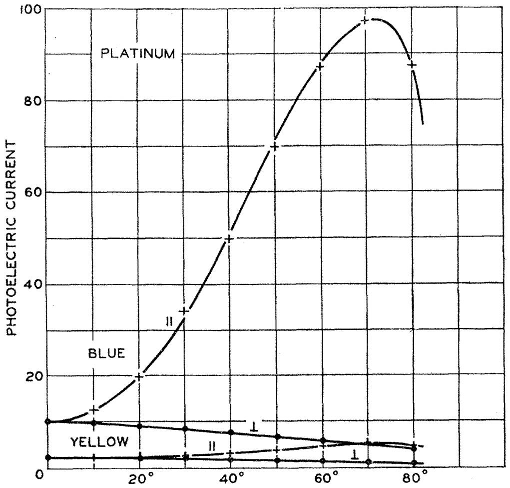

Fig. 1. Photoelectric currents from thin film of potassium on platinum for various angles of incidence, light polarized with electric vector parallel (∥) and perpendicular (⊥) to plane of incidence.

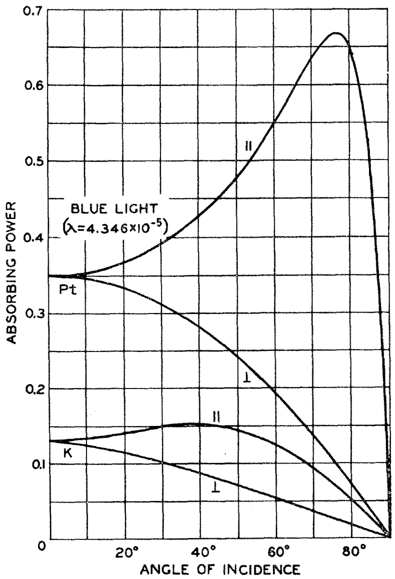

Fig. 2. Absorbing powers of platinum and potassium at various angles of incidence.

at 60° incidence larger than 4. There has consequently appeared to be no quantitative correlation of the vectorial effect with the optical properties of the surface.

In some work now in progress on the photoelectric effect from thin films of alkali metal on silver, in the region of the ultraviolet where silver exhibits a band of low reflecting power (3000 to 3500A) we have found a pronounced influence of the optical properties of the silver on the photoemission. The location of the singularity in the photoemission, however, does not coincide with the minimum of reflecting power of the silver, and, in searching for the exact explanation of the effect, the clue has been found by studying the intensity of the radiant energy *at the surface* of the silver. The work on silver will be reported on later; the present paper deals with some results of applying the same line of reasoning to the photoeffect in the visible spectrum from thin films of alkali metal on platinum.

There is considerable evidence that the photoelectric effect in metals must be a phenomenon of an extremely thin surface layer. That practically as much photoemission occurs from a monatomic film of alkali metal as from the metal in bulk can be interpreted as meaning that the emission comes only from the top layer of atoms; or, the fact that electrons of the speeds characteristic of photoelectrons cannot penetrate metal layers of more than a few atoms depth may be taken as sufficient reason for restricting our attention to distances of atomic magnitude. The optical absorption is on the other hand a process requiring a distance comparable to a wave-length of light, and therefore many times an atomic diameter. If then we want to know the actual absorption of energy involved in the photoelectric effect, it is reasonable to investigate an extremely thin sheet at the metal surface.

In the case of monatomic films of alkali metal, such as potassium, on platinum, we know that the presence of the film cannot be detected by optical examination.[3] Consequently *as a first approximation* in approaching the problem we may assume that the presence of the film does not affect the condition of the light energy appreciably. Qualitatively we know that there exist above the metal surface, *standing waves*. If the metal were perfect, interference between the incident and reflected beams would produce a system of standing waves with a node at the surface, and there would be no energy for the alkali metal film to absorb. However, due to the finite conductivity of the metal, the reflected beam does not quite cancel the incident one at the planes of destructive interference, and moreover the phases are altered so that the metal surface is not a destructive or nodal plane of the pattern. Instead, there is a definite, calculable amount of enery for the photo-sensitive film to absorb. According to the view here developed a thin layer of photoelectrically active material upon a polished platinum plate takes the place of the exceedingly thin photographic layers, by means of which Wiener[4] first demonstrated

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[3] "The Thickness of Spontaneously Deposited Photoelectrically Active Rubidium Films Measured Optically," J.O.S.A. **15,** 374 (1927.)

