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The Depth of Origin of Photoelectrons

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Previous work has shown that the photoelectrons from a silver plate covered with an equilibrium film of alkali metal follow the wave-length distribution of energy just above the silver surface, i.e., in the alkali metal. This question has been further investigated with particular references to alkali metal films in their early stages of development, where their average depth is less than one atom. Computations made on the absorption of light just within the silver surface show that there should be very definite and striking differences in the wave-length distribution of photoemission if emission occurs due to light absorption in the silver, as contrasted with emission from a film on the silver. Experimental tests made with sodium and caesium films show that in the earliest measurable state the emission exhibits characteristics peculiar to the light absorption in silver, and that as the films build up the emission becomes characteristic of the energy above the silver. It is concluded that the photoelectrons originate partly in the underlying metal and partly in the alkali metal film, the relative proportions varying with the film thickness.

IN PREVIOUS papers[1] we have described photoelectric experiments with alkali metal films on silver and on platinum, which show that the photoelectric currents follow the characteristics of the light energy immediately above the supporting metal surface. We have interpreted these experiments as evidence that the photoelectrons originate in the alkali metal film.

The films heretofore studied had reached their complete equilibrium development, and were therefore an atom or more thick, completely covering the supporting metal surface. It is however possible to study photoelectric currents from surfaces during the process of deposition of the alkali metal film, when the average depth may be much less than one atom, in other words, while the surface has upon it isolated atoms or groups of atoms of alkali metal, with uncovered spaces between. Under these conditions, do the photoelectrons originate in the alkali metal, or, as some theories indicate, is the function of the alkali metal centers that of facilitating the escape of electrons released in the underlying metal, but prevented from emerging ordinarily by its high work function?

The experiments described below were made chiefly on partly developed alkali metal films on silver, in the belief that the correlation of optical and photoelectric properties which had proved so informative in the case of fully developed films would here again indicate the place of origin of the photoelectrons. The reasons for expecting information on this point appear from a study of the light energy conditions both above and within the surface of the supporting metal, for these exhibit striking and decisive differences.

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[1] Ives, *The Vectorial Photoelectric Effect*, Phys. Rev. **38**, 1209–1218 (1931).
Ives and Briggs, *The Photoelectric Effect from Thin Films of Alkali Metal on Silver*, Phys. Rev. **38**, 1477–1489 (1931).

In order to make clear these differences, we have in Fig. 1a, reproduced data from an earlier paper showing the computed energy densities above a silver surface, for a range of wave-lengths extending through the ultraviolet absorption band, for perpendicularly incident light ($\underline{\perp}$) and for light incident at 60°, polarized with the electric vector parallel (||) and perpendicular ($\perp$) to the plane of incidence. In Fig. 1c we show the bulk absorbing power, or the fraction of the incident light which is subtracted by an infinitely thick layer of silver. In Fig. 1b we show the "lamellar" absorbing power, or relative amounts of energy absorbed by a thin layer of silver, *just inside* the surface.[2] In view of our conception that the photoelectrons can only escape from the topmost layer of metal it is our expectation that it is this lamellar or surface absorption—which in many respects is transitional in character between the bulk absorption and the energy density above the surface—which would impose its peculiarities on photoemission originating in the silver. Before discussing the significant differences between these curves, we note that of the three sets of curves only Fig. 1c is on an absolute scale, as shown, all absorbing powers lying between zero and unity. The absolute amount of the surface absorption shown in Fig. 1b depends on the thickness of the layer, which enters as a multiplier, while the absorption taking place in a film lying above the surface is a function both of the energy densities shown in Fig. 1a, and of the absorbing power of the film material through this wave-length region.

