Photoelectric Sensitivity of Magnesium

R. J. CASHMAN AND W. S. HUXFORD, *Northwestern University*
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The photoelectric sensitivity of gas free surfaces of magnesium deposited on glass has been determined in the visible region of the spectrum. The long wave limit for all such surfaces deposited in vacuum is approximately 5100A. Air or oxygen in small amounts, or nitrogen activated by a glow discharge, sensitizes the surface to light of longer wave-lengths. Further oxidation of the surface causes the threshold to shift into the ultraviolet region of the spectrum.

A DEPOSIT of magnesium metal on glass is commonly used in the manufacture of certain types of commercial photo-cells. The cathode is prepared by condensing a small amount of the vapor of an alkali metal, which has been carefully purified by distillation in high vacuum, upon an undercoating of magnesium. Caesium cells constructed in this fashion are especially suitable for use in the visual region of the spectrum.[1] In most reports on the use of magnesium undercoatings no mention is made of the photoelectric properties of the magnesium itself, and no extended investigation seems to have been made of the effect of possible variations in the surface structure of the undercoatings on the spectral response of the sensitized cathode in such cells.

In the course of a preliminary investigation of magnesium coatings upon which other metals were to have been deposited, it was found that the magnesium itself was sensitive to visible light. The effect was reproducible and the thresholds the same for all coatings formed by slow vaporization of the metal, although previous coatings "flashed" by means of an induction furnace had not responded uniformly to visible radiation. An extension of the study to include the effect of various gases has shown that small amounts of oxygen render the surface more sensitive to red light, while a thorough oxidation of the surface destroys its response to visible light. Nitrogen, on the other hand, exhibits no effect except when activated by means of a glow discharge within the cell. The results obtained appear to confirm the hypothesis that the thresholds usually assigned to magnesium, which lie between 3300A and 3800A, are not those characteristic of the pure metal, but are due to contaminated magnesium surfaces.

[1] Zworykin and Wilson, J.O.S.A. and R.S.I. 19, 81–89 (1929).

Experimental Photo-Cells

Fig. 1 shows one form of cell employed in the present experiments. Pieces of chemically pure magnesium ribbon, or magnesium turnings, were packed into a small nickel or molybdenum cylinder, usually about 12 mm long and 5 mm in diameter and closed at one end. This was attached to an isolantite heating element through which passed a hairpin tungsten filament. *M* is the cylinder containing the magnesium, with opening at *O*. *A* is a nickel wire loop which

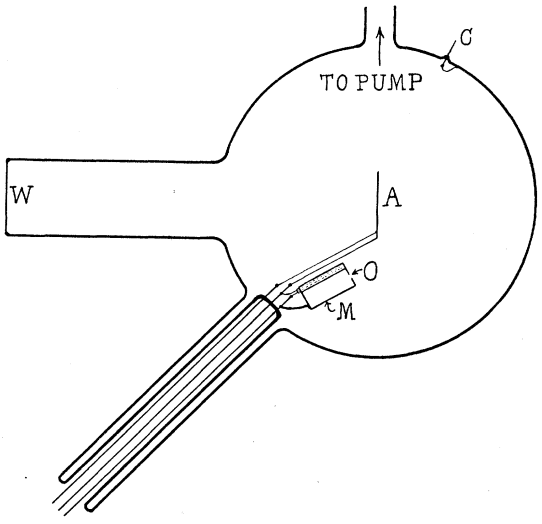

FIG. 1. Experimental photo-cell.

serves as a central anode, and which can be separately heated. *W* is a plane Pyrex window sealed to the bulb, through which light is admitted to the cell. *C* is the cathode lead, and is a tungsten wire sealed through the glass wall and spot welded to a platinum wire which was fused to the inner surface of the bulb for the purpose of making intimate contact with the magnesium coating.

After a cell was sealed on to the pumping system, the metal parts were heated by means of an electric current, and in the later cells, hydrogen was allowed to circulate through the system for about one hour. Each cell was then baked for a period of from 12 to 36 hours in an electric oven at a temperature of 400°C, and evacuated by means of a single stage mercury diffusion pump and Cenco backing pump. Tests for residual gas were made by means of a spark coil, and by observation of the photoelectric emission from the deposited coating. The system contained two liquid air traps and a mercury cut-off in order that a cell could be isolated and observed over a period of several days or weeks.

