STUDIES IN THERMO-LUMINESCENCE.

IV. The Distribution of Light in the Luminescence Spectrum of Sidot Blende.[1]

By C. A. Pierce.

Introductory.

THE characteristic decay curve of phosphorescent substances is well known. If $1 \div \sqrt{I}$ is plotted as ordinates with t as abscissæ, the decay curve appears to consist of two straight lines, of different slopes, which gradually merge into one another. One of the early explanations of the decay of phosphorescence was that by H. Becquerel, who assumed that phosphorescence light was due to molecular vibrations which were set up by the exciting light. It was shown by him that, if the damping forces were proportional to the square of the molecular speed, the decay curve, in the case of a substance which had but one band in its phosphorescence spectrum, would be of the form[2]

$$I = \frac{1}{(a + bt)^2}.$$

For substances which have more than one band, Becquerel proposed for the law of decay of the total light,

$$I = \Sigma \frac{1}{(a + bt)^2}.$$

Using $1 \div \sqrt{I}$ and t as coördinates, the first law gives a straight line curve, while the second law gives a more complicated curve.

Working with a single substance, Sidot blende, Nichols and Merritt showed[3] that the spectrum did not change its form during the first three or four seconds of decay. The measurements were made

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[1] This is a continuation of a preceding article which appeared in the Physical Review, Vol. XXX., No. 6, June, 1910, p. 663.

[2] Comptes Rendus, Vol. 113, p. 618, 1891.

[3] Phys. Rev., Vol. XXI., No. 4, Oct., 1905, p. 247.

upon the one broad bright band of the spectrum. If there were other bands in the spectrum, they decayed too rapidly to be measured.

Later the same authors studied[1] the decay of the same substance at different wave-lengths and found the decay in each case to follow the straight line law for the first ten seconds, although the slopes of the several lines were different, indicating a difference in the rapidity of decay.

Still later the same authors studied[2] the decay of the total band and found the curve to consist of two straight lines, of different slopes, which gradually merged into one another.

In an article[3] on thermo-luminescence, the author of the present article showed that Becquerel's law for the decay of light consisting of two bands represented the decay of the total band, as found by Nichols and Merritt, as closely as could be expected. By assuming that a change of temperature affected the decay of one of the hypothetical bands more than the other, the data on decay curves at different temperatures were accurately explained by the same law. In another article[4] by the present writer, the same law was used to explain the so-called hysteresis effect, which is due to the previous history of the phosphorescent substance.

Since the typical decay curve is always more complex than a single straight line, it is necessary to assume more than one band taking part in the decay in order to apply Becquerel's law. This led to the suggestion in the article above that, if there were always two bands, one might be due to some secondary effect. The assumption of more than one band is in contradiction to the data obtained by Nichols and Merritt, which indicated that the band did not change its shape with decay, but they did not study the band late enough in the decay to be certain that it did not change at the time the decay curve exhibited the typical bending. Their data upon decay curves corresponding to different wave-lengths offer no evidence for or against the existence of two bands, for while the straight line decay found at each wave-length seems to contra-

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[1] PHYS. REV., Vol. XXII., No. 5, May, 1906, p. 279.

[2] PHYS. REV., Vol. XXIII., No. 1, July, 1906, p. 37.

[3] PHYS. REV., Vol. XXVI., No. 4, April, 1908, p. 312.

[4] PHYS. REV., Vol. XXVI., No. 6, June, 1908, p. 454.

ct this view, the different slopes of the straight lines are in agreement with it. The symmetrical smooth-sided band showed in the article preceding this would indicate that, if it were composed of two bands, they must be nearly of equal size.

More recently, in a theoretical article,[1] E. Merritt has considered the effect of different factors upon the form of the decay curve. It was shown by him that absorption of light by the phosphorescent material and irregularities in the distribution of the active component of the powder would explain part of the deviation of the typical decay curve from a straight line, but he decided that the two effects were not of sufficient moment to explain all of the deviation. Complex molecular grouping would account for the whole change. The author stated, however, that no data were available which definitely contradicted Becquerel's law, although several objections could be raised to it.