[4] Vide Woods Optics, 2d Ed., p. 174, *et sequi* for a general discussion of stationary waves in optics.

the existence of standing waves. Instead, however, of placing this film at a small angle with the metal surface, in order to get traces of successive maxima, we shall consider a sensitive film in contact with the metal surface, and shall investigate, by computation, how the light energy on the film is affected by variations of angle of incidence and of polarization. The problem thus becomes one of calculating, from electromagnetic theory, using the refractive index N, and the extinction coefficient K_0, the exact conditions just above the metal surface.

The computations of the electrical intensities in the interference pattern just above the surfaces have been made by the methods explained in a paper by Thornton C. Fry,[5] using values for the optical constants of platinum obtained by W. Meier. In the notation of that paper, when a plane wave of polarized light, whose electric vector has the amplitude E, is incident upon the plane boundary between two media, it gives rise to a reflected wave of amplitude E_2 and a refracted wave of amplitude E_1. These new beams are completely specified by the constants of Tables I and II of the paper in question. By adding E and E_2 vectorially we may obtain the amplitude of the electric force just above the reflecting surface. If we call this resultant $E_\perp$ when it is normal to the plane of incidence (and, therefore, tangent to the reflecting surface) and $E_\parallel$, when it is in the plane of incidence (and, therefore, oblique to the reflecting surface), we readily find that the former has no components in the x or z directions. Hence

$$E_\perp = E_y + E_{y2}.$$

$E_\parallel$, on the other hand, has components in the directions of x (tangential to the reflecting surface) and z (perpendicular to it), given by

$$E_{\parallel x} = E_x + E_{x2},$$
$$E_{\parallel z} = E_z + E_{z2}.$$

These equations refer to reflection from a solid substance, and give the electric force in the medium which contains the incident beam. In their application to our experiment, therefore, they give the force in the air just above the reflecting surface, when the presence of the photosensitive film is ignored. The quantities which we compute, for various angles of incidence, are $|E_\perp{}^2|$ and $|E_\parallel{}^2|$, the latter of which is defined as $|E_{\parallel x}{}^2| + |E_{\parallel z}{}^2|$. These quantities are twice the time average over a complete cycle, of the square of the magnitude of the electric force. In other words, they are twice the mean electric intensity.

There is, however, one other factor which must be taken into account. It is brought into the problem through the experimental fact that, as the angle of incidence I is varied, the size of the spot of light upon the photosensitive material increases. Hence, since the photocurrent must be proportional to the area illuminated, the values of $|E_\perp{}^2|$ and $|E_\parallel{}^2|$ must be multiplied by sec. I before a comparison with experimental data is possible.

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[5] "Plane Waves of Light II," J.O.S.A. **16,** 1–25 (1928).

Inspection of the full line curves of Fig. 3, embodying the results of the above computations for wave-length 4358A, shows at once that we have obtained from this line of attack what has not previously been found, an *optical* explanation of the dominant characteristics of the vectorial effect. These

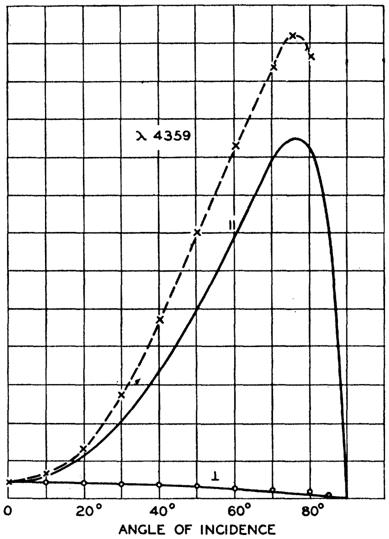

Fig. 3. Electric intensity over surface of platinum (full lines); and photoelectric currents from thin film of potassium on platinum (circles and crosses); blue light.

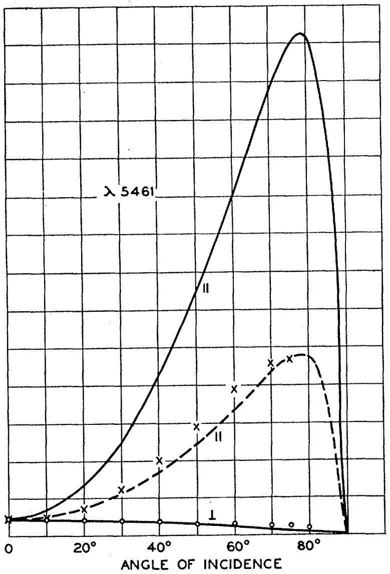

Fig. 4. Electric intensity over surface of platinum (full lines); intensity for || light in thin film of potassium over platinum as computed, (dashed line); photoelectric currents from thin films of potassium on platinum (circles and crosses); green light.

