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THE PHOTOELECTRIC EFFECT FROM THIN FILMS OF ALKALI METAL ON SILVER

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Abstract

The thin films of alkali metals which spontaneously deposit in vacuo on other metals have long been known to exhibit photoelectric effects which vary in amount and character, depending on the underlying material, but the exact nature of this dependence has been obscure. Silver, because of its region of exceedingly low reflecting power in the ultraviolet and the accompanying variation of optical constants, is exceptionally well suited for studying the influence of the underlying metal. It is found that the region of low reflecting power profoundly affects the photoemission, but in a manner not to be explained simply by reduction of light reflected back through the alkali metal film or by the absorption of light by the silver. The results obtained are very satisfactorily explained upon computing, from the optical constants, the intensity at the surface, of the interference pattern formed by reflection just above the silver surface. The positions of the maxima and minima of photoemission, and their variations with angle of illumination and plane of polarization are accurately indicated.

SILVER, in the wave-length region 3200–3500A, exhibits a narrow band of low reflecting and high transmitting power. Measurements of reflecting power for light at normal incidence by Hagan and Rubens,[1] reproduced in Fig. 1, show a value at wave-length 3160A as low as that of glass, and the transmission is sufficiently high so that thin films of silver have been used as filters to transmit a narrow band of ultraviolet energy.

Thin films of alkali metals, spontaneously deposited in vacuo on specular surfaces of metals such as platinum, nickel or silver, give strong photoelectric currents, varying from metal to metal in a manner not heretofore understood.[2] The *vectorial effect* is pronounced, that is, the currents for light polarized with the electric vector parallel to the plane of incidence (symbolized by $\|$) are much greater than for light polarized with the electric vector at right angles to the plane of incidence (symbolized by $\perp$). The ratio of the $\|$ to the $\perp$ currents from a film of a given alkali metal differs with the underlying metal. It has been a fair presumption that these characterisics of the vectorial effect depend upon the optical properties of the metal beneath; but the nature of the dependence has been obscure.

The peculiar optical properties of silver have appeared to be admirably suited for throwing light on the influence of the underlying material on the photoelectric effect from thin films, for the optical properties of silver vary all the way from a typically metallic character in the visible region, through a region where the properties are similar to those of glass, to another region

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[1] Hagen and Rubens, Ann. d. Physik **8**, 1, (1902).

[2] Ives, Astrophys. J. Nov., 1928, p. 60.

in the far ultraviolet where the metallic properties are quite as different as though another metal had been substituted.

The experimental work described below was initiated without any detailed theoretical picture of the results to be expected. One tentative picture would ascribe the photoemission to the silver as well as the alkali metal upon it; on this assumption the photoelectric effect might be expected to follow closely the absorbing power of the silver. Another picture would consider the thin layer of photosensitive alkali metal as lying sufficiently far above the silver reflecting surface so that light would pass through it twice and the photoeffect would be that due to an average of the incident and reflected energy from the silver; the region of low reflecting power of the silver would then again show as a region of reduced photoelectric emission, but the emission would not vary with wave-length in the same manner as on the first assumption. Acutally the experiments have shown that neither of these crude pictures is adequate and we have been led to an interpretation which depends upon a detailed analysis of the optical conditions at the silver surface. This interpolation has given a valuable clew to the nature of the vectorial effect itself, which has been discussed in a previous paper;[3] the present paper deals chiefly with the variation of photoelectric effect with wave-length, as determined by the optical properties of the silver base.

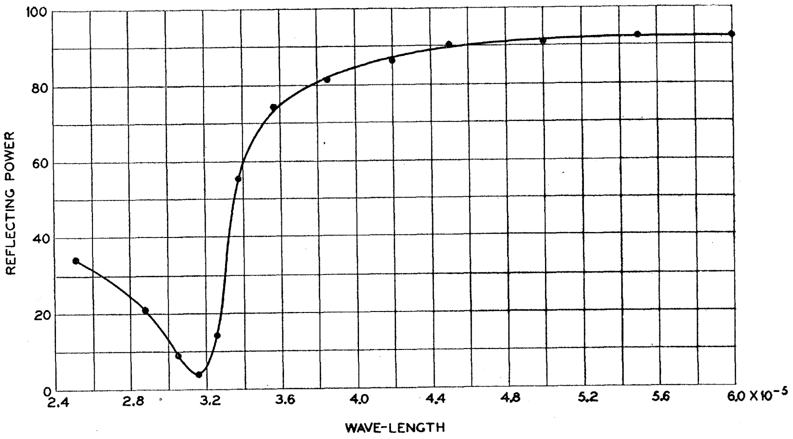

Fig. 1. Reflecting power of silver for perpendicularly incident light, as measured by Hagen and Rubens.