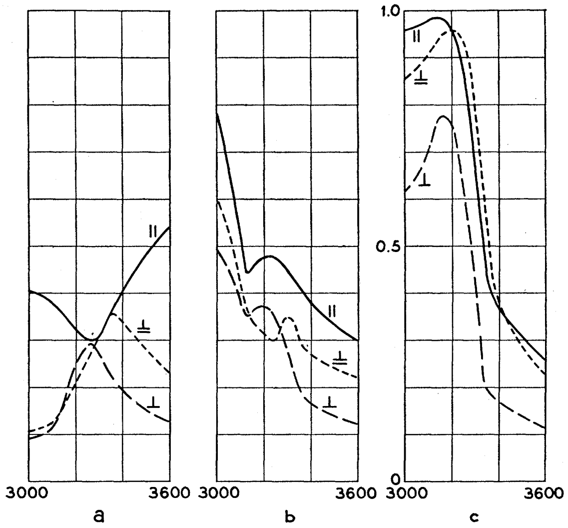

Fig. 1. Optical properties of silver near ultraviolet absorption band, plotted for perpendicular incidence of light ($\underline{\perp}$) and for light incident at 60°, polarized with electric vector parallel to plane of incidence (||) and perpendicular to plane of incidence ($\perp$). (a) Energy density just above surface; (b) Absorption just inside metal; (c) bulk absorbing power.

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[2] We are here using data derived from a study of the absorption of light in thin and thick layers of metal, which will be published shortly by Mr. T. C. Fry. An abstract appears in the program of the meeting of the Optical Society of America of February 27, 1932 under the title, *Plane Waves of Light III.*

Hence, insofar as the absorption of energy is concerned Figs. 1b and 1c give complete information as to relative values from wave-length to wave-length, while Fig. 1a represents relative energy absorbed in the film only if the film absorbs uniformly at all wave-lengths (and conditions of polarization). If the film material has optical singularities, such as absorption bands, in the region under study, they can mask to greater or less degree the characteristic forms of the curves shown. As a further caution on the interpretation of these curves we must recognize as well that the intrinsic photoelectric emission per unit of absorbed light at each wave-length, also enters as a multiplier. Both this factor and the optical constants of the film material, must be known before the problem can be completely elucidated. Nevertheless, by working with films of an alkali metal which shows no evidence of optical singularity in the wave-length interval under observation (as appears to be substantially the case with sodium), and confining our attention chiefly to the *positions* of the characteristic maximum and minimum of absorption and photoemission, rather conclusive information can be derived.

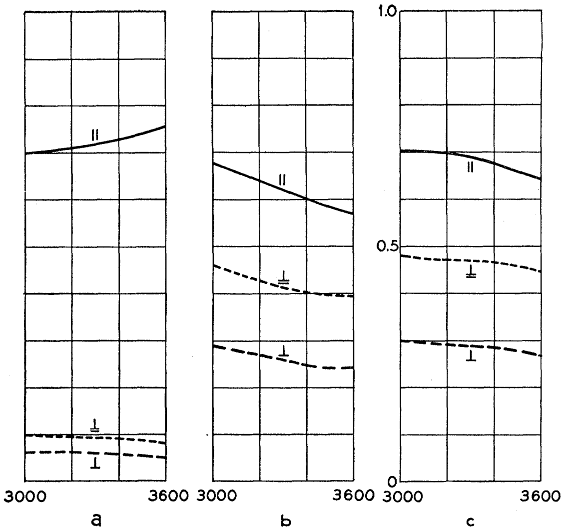

Fig. 2. Optical properties of platinum corresponding to those shown for silver in Fig. 1.

Taking up now in some detail the differences between the silver absorption just inside the surface, and the energy densities just above the surface, consider first the curves for light at 60° incidence polarized with the electric vector parallel to the plane of incidence (||). In these, the minimum or cleft at 3260A characteristic of the energy above the surface, and which was found so strikingly in the fully developed alkali metal films, disappears inside the surface and is replaced by a small peak at 3200A. For light polarized in the other plane, (⊥), the maximum at 3260A found above the surface is shifted to 3200A and greatly reduced in size. The curves representing the surface absorption both rise steeply toward shorter wave-lengths, as compared with the energy above the surface. For light incident perpendicularly ($\underline{\perp}$) the computed curves for the two cases are also materially different. The broad high maximum in the energy above the surface is replaced by a small peak, shifted toward shorter wave-lengths, and the whole curve for the surface absorption rises more steeply toward the shorter wave-lengths.