Magnesium was distilled slowly from the cylinder after the outgassing process was comp'eted, until a heavy mirror coating was deposited upon the Pyrex bulb. All coatings formed in this manner were sensitive to visible light. A spectral response curve was determined for each new surface formed, and the distillation was repeated several times. Sensitivity readings for surfaces which had remained under high vacuum conditions for periods up to fifty hours showed no observable change in the threshold. In some cases the total emission increased slightly with time, finally settling down to a stable value.

Apparatus for Determining Photoelectric Sensitivity

Photocurrents obtained when the magnesium was illuminated by a Mazda test lamp were measured with a Leeds and Northrup galvanometer having a sensitivity of 2.05×10^{-11} amp. per mm. Emission currents obtained with resolved light were measured by means of an FP 54 Pliotron amplifier,[2] a Weston microammeter being used in the plate circuit. The approximate value of unit current on the scale used for most of the photoemission plots in this paper is 1×10^{-13} amp.

A Hilger glass monochromator was used in determining the spectral sensitivity of the magnesium coatings. Light from the linear spiral filament of a 68 watt tungsten lamp was focussed on the collimator slit of the instrument. A slit width of approximately 0.5 mm was used throughout these tests. The energy distribution of the resolved light was determined by means of an improved form of Nichols radiometer.[3]

Long Wave Limit for Magnesium Coatings Deposited in Vacuum

Currents obtained with cell I were originally assumed to be due to impurities on the magnesium surface, a maximum in the total emission plot occurring at 4500A. The results obtained with a second cell, however, were substantially the same, as were those of all subsequent coatings deposited under conditions of a high vacuum in bulbs which had been thoroughly baked and outgassed. The variation in photoemission with wave-length for magnesium coatings deposited in cell II is shown in Fig. 2. Readings of the microammeter in the Pliotron circuit are plotted as ordinates, wave-lengths of resolved light as abscissae. This cell was baked for 36 hours, but was not treated with hydrogen. A window was formed by applying a small flame to the bulb. The long wave limit lies at approximately 5200A.

The second set of emission curves for magnesium coatings deposited in vacuum is given in Fig. 3. Two separate coatings were made with the cell continuously on the pumping system, and in each case the vaporization of the magnesium was allowed to proceed very slowly over a period of from two to three hours. This cell was not given a preliminary hydrogen treatment, and windows were made by flaming the coating from a small area of the bulb. Within the limits of experimental error the long wave limit for these coatings falls at 5100A.

A large number of observations were carried out by using cell V, the construction of which is shown in detail in Fig. 1. Since a side window was provided upon which very little magnesium was

[2] L. A. DuBridge, Phys. Rev. **37**, 392–400 (1931).

[3] B. J. Spence, J.O.S.A. **6**, 625–28 (1922).