Apparatus and Experimental Procedure

The measuring apparatus used in this study consisted of a quartz-ultraviolet spectrometer, used either with a quartz mercury arc or with a quartz windowed tungsten ribbon lamp, to provide monochromatic light. A quartz Rochon prism in the path of the light energy from the spectrometer provided two beams, polarized at right angles to each other. Fused quartz wedges and

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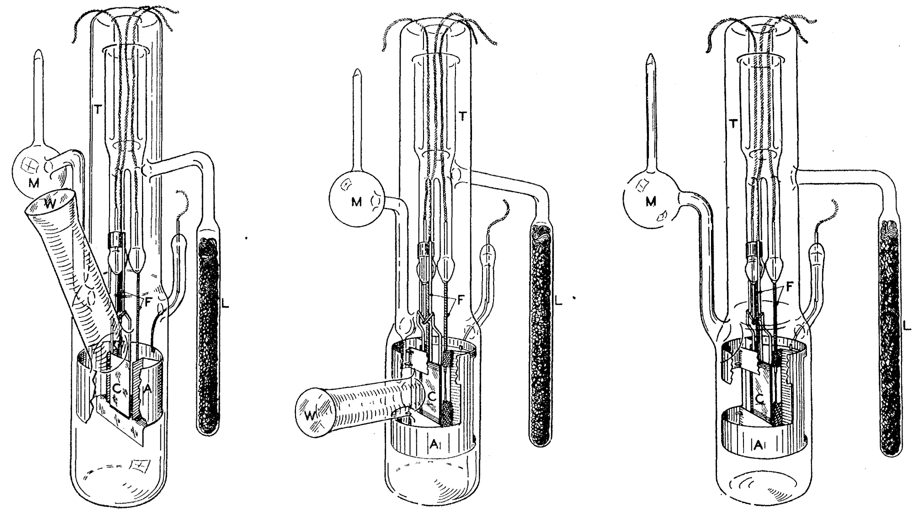
[3] Ives, "The Vectorial Photoelectric Effect," Phys. Rev. Sept. 15, 1931.

prisms were also introduced so that a quick shift could be made from one plane of polarization to the other without shifting the spot of light. The photoelectric currents were measured with a Compton electrometer by the steady deflection method, while the energy values of the radiation were recorded by a thermopile in conjunction with a high sensitivity moving coil galvanometer. With this apparatus it was possible to make reliable simultaneous measurements of photoelectric current and radiant intensity with the mercury arc lines. The tungsten lamp radiation, while sufficient for photoelectric excitation was too small to be satisfactorily measured by the thermopile in the ultraviolet region here in question. Comparison of photocurrents between several cells could, however, be readily made and this possibility was taken advantage of to secure important information.



a b c

Fig. 2. (a) Quartz windowed cell for observation at 60° incidence. *C*, polished silver plate (cathode) on which thin film of alkali metal is spontaneously deposited. *A*, enclosing anode of nickel, with vanes to prevent scattered light from striking back of cathode. *W*, fused quartz window, attached to Pyrex tube by stepped glass seal. F, leads to tungsten filament used for degassing cathode by electronic bombardment. *M*, bulb into which alkali metal is introduced after multiple distillation. *L*, charcoal tube. *T*, reentrant tubulation to reduce leakage caused by formation of alkali metal films on glass parts.

(b) Quartz windowed cell for observation at perpendicular incidence. Parts lettered as in 2a.

(c) Pyrex glass cell for observations at a series of angles. Parts lettered as in 2a.

Several varieties of photoelectric cells were used, which may be listed and illustrated here:

I. Quartz windowed cells for observations at 60° incidence. Fig. 2a.

II. Quartz windowed cells for observations at perpendicular incidence. Fig. 2b.

III. Pyrex glass cells for observations at a series of angles, for the determination of "angle curves." Fig. 2c.

The structural details are sufficiently explained by the legends accompanying the figures.

All these types of cells provided together only what a single cell of type III made entirely of quartz would have given, but the technical difficulty of obtaining clear walled quartz cells forced the resort to several types of cells. These cells were all made up with tungsten filaments behind the plates to permit degassing by electronic bombardment. The alkali metals were introduced after multiple distillation, and were present in large quantities so that sufficient vapor pressure existed to cause photosensitive films to build up spontaneously in very brief periods.