Before proceeding to describe the experiments on silver, we also show, in Fig. 2, the corresponding computed data for platinum, on which we have also obtained data of some significance. No absorption band, such as that exhibited by silver, is present in the wave-length interval shown, and the differences in the three sets of curves are not so spectacular. There is however one of great importance; while the energy above the surface (Fig. 2a) exhibits very large ratios for the two planes of polarization at 60° incidence (about 12:1) immediately the surface is entered the relative absorptions drop to low values (between 2 and 3 to 1), being substantially the same as in the bulk absorbing power. Now in earlier work[3] on thin films of alkali metal on platinum we have found that a characteristic of the very thin, or partly developed films is that they show *low* ratios; in fact the "angle curves" approximate in shape to the bulk absorptions as plotted against angle. These angle curves might then be considered as evidence that with partially developed films the photoelectrons do originate in the absorption of light in the surface of the underlying metal. We shall see however that the experimental data indicate that such an explanation is inadequate and that some additional cause for the low ratios between emission as the plane of polarization is changed, is called for, where the films are very thin.

Apparatus and Experimental Procedure

The majority of the experiments were made with sodium films on silver, and for these the apparatus and methods of observation were in all essentials similar to those described earlier. The tungsten filament quartz-windowed lamp was the only light source used, since as before the significant wave-length region, to which the measurements were restricted, lies between the nearest mercury arc lines. The energy distribution of the lamp was as before determined by interpolated photoelectric measurements on a sodium-on-platinum perpendicular incidence cell, which is presumed to be free of irregularities of emission in this region. With sodium the rate of growth of the films is so slow that, after the introduction of the alkali metal, or after it had been driven off the plate by electron bombardment, ample time was available to make reliable measurements at any stage of development. In order to have some indication of the thickness to which the film had grown, the long wave limit was usually found. This, as is well established,[4] moves toward long wave-lengths as the film develops, reaching the resonance potential value (5893A for sodium) and then recedes somewhat for the final equilibrium film. In the present experiments the long wave limits noted are only approximate, as no

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[3] Ives, *Photoelectric Properties of Thin Films of Alkali Metals,* Astrophysical Journal, **LX,** 4 (1924).

[4] Ives and Olpin, *Maximum Excursion of the Photoelectric Long Wave Limit,* Phys. Rev. **34,** 117–128 (1929).

precautions were taken to cut out stray short wave energy, such as the use of exceedingly fine slits, or color filters.

It was planned to supplement the sodium film measurements by a series on caesium, which because of its greater intrinsic sensitiveness, would permit measurements at much earlier stages of film development. Accordingly, a (60°) tube was designed and built, which in addition to a plate of silver had a platinum plate and twin quartz windows, so that comparative data might be obtained with the two different underlying metals. The caesium was distilled into a bulb on a side tube, and was allowed to diffuse slowly into the main tube. Caesium films are however exceedingly difficult to work with, and our results are quite incomplete, due, first of all, to the rapidity of growth of the film at the earliest stages, and second to the rapid development of surface leakage inside the tube, which completely swamped the small photoelectric currents long before the equilibrium stage was reached. Nevertheless, incomplete as they are the caesium data bring out points of considerable interest.