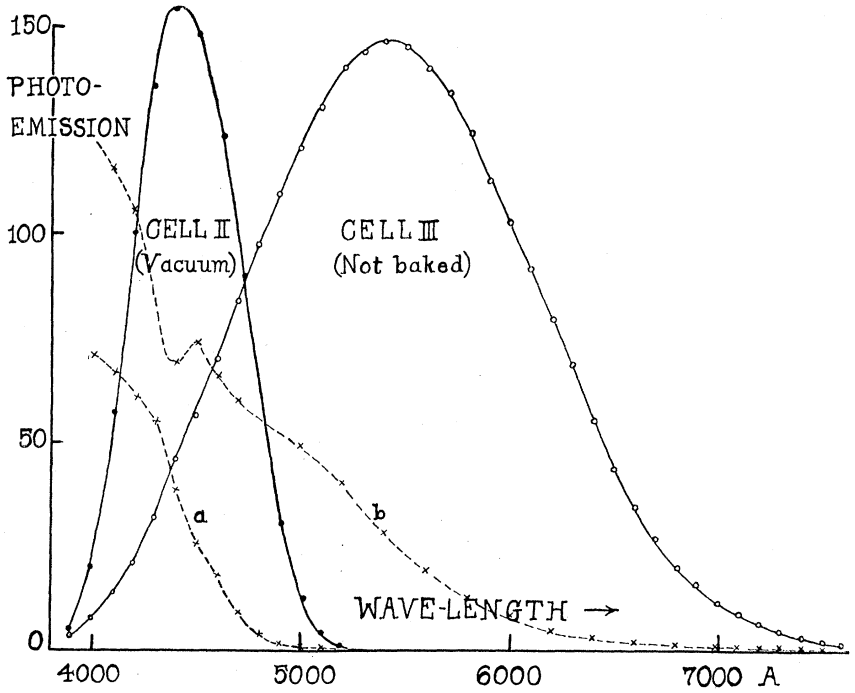

FIG. 2. The solid curves show the total photoemission plotted as a function of the wavelength of light from the monochromator. Curves *a* and *b* are the corresponding emissions per unit of radiant energy.

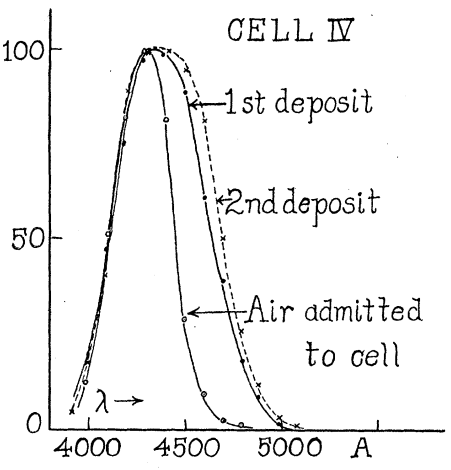

FIG. 3. Total emission curves for two magnesium coatings deposited under conditions of high vacuum, and for one coating after exposure to a small amount of air. The ordinates for these plots, as well as those for Fig. 4, are adjusted to make the maximum readings the same.

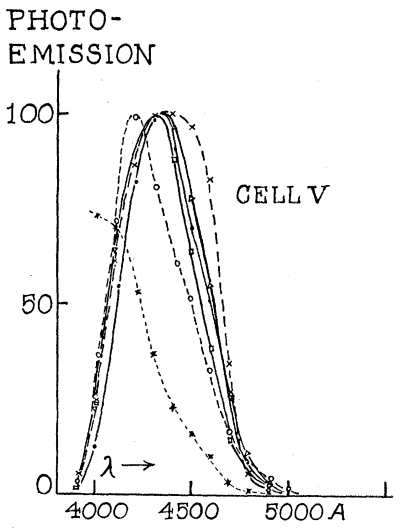

FIG. 4. Total photoemission curves for new coatings in cell V. Dots indicate initial deposit; crosses, two subsequent deposits in vacuum; circles, deposits after air was admitted; triangles and squares, heavy deposits following admission of O_2. The remaining curve shows photoemission per unit radiant energy computed for the initial heavy deposits.

deposited, it was possible to repeat the distillations many times. Spectral response curves were determined for each of six new coatings deposited at intervals while the pumps were in operation, during the course of several weeks of observation. These curves are shown in Fig. 4, ordinates being adjusted so that the value of maximum emission is the same for all. The long wave limit for each of these coatings is approximately 5000A.

It is to be noted that the thresholds for the earlier cells lie some 200A farther to the red end of the spectrum than those for cell V. This discrepancy is larger than the estimated error of measurement, and is probably due to the fact that in the previous cells traces of gas were released when the windows were flamed. On the whole, the measurements taken on ten magnesium coatings are in fair agreement in fixing the long wave limit at about 5100A. Additional information as to the nature of these freshly distilled surfaces is furnished by the tests described in the sections below, which deal with the effect of gases on the photoelectric sensitivity.