angle curves exhibit a ratio of $\|$ to $\perp$ far greater than the ratio of the absorbing powers. For the case shown, this ratio is 29:1 at 60° angle of incidence. In the same figure are plotted recent experimental data obtained at the same wave-length, in a cell containing potassium and provided with a very highly polished plate of pure platinum (free from the microscopic dulling crystals characteristic of commerical platinum). This cell was carefully constructed so that currents from the film-covered glass walls cannot add to the photocurrents from the cathode and so yield spurious values. It is obvious that the experimental curves are closely similar to the computed, showing not only a very high ratio of $\|$ to $\perp$ but the same agular position of the maximum of the $\|$ current.

The agreement between the observed and computed curves is not exact as to magnitude, for the observed $\|$ curve is higher than the computed. Moreover, when we consider the computed and observed curves for green light of wave-length 5461A, shown on Fig. 4, we observe a serious discrepancy, for while the computed curves differ but little from those for blue light, the observed, in agreement with the "yellow" curves of Fig. 1, exhibit a much lower ratio between $\|$ and $\perp$, a phenomenon which has appeared to be general.

These discrepancies are due to the neglect, up to this point, of the effect of the alkali metal film upon the platinum. As already noted, monomolecular films (at least when deposited on metals) do not make an appreciable difference in the electric forces in the air. Hence our calculations of the standing wave amplitudes are practically unaffected by the presence of the film. However, on passing from air into the photosensitive film, while the force components in the x and y directions (tangential to the reflecting surface) are continuous, the component in the z direction is multiplied by a factor $Q = q^2/q_1^2$. In terms of the optical constants,[6] N and K_0 of the photosensitive material, this works out to be

$$Q = \frac{1}{(N + iK_0)^2}\cdot$$

In other words, *inside* the photosensitive film the force components are given to a high degree of approximation by

$$\begin{aligned} E_{\perp} &= E_y + E_{y2}, \\ E_{\|x} &= E_x + E_{x2}, \\ E_{\|z} &= Q(E_z + E_{z2}), \end{aligned}$$

where the quantities E_x, E_y, E_z, E_{x2}, E_{y2}, E_{z2}, are determined without reference to the presence of the photosensitive film, and Q is independent of the nature of the material on which it is deposited.

In order to ascertain the electric intensities in the alkali metal films, Q must be derived from experimental values of N and K_0, and used as a multiplying factor on $E_{\|z}$, before this is used to compute.

$$|E_{\|}^2| = |E_{\|x}^2| + |Q^2||E_{\|z}^2|.$$

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[6] For a precise definition of these constants, concerning the latter of which there is much confusion in the literature, see "Plane Waves of Light I," J.O.S.A. **15**, 137–161, (1927), especially the picture on p. 143.

In Fig. 5 are shown, first, values computed through the visible spectrum for platinum of $|E_1{}^2|$ sec. I, $(|E_{\|x}{}^2|+|E_{\|z}{}^2|)$ sec θ, for $I=60°$; and also of $|E_{\perp}{}^2|$ for perpendicular incidence. The optical constants for platinum are taken from Meier.[7] Second are shown the results of using the computations involving Q, for Na, K, Rb and Cs, taking values of the alkali metal optical constants from the literature.[8] These yield new $\|$ curves, the $\perp$ curves being unaffected, for they are determined solely by the underlying metal.

The curves embodying the multiplying factors show at once that the effect of the film is, in general, with all four alkali metals, to *decrease* the ratio of $\|$ to $\perp$ for the long wave region, and to *increase* it for the short wave region, over the ratios indicated by the platinum alone. This is in agreement with experiment. Furthermore it is indicated that low ratios should be obtained with sodium, and high ratios with rubidium and caesium, which is exactly what we have known experimentally for a long time.