The metal plates were in all cases given as high a polish as could be obtained. This was much higher in the case of the platinum plates used for reference purposes than in the case of the silver plates. Moreover the latter could not be raised to nearly as high a temperature for degassing, as could the platinum, without the surface disintegrating and becoming rough. For these reasons the results obtained with the silver plates are probably somewhat less clear-cut than would be desirable for exact quantitative check with any theory correlating photoeffect with optical properties.

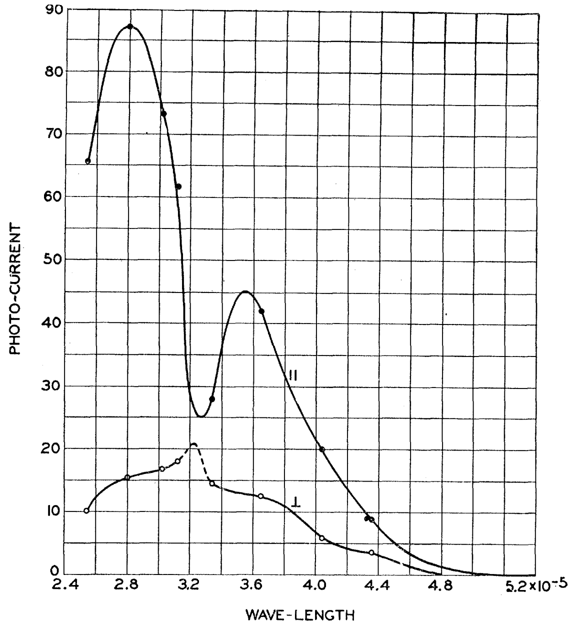


Fig. 3. Photoelectric currents per unit energy incident at 60°, plotted against wave-length, thin film of sodium or silver. Circles, electric vector perpendicular to plane of incidence; dots, electric vector parallel to plane of incidence.

Preliminary Experimental Results

In Fig. 3 are shown photoemission curves for sodium on silver, for light incident at 60°, for the || and ⊥ cases; in Fig. 4 similar curves for potassium on silver, and in Fig. 5 for caesium on silver. In Fig. 4 is shown, in the dashed curve, the || emission from a thin film of potassium on platinum. It will be seen at once that the films on silver exhibit a pronounced influence of the silver plate beneath. There is a deep cleft in the || curves for all cases shown.

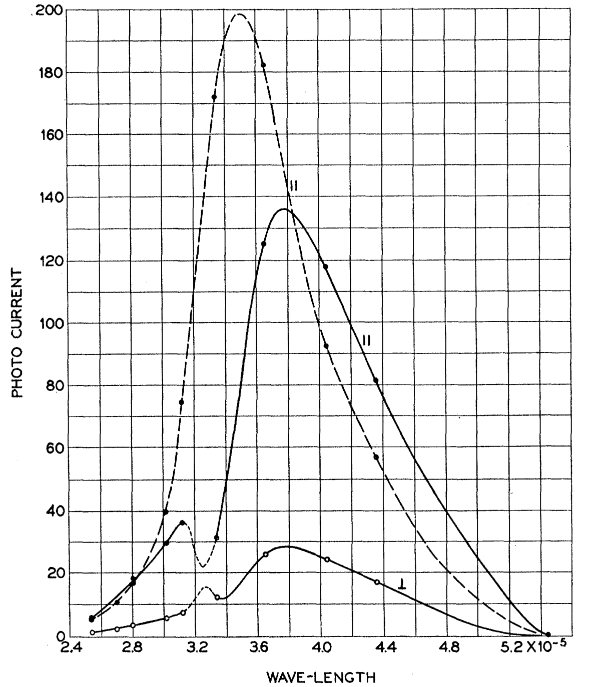


Fig. 4. Photoelectric currents per unit energy incident at 60° plotted against wave-length. Full lines, thin film of potassium on silver. Circles; electric vector perpendicular to plane of incidence; dots, electric vector parallel to plane of incidence. Dashed line, emission from thin film of potassium on platinum, electric vector parallel to plane of incidence.

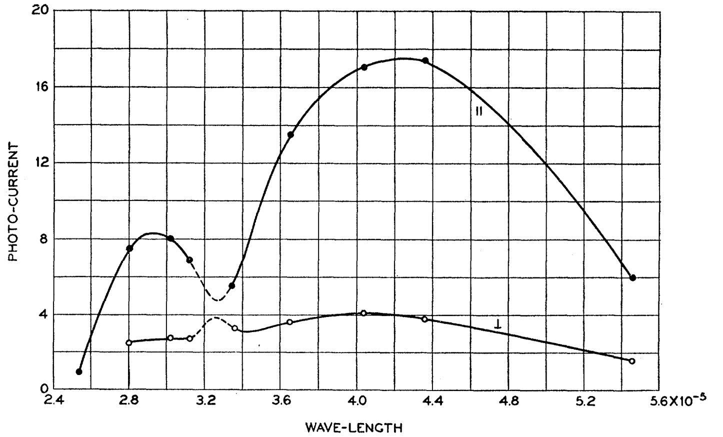


Fig. 5. Thin film of caesium on silver. Circles; electric vector perpendicular to plane of incidence dots, electric vector parallel to plane of incidence.