Effect of Air on Photosensitivity

That alkali metal surfaces may be sensitized by the application of various gases and vapors has been known since the time of the early experiments by Elster and Geitel. In order to test the possible effects of poor cleaning and evacuation, a cell was made through which hydrogen was not passed, and which was not baked in the electric furnace. After pumping and sealing off the bulb, magnesium was vaporized by heating the cylinder and a heavy coating deposited upon the walls of the tube. A window was formed by flaming a clear spot on the side wall. Tests on the variation of photocurrent with potential showed that the cell was gassy. Fig. 2 shows a spectral response curve for this cell (cell III) with an accelerating potential of 240 volts. Although the long wave limit lies at about 7500A, the efficiency of the cell is very small by comparison to a Cs-Mg gas photo-cell. Duplication of this type of surface by direct application of gases, or by means of glow discharges set up within the cell, has so far been impossible, and it is believed that this extreme sensitization to red light is due to the release of air and possibly water vapor from the unbaked glass walls.

An attempt was made to determine the effect of air upon the sensitivity of the second coating deposited in cell IV. The admission of air at a pressure of less than 0.5 of a micron resulted in an initial increase in the emission, followed by a considerable decrease, and the cell was immediately evacuated by means of the diffusion pump. The spectral response of the coating was then measured, the readings being shown in the third curve of Fig. 3. When air was admitted a second time, the emission fell to a value too small to be detected.

The study was continued by admitting still smaller amounts of air to cell V. The oxygen content of the air was considerably reduced by bubbling it through a solution of pyrogallic acid and potassium hydroxide. The results are shown in Fig. 5.

Curve *A*, of Fig. 5, gives the emission obtained from the second coating of magnesium plotted as a function of the wave-length of incident light. Curve *B* indicates a similar test after air had been admitted and pumped out. Curve *C* shows the increase in emission and in red sensitivity of the coating produced by admitting a second dose

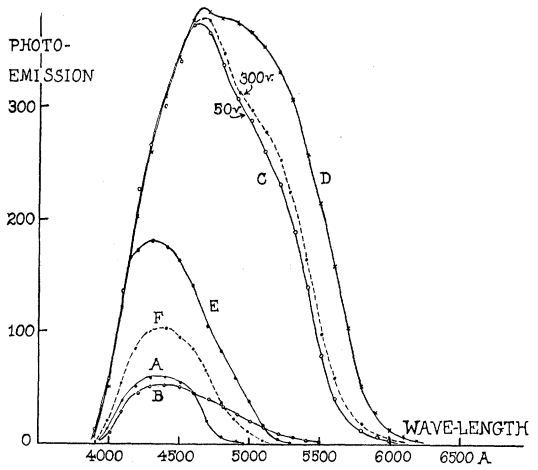

Fig. 5. Sensitization of a magnesium surface by contact with air. Curve *A* shows sensitivity of the coating as deposited in vacuum; *B*, sensitivity after first dose of air; *C*, sensitivity after second dose. *D* shows the effect of depositing a minute amount of magnesium upon the gas contaminated surface, *C*. *E* and *F* show the effects of further heavy magnesium deposits. The amplitudes shown are only rough approximations of the relative response of the various surfaces.

of air and leaving it continuously in contact with the surface for a period of 72 hours. This test was followed by a very slow heating of the magnesium cylinder in an effort to determine the effect of a deposit of a thin film of the metal upon an oxidized undercoating. Curve *D* shows the result of what was regarded as the maximum sensitization procurable by this process. A fourth deposit of the metal resulted in an immediate decrease in total emission, and response curve *E* shows that the long wave limit has shifted from a maximum at 6300A to about 5300A. Further deposits of magnesium in the presence of the residual gas indicated that the new surface was similar to that formed by initial deposits in high vacuum, the long wave limit finally decreasing to 5100A, as shown by curve *F*. The gas pressure likewise was found to be decreasing somewhat during this time, and a glow discharge indicated the presence of nitrogen only within the cell.

Effect of Oxygen on Photosensitivity

The influence of small amounts of oxygen admitted to cell V is shown in the plots of Fig. 6. Curve *A* shows the response for a freshly deposited surface formed after the cell had been thoroughly evacuated following the tests with air. The vacuum system up to the mercury cut-off was flushed several times with thoroughly dried tank oxygen, and the pumps allowed to operate until the pressure was very low on the high vacuum side of the diffusion pump. The mercury cut-off was then lowered, but no effect was observed in the photoemission.