The present article and the one preceding it were undertaken to provide data with which to prove or disprove the two-band theory of phosphorescence decay. The work is based on the assumption that the typical decay curve is represented accurately by the summation of two straight-line decay curves. It has been suggested that the decay curve in its earliest parts is not in accordance with such an assumption, but recent data[2] by C. A. Zeller would seem to definitely prove the fallacy of these suggestions. The straight-line component parts of the typical decay curve differ widely in slope. Hence, on the assumption of two bands, most of the light before the bend in the curve is due to the band corresponding to the steeper straight line[3]; at the bend, the light is due more or less equally to both bands; and after the bend, the light is due mostly to the second band. With a method available for studying the light distribution before and after the bend, the two-band explanation would be proved or disproved depending on whether a change was or was not found in the distribution of light.

A method was developed in the first of these two articles with which the energy distribution of fluorescence light could be

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[1] Phys. Rev., Vol. XXVII., No. 5, Nov., 1908, p. 367.

[2] Phys. Rev., Vol. XXXI., No. 4, Oct., 1910, p. 367.

[3] Fig. 3, p. 316, Phys. Rev., Vol. XXVI., No. 4, April, 1908.

studied by photographic means. This method was developed in such a manner as to avoid the assumption that a constant product of intensity of light at any wave-length times the length of exposure would give a constant density on the photographic negative, an assumption which was found not to hold even approximately.

The results of the first part of the work showed that the energy distribution of the fluorescence light of the substance used consisted of one prominent, symmetrical, smooth-sided band with a maximum at about $\mu = 0.55$. The band extended, approximately, from $\mu = 0.46$ to $\mu = 0.60$. Furthermore, the energy distribution immediately after excitation is the same as in the fluorescence light.

The present article is concerned with the light distribution before and after the bend in the decay curve and also with the effect of different temperatures and the effect of infra-radiation upon the fluorescence spectrum.

EXPERIMENTAL.

The method employed to photograph the decaying band of phosphorescence was based on the assumption that the conditions and phenomena could be reproduced indefinitely, a fact practically proven true for the substance under investigation. The phosphorescent powder, except in the case of Fig. 49, was emanations pulver, called by the writer Sidot blende, the same sample of powder having been used in the investigations previously published.

The apparatus was practically that used in the previous investigation, except electrically operated shutters were substituted to excite the powder, to expose the plate and to kill off the remaining phosphorescence with infra-radiations before repeating the excitation. With this apparatus the decay curve could be photographed between any two points time and time again until an impression had been made on the photographic plate. Since, at best, the necessary exposure was very long, varying from a few hours to a much longer time, no attempt was made to deduce the energy distribution, but the photographic spectra were compared with each other, the principle weight being attached to the position of the maximum of the band. The necessary attention was given to obtain negatives of about the same average density and of not too great density so that no complications could result from widely different or complete chemical change of the films at any wave-length. With these precautions, negatives were obtained which showed definite maxima and the results could be repeated as many times as desired.

The distribution of deneseness on the photographic film was measured, at first, with a photometer, as in the previous article, but this method was soon abandoned because of the eye strain induced by comparing very faint fields of light. The apparatus which was substituted consisted of a brightly illuminated slit placed before a very sensitive thermo-couple system. The photographic plate was pushed past the slit by means of a screw calibrated in wave-lengths. Since the deflection of the galvanometer, which measured the current from the thermo-couple, depended upon the length of time that light was allowed to pass through the slit, a pendulum switch was made which would light and turn out the electric lamp, which illuminated the slit, at predetermined intervals. With this apparatus, results were obtained which were consistent with those obtained with the photometer, and the results could be repeated.

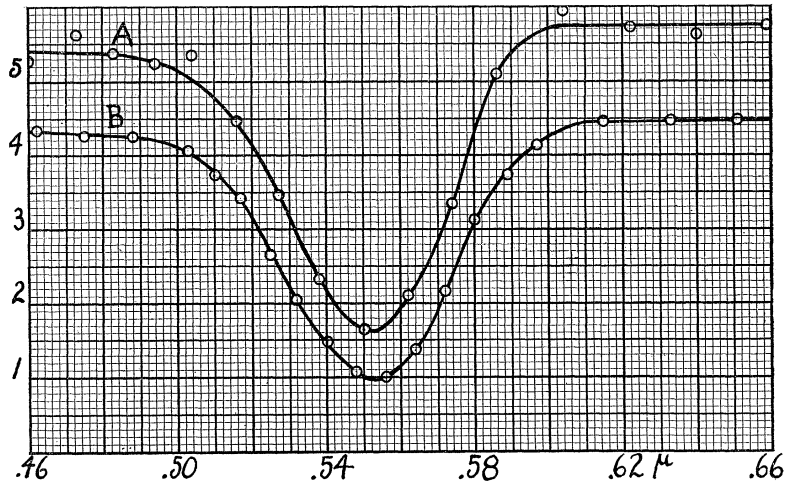

Fig. 47.