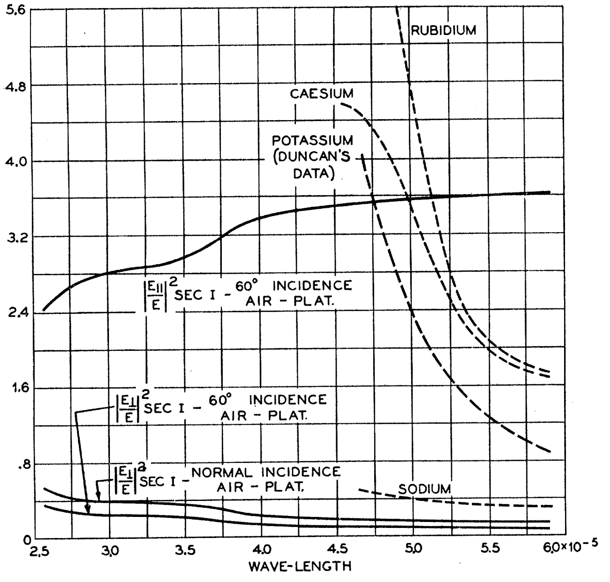

Fig. 5. Electric intensity over platinum for light incident normally, and at 60° for both planes of polarization (full lines). Intensities computed in thin films of alkali metals on platinum for $\|$ light (dashed lines).

The available data regarding the optical constants of the alkali metals are too scattering and too restricted in spectral range to be of much value for the purpose of a quantitative check. Taking, however, the potassium multiplying factor, for λ5461, which is calculated from the mean curves drawn through

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[7] Ann. d. Physik, **31,** 1017 (1910).

[8] The values used were obtained by graphical averaging of data by Duncan, Nathanson and others, which exhibit considerable spread. Our own experimental determination of constants for Rb at λ5461 made in vacuo (vide note 3) differs from Nathanson's value so considerably as to suggest that a real check of the theory here presented will only be possible when all the optical constants involved are determined under the exact conditions of the photoelectric experiments.

Duncan's two sets of potassium constants, as shown in Fig. 6, the dashed curve of Fig. 4 is computed, which agrees reasonably well with the observed values. The potassium data do not extend far enough into the blue to check the λ4358 experimental curve. A straight extrapolation from the same mean data gives a || curve of about twice the ordinates of the platinum curve, while the experimental potassium points lie only about 30 percent higher. It would be easy to pick an extrapolation well within the range of the experimental values of the potassium optical constants which would give an exact check, but study of this region may much better wait until more satisfactory constants are available.

As an additional check on the theory, computations have been made for the case of a thin film of rubidium on glass, previously studied experimentally.[3] The angle curves obtained (Fig. 7, dots and crosses) were quite different from those observed with films on metals, and no explanation was established. Computations of the sort here described yield the full line curves, the optical constants of the glass being taken as $N=1.51$, and $K_0=0$. By using the multiplying factor for rubidium from Fig. 5, corresponding to wave-length 4890, the dashed || curve is obtained, both || and ⊥ curves exhibiting close agreement with the experimental data. Actually the measurements were made for continuous spectrum light from a tungsten lamp, but in view of the predominant sensitiveness of the rubidium film for short wave energy, the "equivalent" wave-length must be somewhere in the blue, so that while the almost exact quantitative agreement shown depends upon the wave-length chosen, this wave-length is closely that which is indicated from the conditions of the experiment.

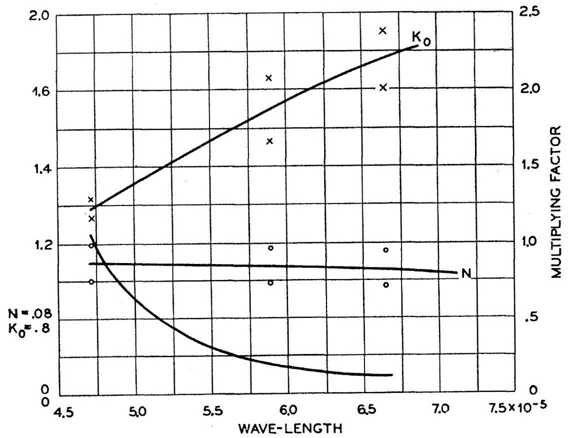

Fig. 6. Computation of multiplying factor for perpendicular light vector from optical constants of potassium.

It must be pointed out in fairness that our assumption that the film of alkali metal does not affect the standing wave system formed by the underlying material is violated in the case of glass, for we have previously used the just measurable phase shift caused by the alkali metal film on glass to arrive at the thickness of the film. However, the standing waves formed over glass have a smaller variation of amplitude than do those over metal, so that a small phase shift will alter the computed values of Fig. 7 but little.