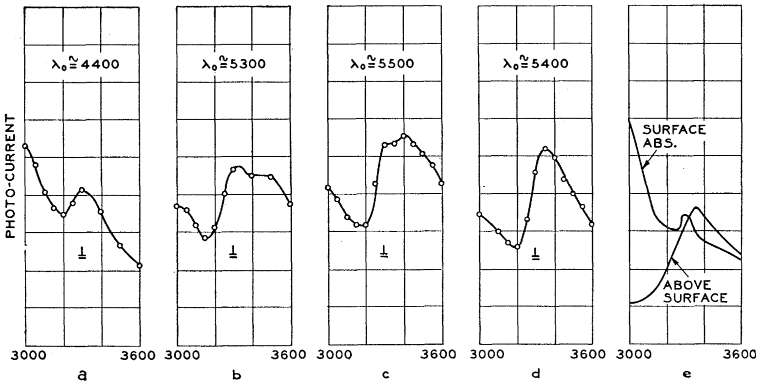

Fig. 3. Photocurrents from thin films of sodium on silver, light incident perpendicularly. Figs. a, b, c and d show successive stages, as indicated by the approximate long wave limits. Fig. e reproduces from Fig. 1, a and b, the surface absorption and supra-surface energy density.

Experimental Results

Silver

As a preliminary to the discussion of the photoemission from silver plates on which alkali metal films are allowed to form, it is pertinent to record that silver itself shows no detectable photoemission in this wave-length interval. All the photoelectric emission is due, whatever the exact mechanism may be, to the presence of the alkali metal film.

Sodium, perpendicular incidence, Fig. 3

The earliest stage of film deposition for which reliable measurements could be obtained exhibited a long wave limit at approximately 4400A. In this condition, (a), the photocurrent rises steeply toward short wave-lengths, showing however a well marked maximum at 3300A. As the film grows and the long wave limit increases (b) and (c) the short wave emission decreases relatively to the maximum value, and the long wave side of the emission maximum builds up. For the fully developed film (d) this process has continued until the position of the maximum has shifted to 3350A, and the emission on the short wave side is nowhere as great as at the maximum.

At (e) are shown the computed surface absorption and supra-surface energy density, copied from Fig. 1, (a) and (b), for this condition of illumination. Comparing these with the experimental results we note that the final state (d) is clearly dominated by the supra-surface energy density, that is, as previously concluded, the photoelectrons originate in the alkali metal film. Now, comparing (e) and (a) we see that the film in its earliest measured state definitely shows characteristics peculiar to the absorption in the silver surface. These are, the trend upward toward short wave-lengths, and, of greater significance, a maximum at 3300A. It is true that the "fine structure" of this maximum as computed in (e) is not shown in (a), but it is to be remembered on the one hand, that the experimental observations are of necessity made with spectrometer slits of considerable width, and on the other hand, that the computed curves themselves rest on experimental determinations of the optical constants of silver, which must not be accepted as infallible. Bearing these facts in mind, the data present clear evidence, we believe, that *in the earlier stages of film deposition the photoelectrons come from the underlying metal.*

Sodium, oblique incidence, Fig. 4

Inspection of the data shown in the curves, (a) to (e), reveals that we have here again the same general shift of characteristics from those of the silver surface to those of the space immediately above the surface. In the earliest stages both planes of polarization show a maximum at 3200A, characteristic of the absorption just inside the silver surface. In the completely developed film (e) the one plane of polarization ($\|$) exhibits the deep minimum at 3300A, the other ($\perp$) the maximum between 3200A and 3300A characteristic of the energy density above the surface. There are however several features in the structure of the curves which complicate the simple interpretation indicated by the perpendicular incidence data.

One peculiarity is that the characteristics of both regions of absorption are always present to some degree. Thus in the fully developed film the silver absorption peak at 3200A still shows its influence, by a small shoulder on the $\|$ curve,[5] and by the fact that the $\perp$ maximum is shifted to somewhat shorter wave-lengths than the computed curve (3230A as against 3270A). At the first stage of deposition measured, which is considerably earlier than for perpendicularly incident light, ($\lambda_0 \cong 4000$A as against 4400A) the $\|$ curve shows definite indication of the depression at 3300A characteristic of the energy density above the surface. In immediately succeeding stages, not here reproduced, the $\|$ curve quickly takes the shape shown in (b), where the minimum at 3300A is pronounced. It is not of course out of order that there should be