Fig. 47 shows the data obtained by measuring a film with the photometer, curve *A*, and with the thermo-couple, curve *B*. In this article all ordinates represent intensities of transmitted light. These two curves are consistent as regards general shape and position of the minima points of the curves. Since intensities of transmitted light are plotted, the minima of the curves correspond to the maxima intensities of the spectra. Inspection will show that curve *B* is not the exact duplicate of curve *A*; the ratios of the ordinates at long wave-lengths are not the same as at shorter wave-lengths. This lack of similarity did not exist in many of the comparisons and was, quite likely, due either to eye fatigue or else to the gradual warming up of the plate under successive exposures to the light which illuminated the slit.

Fig. 48 shows three curves corresponding to the decay of phosphorescence. In curve *A*, the Sidot blende was excited for 9¾ sec. and the plate was exposed for 8½ sec. immediately after excitation. Then the powder was exposed for about one minute to infrared rays and the process repeated. In curve *B* the powder was excited for 21 sec., allowed to decay for 14 sec., then the plate was exposed for 15 sec. In curve *B* the x-axis was raised so that curve *B* would not intersect with curve *A*. In curve *C*, the excitation was 5½ min., the decay 1½ min. and the plate was then exposed for one minute. The total time to produce the negative from which curve *C* was made was 72 hours. The negative was faint and the

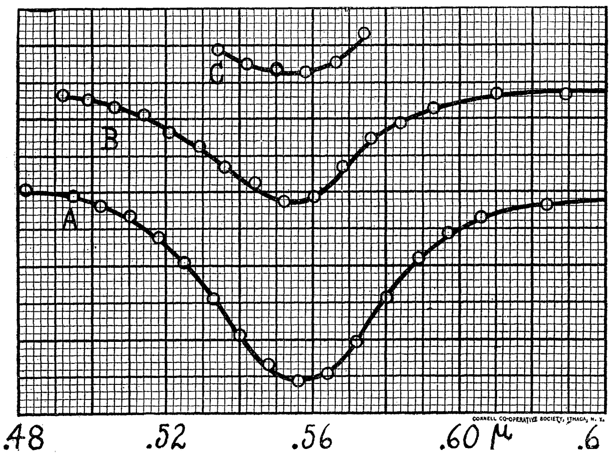

Fig. 48.

film was somewhat fogged, but remeasurements on the film always gave approximately the same curve. In fact, curve *C* is the average of several remeasurements. The minima of these curves occur at wave-length $\mu = 0.555 \pm 0.003$.

The bend in the curve of decay of the phosphorescence of Sidot blende occurs between 10 and 20 sec. after the end of excitation and is more pronounced the longer the excitation. Hence curve *A*, in Fig. 48, is due mostly to the light corresponding to the decay before the bend, while curve *B* corresponds to conditions near the bend, and curve *C* corresponds to conditions far beyond the bend. Or in terms of the two band theory, curve *A* corresponds mainly to band 1; curve 2, to bands 1 and 2; and curve 3 to band 2 almost entirely. This set of curves shows no change in the maxima of the spectra, and no set was obtained which showed any appreciable change.

Because Balmain's paint, a powder on which data for a previous article were obtained, shows a more pronounced bend in the decay curve than Sidot blende, two curves, Fig. 49, were obtained showing the spectrum before and after the bend. For each curve, the excitation was 5 min. For curve *A*, the plate was exposed 20 sec. immediately after excitation. For curve *B*, the phosphorescence was allowed to decay 1½ min., then the plate was exposed for one minute. No shift in the minima of the curves is evident, while a decided shift in the minima or a decided change in the shape of the curves would be expected if the two-band theory is correct.

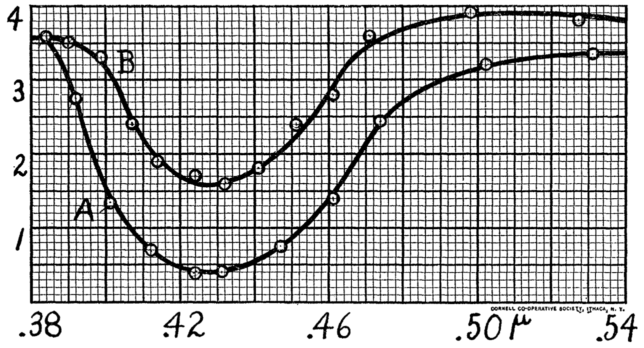

Fig. 49.