A small amount of oxygen gas at approximately 0.01 mm pressure was trapped in a volume of about 100 cm^3 in the tube joining forevacuum pump and the mercury pump. The diffusion pump was then shut off and the gas allowed to diffuse up to the mercury cut-off. The cut-off was then lowered slightly for an instant, the result being an immediate increase in the photoemission produced by the test lamp. Readings taken with resolved light showed some increase in red sensitivity. A second momentary opening of the cut-off resulted in a three-fold increase in photocurrent, and it was evident that more than enough oxygen had been admitted than that required to give maximum sensitization. The data on the spectral sensitivity produced are given by curve *B* of Fig. 6. The cut-off was permanently lowered, and curve *C* shows the spectral response obtained after the surface had been exposed to the action of the oxygen for a period of 36 hours, after which

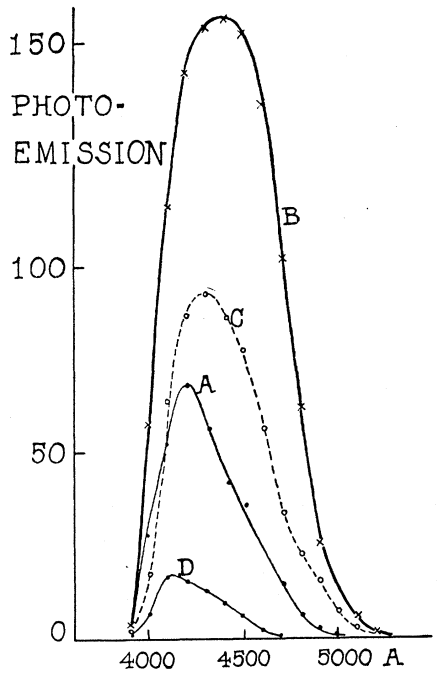

Fig. 6. Effect of O_2 on sensitivity of magnesium coating. *A*, coating deposited in vacuum. Curve *B* shows effect of admitting a trace of O_2; curve *C* indicates the effect of a second dose of gas, while *D* shows the decrease in sensitivity produced by a third treatment.

time spark coil tests showed that the oxygen had been completely cleaned up.

The entire procedure described above was then repeated, the final result being illustrated by curve *D*, the response to visible light now being very small. A third dosage of oxygen lowered the response to visible light to such a point that no emission could be detected. By placing a quartz mercury arc directly in front of the cell window, however, it was found that the oxidized surface responded to emission lines in the ultraviolet which were not absorbed by the Pyrex. A deflection of about 7 mm with the high sensitivity galvanometer was obtained in this manner. It thus appears that an oxidized magnesium surface has a threshold somewhere below 4000A, the

limit of the visible spectrum tests, and above 3650A, the only intense line in the ultraviolet spectrum of mercury that is transmitted by Pyrex. Since further oxidation did not destroy this response to the light from the arc, it seems very probable that the long wave limit for oxidized magnesium is approximately 3800A.

Effect of Nitrogen on Photosensitivity

The cell was evacuated and fresh surfaces of magnesium were deposited following the test with oxygen, plots for these surfaces being included with those shown in Fig. 4. The entire vacuum system up to the cut-off was then washed out several times with nitrogen which had been completely freed of oxygen and dried. Results of the tests with N_2 are shown in Fig. 7. The lower amplitude for curve *B* showing the emission from the surface following the second deposit is due to a slight fogging of the window caused by the vaporized magnesium. Curves *C* and *D* show the results of admitting nitrogen to the photo-cell. Curve *E* is a plot of *B* multiplied by a factor 7.2, and shows that the gas acts merely to amplify the photocurrents, the spectral sensitivity and long wave limit being essentially the same for *D* as for *B*.

When a glow discharge is set up in nitrogen, however, the emitting surface is changed, probably by the formation of magnesium nitride.[4] Another possibility, although a doubtful one, is that the sensitivity at 5100A of a new surface is due to an adsorbed gas layer which is removed by the electric discharge. The spectral response of the surface following this treatment is given by curve *F* of Fig. 8, which shows a shift in the long wave limit from 5000 to 5400A. Additional glowing of the gas did not seem to increase further the sensitivity of the surface, a prolonged and rather heavy discharge eventually destroying the response to visible light. A further investigation of the change in photoelectric properties of magnesium when a glow discharge is set up should be valuable in obtaining information as to the manner in which magnesium cleans up various gases when used as a "getter" in vacuum tubes. (See also Fig. 9.)