Comparing this cleft with the minimum of reflecting power for silver shown in Fig. 1 several questions are at once raised. First of all, the photoemission curves show their depressions at about 3260A. while the reflection minimum is at 3160A. Second, the depression of photoemission appears to be absent for light polarized with the electric vector perpendicular to the plane of incidence. In the figures we have in fact dotted in an *increase* of emission for this case, the warrant for which we will give later.

It was immediately thought that these peculiarities might be explained when the reflecting power curves were computed for 60° incidence. This was accordingly done, using Minor's very full data[4] for the optical constants n and k, yielding the curves shown in Fig. 6, on which the computed reflecting power for perpendicular incidence is also plotted, agreeing quite well with Hagen and Rubens direct determination. It appears from these computations that at 60° the minimum of reflecting power is indeed shifted along the spectrum, but not nearly enough to agree in position with the photoemission minimum. Also it appears that the minimum is less for ⊥ light than for ||, but again the difference is not enough to account for the apparent absence of the ⊥ minimum found experimentally.

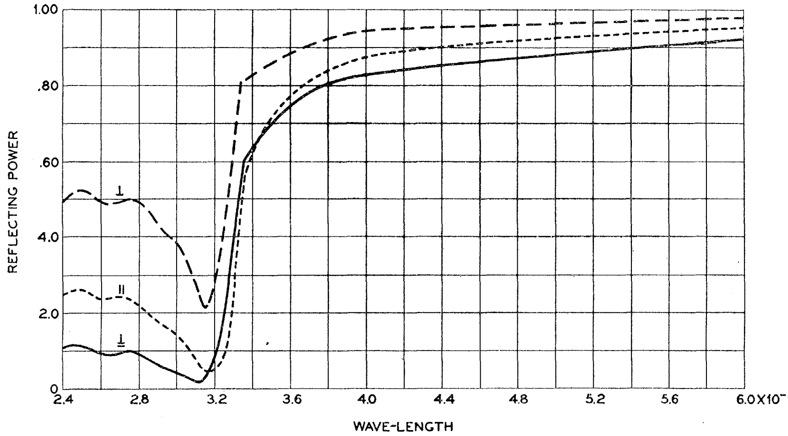


Fig. 6. Reflecting power of silver as computed from Minor's determination of optical constants. Full line; perpendicular incidence. Dotted and dashed lines, light incident at 60°; dots, electric vector parallel to plane of incidence; dashes, electric vector perpendicular to plane of incidence.

THEORY FOR TRIAL

In order to explain our experimental results we have evolved a theory whose essential postulates are:

(a) That the photoelectrons come entirely from the thin film of alkali metal.

(b) That the effective light intensity is that at the metal-vacuum surface.

In order to test this theory it becomes necessary to determine the effective light intensity called for by (b). We are aided in this by an experimental result

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[4] Minor, Ann. d. Physik 10, 581 (1903).

previously obtained,[5] namely, that the *presence of the thin alkali metal film does not appreciably affect the condition of the light as reflected by the metal plate beneath.* In consequence of this fact, the determination of the light intensity at the metal-vacuum surface can be arrived at by computation, using the *refractive index and extinction coefficient of the metal underlying the photosensitive film.*

This theory has been discussed in some detail in a previous paper[3] where it is shown that the large differences in emission from thin films on platinum for illumination by light polarized in the two chief planes follow directly from the computed light intensities just above the platinum surface. That paper should be consulted for details of the theory and the computations.

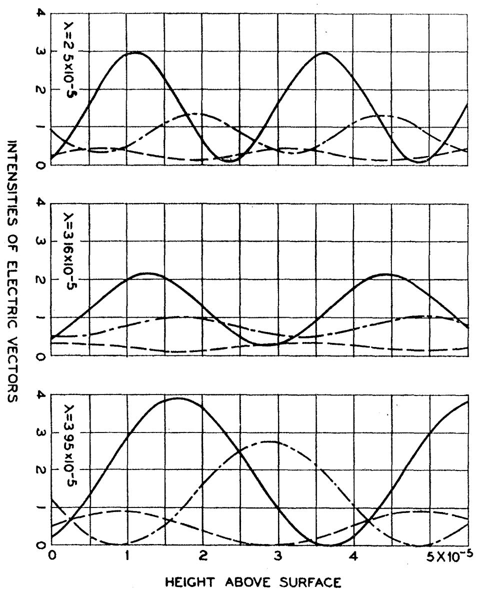

Fig. 7. Standing wave intensities above silver surface for light incident at 60°. Full line; the y component, electric vector perpendicular to plane of incidence. Dashed line, the x component; dot and dashed line, the z component, electric vector parallel to plane of incidence.