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[5] This shoulder is shown by the points in the previously published curves (reference 1 above) but its significance was not understood.

a transition from one set of characteristics to the other, however there is one feature in which this transition does not fit the computed curves of Fig. 1. According to the || curve in Figs. 1a and 1b, the early maximum at 3200, and the final minimum at 3300 are of such breadth that if both are present together they should very nearly neutralize each other, resulting in a nearly smooth emission curve. Actually the behavior is as if the maximum and minimum in question were very much sharper than the computations show so that they do not overlap to such an extent as to neutralize. Here again the caution with regard to accepting the optical constants as infallible must be stressed. For one thing these were determined from silver plates in air, while our plates were outgassed and worked with in vacuo; this difference in conditions may of itself, quite apart from experimental uncertainties, be sufficient explanation for the much narrower singularities which our photoelectric data appear to reflect. In any event there is no reason to modify the general conclusion already drawn from the data at perpendicular incidence, that *the photoelectrons come largely from the silver in the early stages, and chiefly from the sodium film in the later stages of deposition.*

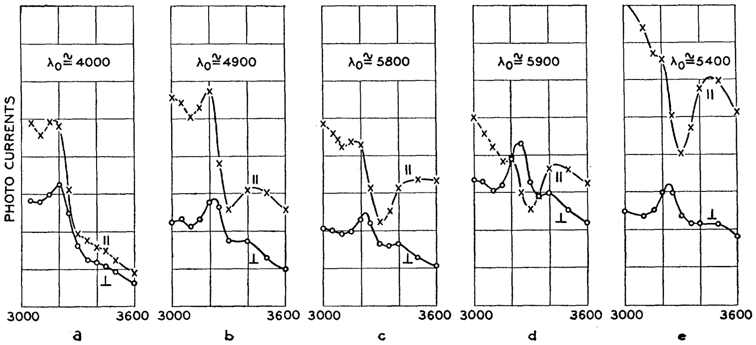

Fig. 4. Photocurrents from thin films of sodium on silver, light incident at 60°, successive stages.

Directing our attention to Fig. 4d we find a condition which has a vital bearing on the question whether the low ratios of || to ⊥ emission found with partially developed films are to be ascribed to the emission originating in the supporting metal, for which these ratios are low. We observe here that around 3300A this ratio is actually *inverted*, there is a smaller emission for light polarized with the electric vector parallel to the plane of incidence than when it is perpendicular thereto. Now the occurrence of such an inversion is not characteristic of the silver, for which this ratio is always greater than unity. Moreover it occurs at a late stage of film formation, where the characteristics with respect to wave-length of the energy density above the surface are predominant. It is not a characteristic of the unmodified energy density above the silver, for which the ratio in question is nearly unity at 3270A. It must, in accordance with our previous findings depend upon the optical properties of the alkali metal occupying the space just above the silver. The occurrence of low ratios in partially developed films must therefore be due in part to peculiar optical properties of such films.

Caesium, oblique incidence, Fig. 5

Our results for caesium are incomplete for reasons already stated, but are recorded partly because they confirm the sodium results and partly because they exhibit some new phenomena which are interesting in connection with our general study of the correlation of optical and photoelectric properties.

Referring to Fig. 5 we have at (a) again the exhibition in the earliest stages of film development of maxima of emission at 3200A for both planes of polarization of incident light. As the film grows (b to e) the maximum for $\perp$ light shifts to longer wave-lengths and the emission curve is lower in relative value on the short-wave side, following in general the behavior of the sodium film. For $\parallel$ light the growth history presents new features. The maximum at 3200A quickly irons out, the whole curve drops, showing the inverted $\parallel/\perp$ ratio over a wide wave-length region; the minimum at 3300, which is so striking in the sodium film, is merely suggested for a period, to be lost in the appearance of a new minimum at 3150A as the film passes its maximum long wave limit condition.