[4] Lukirsky and Ptizyn, Zeits. f. Physik **71**, 339–49 (1931).

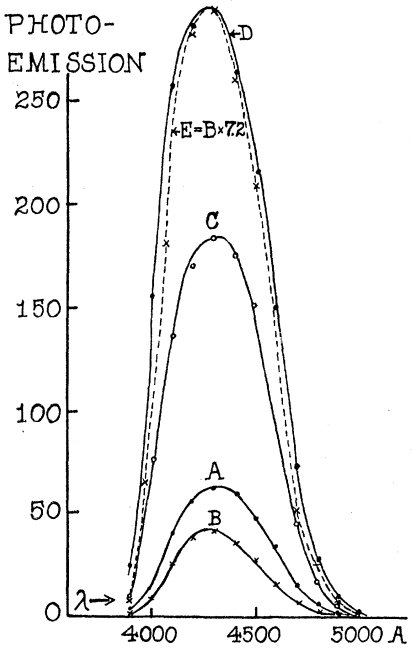

Fig. 7. Effect of nitrogen upon the photosensitivity of magnesium coatings. The long wave limit is not changed when gas is admitted.

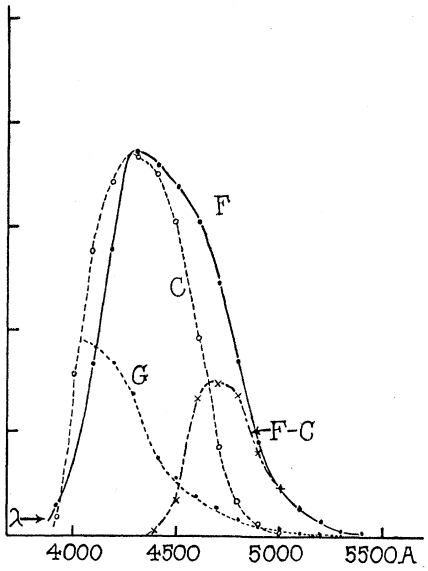

Fig. 8. Curve *F* shows the increase in red sensitivity of magnesium caused by a glow discharge in N_2. *G* is the emission per unit energy corresponding to the total emission curve *F*. *F*−*C* is the difference between *F* and *C*.

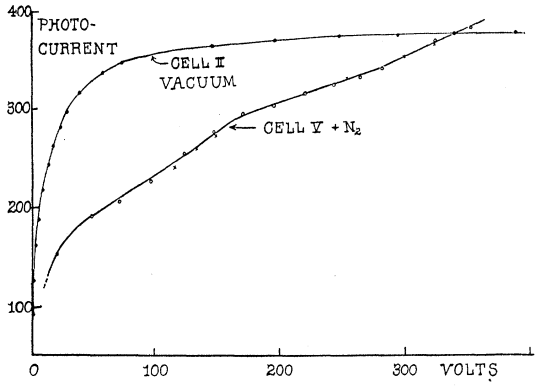

FIG. 9. Current-potential plots for a vacuum cell (II), and for cell V after admitting nitrogen gas.

DISCUSSION OF RESULTS

The deposition of magnesium by careful distillation in a good vacuum, results in a surface which has a long wave limit of approximately 5100A. If the photoelectric properties of such coatings are determined by the formation of a compound surface, or by the adsorption of a gas layer, then these properties might be expected to vary considerably from cell to cell as conditions of heat treatment and evacuation are varied. But within the limit of error of the measurements the same threshold was found for repeated distillations in the same cell, and for new deposits from different magnesium samples in several cells. Moreover, if the active surface layer is one formed of a stable compound the repeated formation of which is not hard to attain, then one should not expect slight additions of O_2, or of active N_2 formed in a glow discharge, to further sensitize the surface as has been found in these experiments.