For the purposes of the present discussion the essential physical phenomenon is the formation, above the metallic reflecting surface, of an interference pattern whose phase and amplitude are dependent on the refractive index (N) and extinction coefficient (K_0) of the metal, and vary with the plane of polarization and angle of incidence.

In order to make this conception concrete, we show, in Fig. 7, the standing wave system as present over silver, for three wave-lengths in the neighborhood of its region of low reflection, as computed from the optical constants determined by Minor. In this are shown the electric intensities of the x and z components (dashed, dot-and-dashed lines) for light incident at 60°, polarized with the electric vector parallel to the plane of incidence $(\|)$ and (full

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[5] Ives and Johnsrud, J. Opt. Soc. **15**, 374 (1927).

lines) the y component (the only one in question) for light polarized with the electric vector perpendicular to the plane of incidence ($\perp$).

On inspecting these plots we note that while the $\perp$ standing wave system is very near a node at the metal surface for all three wave-lengths shown, the two components of the $\|$ standing wave system are well away from a node, except for the z component in the region of minimum reflection, which is near a node, but has considerable amplitude. On the scale of this plot the monatomic layer of alkali metal is too thin (circa 10^{-8} cm) to be indicated other than as a line coincident with the silver surface. For the purpose of the present study the intercepts of the standing wave systems, of which the three of Fig. 7 are samples, have been computed at short wave-length intervals throughout the low reflection region, and from these the electric intensities just above the silver surface have been computed for perpendicular incidence ($\perp$), and for the two planes of polarization at 60° incidence, ($\|$ and $\perp$). These computations are potted in Fig. 8.

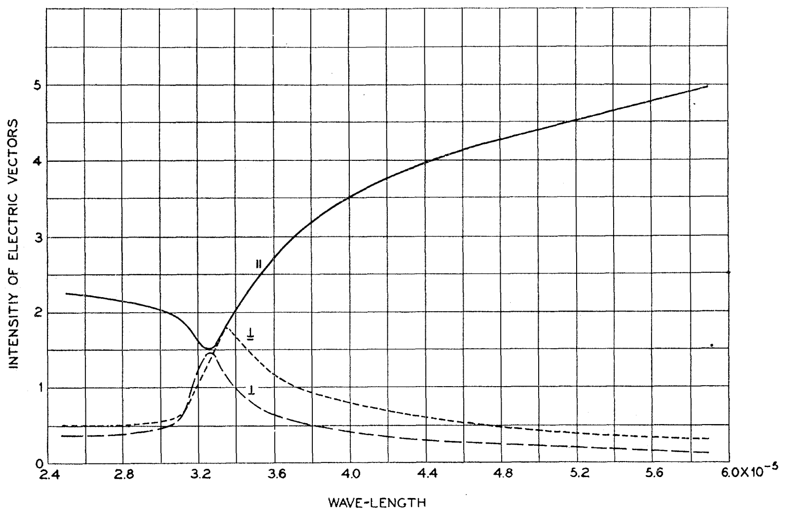

Fig. 8. Intensities of electric vectors just above silver surface, as computed from optical constants. Full line, light incident at 60°, electric vector parallel to plane of incidence. Dashed line, light incident at 60°, electric vector perpendicular to plane of incidence. Dotted line, perpendicularly incident light.

If now we could assume the photoemission to be proportional directly to the electric intensity in the alkali metal film, Fig. 8 gives the photoemission to be expected. We see at once that not only is the minimum of emission for the $\|$ case shifted by about 100 angstroms from the minimum of reflection, that is, from 3160A to 3260A, but for the $\perp$ case there should be a *maximum* of emission. Furthermore, for perpendicular incidence, in place of a strong minimum, as shown by the reflecting power, there is a very pronounced *maximum*. Considering further the variation of emission with angle of illumination, it appears that in the neighborhood of 3200A the $\perp$ angle curve should rise higher for 60° incidence than for perpendicular incidence, unlike the angle curves ordinarily obtained from metals, which exhibit a steady decline in value toward the higher angles of incidence.