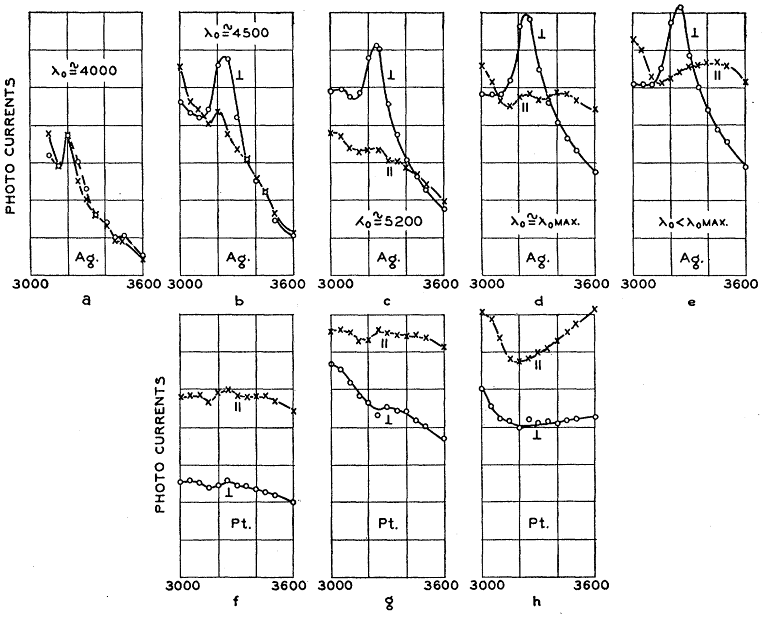

Fig. 5. Photocurrents from thin films of caesium on silver and platinum; light incident at 60°, successive stages.

The behavior of the $\parallel$ emission in its later stages appears to have little relationship to the optical properties of silver plotted in Fig. 1. For the explanation of the inverted ratio of $\parallel/\perp$ emission, we must, as with sodium, ascribe it to a property of the alkali metal, on which more will be said later. For the peculiar shape of the curve we derive an explanation from data taken on a platinum plate in the same tube, shown in Fig. 5 (f) (g) (h) at intervals between (b) (c) (d) and (e) approximately as their positions with respect to the upper diagrams show. The significant fact shown by these curves is that, in the later stages of film deposition (h) the caesium film on platinum exhibits precisely the same minimum of emission at 3150A as on silver. We have here a clear indication that caesium has in this spectral region an optical singularity (probably an absorption band) which is masking the silver characteristic. We have earlier emphasized the necessity for working with films which possess no optical singularities in the wave-length region under study if the indications of our guiding theory are to be tested without ambiguity. This condition is met with sodium, but not with caesium. Insofar however as we are asking the question, where the photoelectrons originate, this complication has not affected the answer. The minimum of emission at 3150A is shown by its occurrence both with platinum and silver to be a characteristic of caesium.

DISCUSSION OF RESULTS

By comparison of the experimental data of Figs. 3, 4 and 5 with the computed supra-surface energy and surface absorption curves of Figs. 1 and 2, the following broad conclusions may be drawn:

1. At the very earliest stages of alkali metal film deposition the photoelectric emission exhibits a spectral distribution containing characteristics of the absorption of the underlying metal. These characteristics become less noticeable as the film builds up.
2. During the greater part of the film growth period the photoelectric emission clearly exhibits spectral distribution features characteristic of the energy distribution above the supporting metal surface. These characteristic features dominate in the final stages of film growth.

In terms of the title of this communication, these conclusions may be recast as follows:

In the initial stages of alkali metal film growth photoelectrons are emitted which originate in the supporting metal; as the film increases in thickness more and more photoelectrons originate in the alkali metal; in the completely covered surface practically all the photoelectrons come from the alkali metal film.