The effect of infra-red radiations in suppressing phosphorescence and fluorescence is well known. Nichols and Merritt[1] found that all parts of the fluorescence spectrum were suppressed in the same ratio. As a check on the above work and on the present work, and because, on the basis of the two-band theory, all available data lead to an assumption that one band is suppressed more than the other, several runs were made in which the fluorescence spectrum of Sidot blende under the influence of infra-red rays was photographed. These rays were obtained, as in the whole work, from a 16 c.p. lamp held two inches from the powder. The visible portion of light was screened off by means of thin rubber.

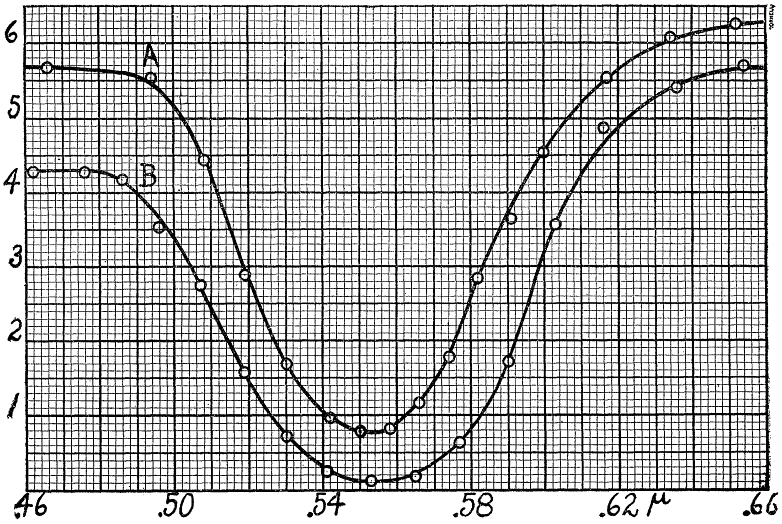

Fig. 50.

In Fig. 50 curve *A* corresponds to the fluorescence spectrum without infra-red excitation, and curve *B*, with infra-red. The exposure of the plate in the latter was twice as long as in the former case. The minimum is not changed appreciably from $\mu = 0.555$, and the curves correspond very well except at short wave-lengths.

In Fig. 51 curve *A* corresponds to the fluorescence spectrum without infra-red; curve *B*, with infra-red; and curve *C* corresponds to the phosphorescence spectrum just after excitation and is added

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[1] Phys. Rev., Vol. XXV., No. 5, Nov., 1907, p. 362.

for ease of comparison. In each case the minimum of the curve occurs at $\mu = 0.555$ approximately.

The only effect of infra-red excitation on the fluorescence spectrum, according to all of the curves obtained, is to decrease the intensity of the band, but not to change its general shape. This result is in accordance with that found by Nichols and Merritt and is not in favor of the two-band theory of decay.

It is known that bands in the spectrum of fluorescent substances grow brighter or die out with changes in the temperature of the substance. This effect is due to the temperature change alone since many of the substances will show normal spectra when the temperature is brought back to normal. Some runs were made to see if any change could be detected in the fluorescence band of Sidot blende at different temperatures higher than normal. It is well known that the phosphorescence decay varies in rapidity with change of temperature and this could be easily explained by means of the two-band theory of decay.