Before proceeding to describe the experimental tests of these findings it is important to recall, from the previous paper, just how far the theory, as developed, can be verified at the present time, and what limitations are imposed to its full application, principally through our ignorance of the optical constants of the alkali metals in the ultraviolet. It is important to note that the curves of Fig. 8 do not take account of the specific absorbing and emitting properties of the film. In other words, if the film absorbed energy equally well at all wave-lengths, and emitted the same photoelectric current for the same effective energy density at all wave-lengths, the emission by wave-length would be given at once by Fig. 8. Actually, however, the absorption of energy in a film is determined by the optical constants and thickness of the film;[6] and the photoemission per unit of absorbed energy is at present an unknown function of wave-length. When the optical constants of the alkali metals are completely known, the absorption of energy in a thin film will be capable of computation for all conditions of incidence and polarization of the light, all through the spectrum. It will then be possible to find the specific photoemission as a function of wave-length, and thus have all the factors necessary for the complete description of the thin film photoelectric phenomenon. At the present stage of the investigation, however, lacking the optical constants of the alkali metals, all the indication of the theory that we can expect to verify are:

(1) The occurrence of the several maxima and minima of emission shown by Fig. 8, at approximately their computed places (provided the alkali metal has no considerable singularity itself in its optical constants through this region).

(2) The shape of the $\perp$ angle curves for monochromatic light.

EXPERIMENTS TO TEST THEORY

Inspection of the curves plotted in Fig. 8 shows that *the most interesting and significant regions for testing the theory lie between the mercury arc lines which were used in the initial measurements.* What is required for an adequate test is a continuous light source of sufficient intensity to permit of accurate energy measurements at each point of interest. Such a source was not available. Instead a procedure was worked out which consists essentially in making relative photoelectric measurements by comparison with a photosensitive surface whose wave-length emission curve could be established beyond reasonable question all through the region in question. For this purpose a sodium-on-platinum cell was constructed of the type II, shown in Fig. 2b. This was measured with great care for light incident perpendicularly, using the mercury arc as a source of radiation, yielding the emission curve shown in Fig. 9 (circles). This curve shows a uniform slow rise in value through the wave-length region in which we are interested, and, since platinum has no

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[6] A full treatment of the absorption of light in thin films will be given in a paper now in preparation by Mr. T. C. Fry.

singularities in its optical properties in this region, it is quite safe to interpolate the smooth curve shown between the mercury arc points. This curve constitutes our reference standard.

A second cell of the same type was then made up with a silver plate, and this was likewise filled with sodium. This alkali metal was chosen in part in order to use the same material as the reference standard, and in part because sodium is more suited to delicate measurements, due to the greater freedom of sodium cells from leakage currents. This second cell was mounted alongside the reference cell on a sliding carriage, so that they could be exposed alternately, in quick succession, to the light from the spectrometer, and the photocurrents measured. Measurements of this sort were made, using first the mercury arc, and then the tungsten ribbon lamp with a quartz window. In this way the whole region from 3200A to 4359A was covered at sufficiently small intervals to establish the perpendicular incidence emission curve with great accuracy. The curve so obtained is also shown in Fig. 9 where the points interpolated by the use of the tungsten lamp are shown by the small crosses. It will be seen that it exhibits in striking fashion the maximum at 3350A predicted in Fig. 8.

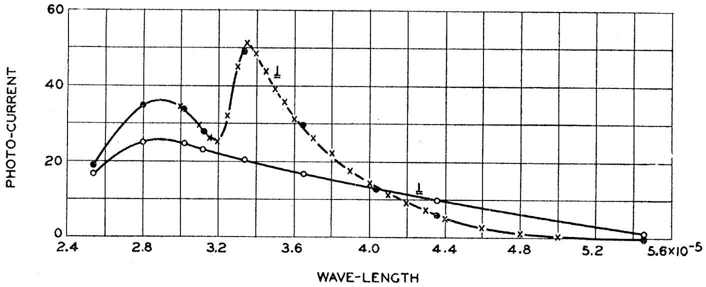

Fig. 9. Data from perpendicular incidence cells, type II. Circles, thin film of sodium on platinum, mercury arc lines. Dots, thin film of sodium on silver, mercury arc line. Crosses, points obtained by relative values of photocurrents in two cells, with tungsten ribbon source.