Several points with regard to the films on platinum deserve further comment. As pointed out above, the ⊥ curves should be characteristic of the metal on which the alkali metal film is deposited. There should, therefore, be an exact check in Figs. 3 and 4 between the photocurrent angle curves observed from the thin films for ⊥ light and the electric intensity curves computed for platinum. The agreement, while very close, is not, however, exact. In every case the ⊥ emission, plotted against angle of incidence, yields curves which are somewhat too flat, that is, too high at the higher angles of incidence. While this difference hardly shows on the scale to which the curves are here plotted, due to the small value of the ⊥ emission, it has been carefully checked by studies of the shapes of the ⊥ curves alone. At 60° incidence the emission should usually be only slightly greater than half that at 0°, while experimentally it approaches $\frac{2}{3}$.

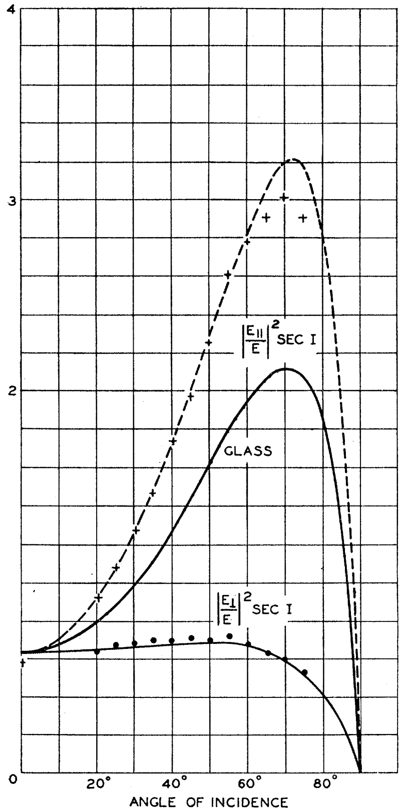

Fig. 7. Electric intensity over glass (full lines); intensity for || light as computed for thin film of Rb on glass (dashed line); photoelectric currents from thin films of Rb on glass (dots and crosses).

The cause of this discrepancy is not yet established. It may be due to anisotropy of the thin film, caused by an orienting of the alkali metal atoms. It may possibly lie in some small phase shift such as polishing operations are well known to produce. Inspection of plots of the standing wave amplitudes over the metal surface, shows that while the E^2 component is fairly far from a node, the E_y component is so close to a node that a very slight phase shift can produce a relatively large change of amplitude. It must, of course, be recognized that the attack on this problem through the standing wave pattern is only the first step toward a rigorous study of the actual energy absorption in the thin films without simplifying assumptions such as are here made.

Another matter may be touched on. With partially developed very thin films ($<$ one atom average thickness) the ratio of $\|$ to $\perp$ is much less, dropping indeed to 3:1 or 2:1 or indeed on some cases we have observed, to 1:1. One might reasonably expect this condition to be one where the standing wave system over the platinum would be least affected by the alkali metal, that is, that the values computed for platinum alone would be most closely approximated. On the other hand—and this is as far as consideration of this condition will be taken here—there is the possibility that some of the photoelectrons in this case originate in the platinum, so that the multiplying factor due to the dielectric constant of the surface will not be that computed from the alkali metal. The value of $Q=1/(N+iK_0)^2$, for platinum is much smaller than for the alkali metals, so that if the effective value of Q approximates to that for platinum as the film becomes thinner, a rapid reduction of the $\|$ emission would be called for, with consequent low ratios, as found.

The subject matter of this paper has been purposely confined to the *vectorial* effect, exhibited by *thin films* of alkali metal on other metals or bases. The study can obviously be extended to the distribution of photoemission through the spectrum, whereby the specific photoemission, or emission per unit of energy actually absorbed in the thin film can be determined at each wave-length. Furthermore, there is no reason to limit the application of these ideas to thin films. The bulk alkali metals and alloys can perhaps be looked upon as reflecting surfaces overlaid by photosensitive films of the same optical constants. If these overlaid films are not effectively much thicker than the films on other metals, the same treatment will apply. If they are effectively much thicker the theoretical treatment here given should serve as a useful starting point. For the extension of the study along these lines, however, it is essential that the optical constants involved be determined for the actual metal surfaces used, and the work be carried into the ultraviolet where the pure alkali metals exhibit their most marked "selective" effects. No optical constants are available for the alkali metals in the ultraviolet, so that these must be determined before the work can be carried to a satisfactory conclusion. Meanwhile it is believed the material here presented shows pretty clearly that *the vectorial photoelectric effect is predominantly an optical phenomenon.*

In conclusion I wish to acknowledge my great indebtedness to Dr. T. C. Fry for discussions of many points involved in this paper, to Miss C. L. Froelich for the computations, and Dr. H. B. Briggs for making certain of the measurements quoted.