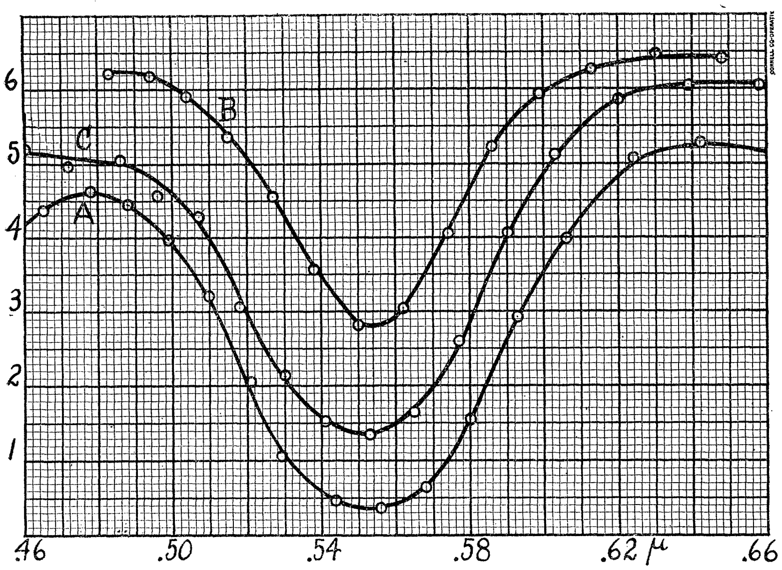

Fig. 51.

Fig. 52 shows four curves corresponding to the fluorescence of Sidot blende at different temperatures. In each case the length of excitation was varied so as to give, approximately, negatives of equal average density, hence the dimming of the band at higher temperatures is not evident, though it occurred, the powder practically ceasing to exhibit fluorescence when the temperature was raised sufficiently. When the temperature was lowered, the powder would again show the same spectrum as before if a certain critical temperature was not reached. The x-axis is changed for each curve so that the points may be entirely distinct from one another. Curves A, B, C and D were obtained at temperatures 22°, 67°, 88° and 120° respectively. No shifting of the minimum is evident.

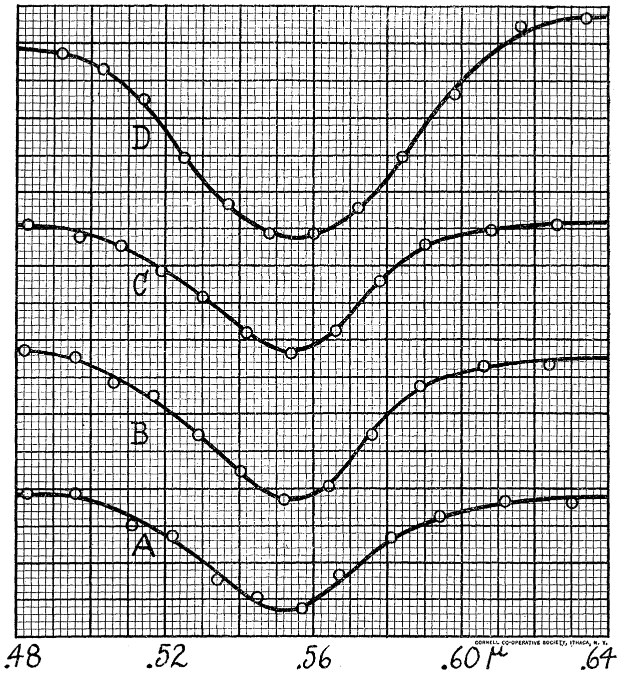

Fig. 52.

Discussion of Results and Conclusions.

The accuracy of measurements made with a non-direct method, as the one above, is not great. Conclusions must be drawn from the indications of many runs, rather than from the too exact interpretation of a single run. A general survey of the curves shown will lead to the conclusion that the minima of all of the curves occur within the limits, $\lambda = 0.555\mu \pm 0.003$. These limits were seldom exceeded and the variations were not consistent with each other. For some sets of curves, the limits could be contracted to $\pm 0.002\mu$ or possibly to $\pm 0.001\mu$. Hence, if the maximum of the band changed under any of the conditions it must have been within the limits $\pm 0.003\mu$ and probably within even smaller limits. From certain considerations, such as the bend in the decay curve of phosphorescence, and the smooth symmetrical shape of the whole band, one would expect, if the two-band theory is correct, a considerable change in the band under the conditions studied. No changes were found that were not explained by the limitations of the method.

Hence the following conclusions are drawn from the work above:

1. That the fluorescence and phosphorescence bands of Sidot blende coincide with each other.
2. That no change in the position of the band of phosphorescence occurs with decay.
3. That no change in the position of the band of fluorescence occurs under the action of infra-red rays.
4. That no change in the position of the band of fluorescence occurs with a change in temperature of the powder.
5. That no evident change in the shape of the band was found under the above conditions.
6. That no change in the position or shape of the band of phosphorescence of Balmain's paint occurs with decay.
7. That the two-band theory of the decay of phosphorescence is not sustained.

Physical Laboratory,
Cornell University,
August 22, 1910.