The next step was to build up the 60° emission curves. This was done by obtaining "angle curves" for monochromatic light, using a cell of type III shown in Fig. 2c, and taking off from these angle curves the relative values for the 60° emission as compared with the 0°. Multiplying the perpendicular incidence curve of Fig. 9 by these ratios gave at once the 60° emission, the derived points being shown by the small crosses. Due to the absorption of the Pyrex glass in the angle-curve cells no measurements could be made below 3100A, but this fortunately was not an obstacle to obtaining data in just the region desired. Examples of the angle curves used for this purpose are shown in Fig. 10. Attention may be called to the dashed curve shown for 3260A, which is computed from the optical constants of silver, and agrees closely with the experimental finding, of curves rising with increasing angle of incidence.

The 60° emission curves for both planes of polarization are shown, together with the perpendicular incidence curve from which they are derived, in Fig. 11. Inspection of this figure shows that the predictions of the theory are strikingly confirmed. With light polarized with the electric vector parallel to the plane of incidence there is a *minimum* of emission at 3260A, as the curves for potassium and caesium thin films already indicated. With light polarized with the electric vector perpendicular to the plane of incidence there is a *maximum* of emission at the same wave-length. Around 3200A the currents for 60° angle of incidence, with the electric vector perpendicular to the plane of incidence, are greater than for perpendicular incidence.

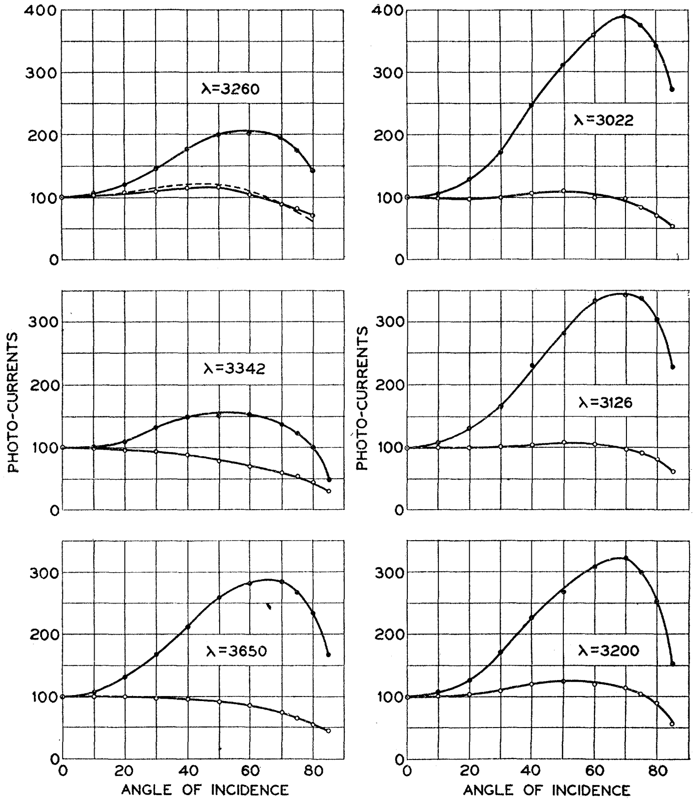

Fig. 10. Angle curves at various wave-lengths; sodium film on silver. Circles, electric vector perpendicular to plane of incidence; dots, electric vector parallel to plane of incidence. Dashed curve of 3260A, computed from optical constants of silver.

The success of our substitution method of filling in the wave-length interval around 3200A, as just described, suggested its use with the 60° type of cell (Fig. 2a) as well to get a still further check on this important region. Accordingly a 60° cell[7] was mounted alongside the perpendicular-incidence platinum-plate cell and alternating measurements made, with both the mer-

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[7] This is a different cell from that used to get the data of Fig. 3, and the actual angle was nearer 55° than 60°.

cury arc and the tungsten ribbon. The data so obtained are shown in Fig. 12, where the $\|$ and $\perp$ curves are for the silver plate 60° cell, and the $\underline{\perp}$ curves for the sodium on platinum normal incidence cell. These curves fully confirm the findings of Fig. 11, and agree well with the preliminary curve shown in Fig. 3. The agreement between the various sets of sodium data is considered excellent for this kind of work, remembering that measurements on four different sodium-on-silver cells are represented.

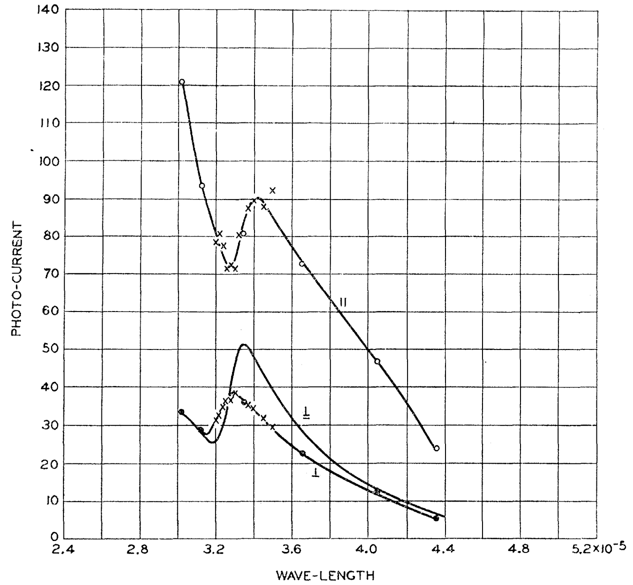

Fig. 11. Thin film of sodium on silver, photoemission at 60° and at 0° as derived from angle curves from perpendicular incidence data of Fig. 9.