It is interesting to compare the results of the present experiments with those obtained by other investigators. Pohl and Pringsheim[5] found a continual increase in photosensitiveness of distilled magnesium surfaces with time over a period of 24 hours, the long wave limit in one instance increasing to approximately 7000A. In the present investigation the increase in photoemission under standard test conditions was less than 12 percent over a period of 54 hours in the case of cell V, and there was no appreciable change in the long wave limit while the cell was isolated with liquid air trap between cell and mercury cut-off. Moreover, no decrease in emission was noted in these freshly deposited coatings. Absence of fatigue may be taken as indicating the absence of gas layers on the metal surface.[6] It has been the experience of many investigators that denuding a surface of gas shifts the long wave limit to the red end of the spectrum.[7] Others have shown an initial sensitization to red light, probably due to the adsorption of a monomolecular layer of gas, and an eventual shift of threshold to shorter wave-lengths (or at least a marked decrease in emission) with additional adsorption of gas.[8]

The authors believe their results on the effect of gases are to be explained in terms of the formation of a surface compound of magnesium. If this is true the early results for magnesium metal scraped with a steel tool under vacuum conditions which were obviously poor in all probability gave a long wave limit not characteristic of a clean magnesium surface, but one which is characteristic of magnesium oxide. This contention is of course supported in a definite way by the present tests on the response of an oxidized surface to the radiation from a mercury arc.

Recent reports on the photoelectric properties of magnesium deposited in various ways seem to lend support to the above interpretation, when account is taken of working conditions and methods used. For layers *sputtered* in an atmosphere of inert gas, it is quite certain that the coating formed will contain most, if not all, of the magnesium compounds existing in the original sample. Results obtained by Rentschler, Henry and Smith[9] for magnesium surfaces prepared in this manner indicate a threshold at 3700A in good agreement with that obtained by many observers for the bulk metal scraped in vacuum. Locher,[10] not attempting to work under conditions of a high vacuum, found a long wave limit for MgO on Mg somewhere between 3400

[5] Pohl and Pringsheim, Verh. d. Deutsch. Phys. Ges. **14**, 546 (1912); **15**, 111 (1913).

[6] L. W. Morris, Phys. Rev. **37**, 1263–68 (1931).

[7] R. P. Winch, Phys. Rev. **37**, 1269–75 (1931).

[8] S. Rijanoff, Zeits. f. Physik **71**, 325 (1931).

[9] Rentschler, Henry and Smith, Rev. Sci. Inst. **3**, 794–802 (1932).

[10] Locher, Phys. Rev. **42**, 534 (1932).

and 4000A, again in approximate agreement with the results of previous workers.

When great care is taken to obtain a pure surface in high vacuum, it has been shown by at least two recent observers that magnesium responds to visible radiation. For relatively gas-free magnesium surfaces deposited upon thoroughly outgassed tungsten, Kenty[11] reports a work function of less than 3 volts, or a long wave limit which is greater than 4100A. The threshold was located approximately by the method of filters with quartz mercury lamp as source. De Laszlo[12] has investigated the photoelectric sensitivity of magnesium films deposited on glass from samples of the metal which previously had been distilled in high vacuum. A quartz monochromator was used with a mercury arc as source. His sensitivity curve indicates a long wave limit for magnesium lying somewhere between 4500A and the long wave limit for lithium, which falls well beyond 5000A. He concludes with the statement that the photoelectric efficiency of magnesium is exceptionally high between 2800A and 2400A, and that it would be of practical use as far out as 4000A.

[11] Carl Kenty, Phys. Rev. **43**, 776A (1933).
[12] H. de Laszlo, Phil. Mag. **13**, 1171 (1932).

Conclusion

These experiments on magnesium coatings show that the photoelectric threshold for layers deposited by slow distillation in high vacuum falls in the visible region of the spectrum. The measured long wave limit lies in the range 5000 to 5200A. The formation of a light surface film of magnesium oxide, or nitride, sensitizes the metal to light of longer wave-lengths, a result which has been observed in the case of the alkali metals. With continued oxidation the sensitivity of the coating to visible light decreases, and tests show that for well oxidized magnesium the threshold lies in the neighborhood of 3800A.