These experimental results lend support to the idea that the alkali metal atoms (or ions) on the surface of another metal decrease the work function of the surface, extend the long wave limit and allow electrons originating in the underlying metal to escape. They show however that only a part (and during most of the development history of the film only a small part) of the photoelectrons are thus to be accounted for. On the face of the evidence at least equal emphasis should be placed on the conception that restraining forces due to the underlying metal act upon the electrons originating in the alkali metal film and cause the limitation of the long wave response while the film is only partially developed.

Accepting these conclusions, we must now recur to one of the original questions asked, namely, why is the ratio of the emissions for excitation by obliquely incident light polarized in the two chief planes ($\|$ and $\perp$) low (such as 2 or 3 to 1) in the partially developed films, when the energy density above the supporting metal calls for high ratios, such as 10 or 20 to 1? Our experimental results show the possibility that these low ratios are due, in the very early stages of film growth, to the emission originating in the supporting metal. But that this explanation is not adequate is very clear from the data of Figs. 4 and 5, in which a stage of film development appears where the ratio of $\|$ to $\perp$ emission is actually *inverted*, that is, the $\perp$ emission is greater than the $\|$, a condition which does not occur in the absorption in the silver. It is apparent that some other contributory cause for these low (and inverted) ratios of emission for partially deposited films, must be found.

Now the occurrence of an inverted ratio, while surprising at first glance, is actually entirely in accord with our previously found explanation of the low ratios occurring in the long wave visible region for all of the alkali metals.[1] A ratio lower than that exhibited by the energy density above the surface follows at once when the refractive index N and the extinction coefficient K_0 have such values that $1/(N+iK_0)^2$ is less than unity. In the case of sodium on platinum as the underlying metal, this factor in the long wave region reduced ratios of 30:1 down to 4 or 5 to 1. This same kind of reduction, applied to an energy density ratio of approximately unity, as in silver near 3250A would at once give ratios less than unity. What does require further explanation however is the fact that this ratio rises again with increasing film deposition, as shown in Fig. 4e, for sodium, and (as we have verified by angle curves) with caesium.

It is possible that an explanation is to be found in the peculiar optical constants of the alkali metals exhibited when they are in a dispersed form. Garnett[6] has shown that the colors of glass containing dissolved metals, and of alkali metal films on glass, can be correlated with new optical constants which bear a complicated relationship to the bulk constants, varying with the amount of material per unit volume. The alteration of values in the perpendicular electric vector upon entering the alkali metal film—which has been previously shown to explain the variation of the vectorial effect with wavelength—will of necessity be calculated for partially deposited films only in terms of optical constants applying to such film structures as arrived at by studies similar to those of Garnett. The optical constants which Garnett calculates for isolated aggregates of atoms call for sharp singularities of absorption, both as to wave-length and as to state of development of the film. The constants can moreover be different depending on the plane of polarization of the light. While Garnett's assumed film structures may not correspond exactly to those with which we are dealing[7] his work at any rate indicates the possibility that the low ratios in question may find their explanation in part

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[6] Phil. Trans. Royal Soc. A, **V203,** 385–420 (1904); **205,** 237–288 (1905).

[7] Inverted ratios, which we have noted on several occasions, appear to occur under rather special conditions, not reproducible at will, and apparently dependent on the way in which the alkali metal film builds up, as conditioned by vapor pressure, temperature and preparation of the underlying metal. Thus we observed this condition in very thin films of sodium which showed a departure from Lambert's law (Phys. Rev. **35,** 669, (1930)). A departure from Lambert's law is one of the effects to be expected from isolated aggregates of metal, which is the condition studied by Garnett.

in the properties of the alkali metal film in its partially developed state. The complete elucidation of thin film photoemission in its early stages must wait upon more complete knowledge than we now have of the optical constants of the alkali metals. Our conclusions as to the depth of origin of the photoelectrons are however not dependent on the complete explanation of this phase of the problem, and remain unaffected.