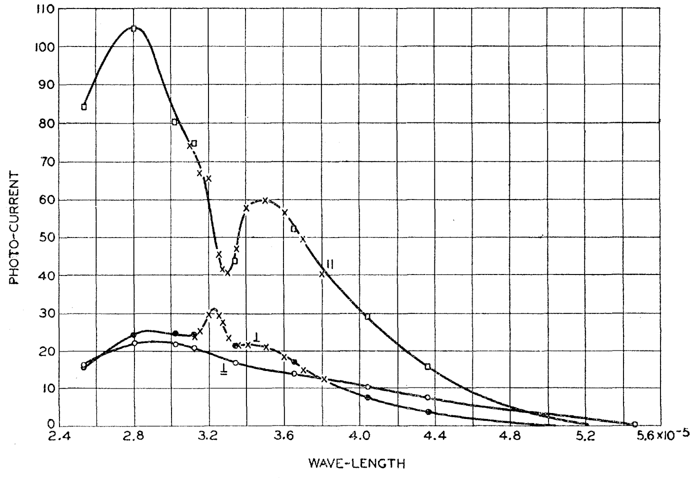

Fig. 12. Upper curves (dots and squares) are photocurrents from thin film of sodium on silver, light incident at 60°, as obtained by substitution measurements from thin film of sodium on platinum (perpendicular incidence) shown in lowest curve (circles).

In the very satisfactory agreement with the essential predictions of our theory which is shown by the curves of Figures 11 and 12, for the case of light with the electric vector perpendicular to the plane of incidence, it will be noted that the peak of emission near 3260 is considerably smaller than would be expected if the values in the computed curves of Figure 8 were used as direct multiplying factors on an emission uniform or smoothly varying with wave-length. While this diminished prominence of the emission peaks may be real, and be explicable by further refinement of the theory, it is rather more likely to be due to a condition we have already pointed out, namely the lack of perfect polish of the silver surfaces, whereby some admixture of light polarized with the electric vector parallel to the plane of incidence occurs. Since excitation with this light shows a marked depression in the emission curve at this same point, a smoothing out of the peaks as found is exactly what would be expected in mixed light. In addition to this, the peaks in question are established entirely by measurements with a continuous spectrum source, for which the slits used in the spectrometer were of necessity of considerable width, which would have the effect of decreasing the measured magnitude of the peaks. In short, the agreement found with theory in the relative positions of the curves, and in the positions of their maxima and minima, can be interpreted, we believe, as a complete confirmation of the theory despite the apparent discrepancy in the magnitudes.

DISCUSSION

The most important outcome of this study of alkali metal films on silver is the proof which it gives that the energy that must be considered in studying the photoelectric effect is not the incident, nor the absorbed energy, is ordinarily considered, but the *energy density at the surface*. While this has been demonstrated here only for the case of thin films, the fact that the photoemission from thin films is of the same order of magnitude as that from bulk alkali metals, is strong reason for believing that in the latter case the photoelectrons escaping all come from the top layer of atoms, so that the conclusion just drawn will be of general applicability. Speculations based on the positions of maxima of emission under excitation by an "equal energy" spectrum are, on this view, of little significance. Until the optical constants of the photoactive metals have been determined through the whole spectrum, and the absorptions in their surfaces computed there-from, the intrinsic emissivities cannot be considered known. The important question whether there is indeed any real difference in the emissive properties of the alkali metals with plane of polarization of the light ("normal" and "selective" effects) must be considered open until it is ascertained whether the apparent differences are not to be correlated with optical properties, along the lines here followed.

ACKNOWLEDGMENT

We are greatly indebted in this work to Mr. T. C. Fry for his mathematical studies of the optical properties of metals,[8] utilized extensively in the computations necessary for this paper, and to Miss C. L. Froelich for carrying through these computations.

[8] T. C. Fry, "Plane Waves of Light," J. Opt. Soc. **15**, 137 (1927); **16**, 1 (1928).