MAY 1, 1931 PHYSICAL REVIEW VOLUME 37

LUMINESCENCE DUE TO RADIOACTIVITY

BY D. H. KABAKJIAN
RANDAL MORGAN LABORATORY OF PHYSICS, UNIVERSITY OF PENNSYLVANIA

(Received March 16, 1931)

ABSTRACT

Results of several investigations on luminescence due to radioactivity carried on under the direction of the author are reviewed. It is shown that these results cannot be explained on the well-known active center theory advanced by Rutherford, or any modification of the same such as that proposed by Walsh. In certain substances, including zinc sulphide, there is an initial rise in brightness of the irradiated samples followed by a decay which cannot be represented by a simple exponential curve. It is also found that the rate of decay of brightness is not strictly proportional to the rate of emission of luminous energy as required by the theory. The observed facts can be explained qualitatively by assuming that the alpha, beta and gamma-rays produce excited molecules in the luminescent material. Return of these molecules to their initial state of more stable equilibrium results in emission of luminous energy. The rays also affect the transmission coefficient of the materials, and the apparent decay of brightness is explained as due to the increased absorption of light by the material itself, rather than to the destruction of the hypothetical active centers. This is evidenced also by the fact that in the materials studied, heating the samples usually restores the initial brightness. Quantitative application of these suggestions to the experimental curves was not possible, since the nature of the change in light absorption coefficients resulting from irradiation is not definitely determined.

LUMINESCENCE of certain chemical compounds under the excitation of rays from radioactive substances has been studied by various investigators and theories have been advanced to explain the gradual decay of brightness in these materials.

Rutherford in 1910[1] advanced a theory to explain Marsden's observations on the decay of brightness of phosphorescent zinc sulphide under the action of alpha rays from radon and its decay products. According to his theory, which we shall call the active center theory, phosphorescent zinc sulphide contains initially a number of molecular aggregates known as active centers. Passage of alpha-rays through the compound destroys a number of these active centers resulting in flashes of light known as scintillations. Active centers once destroyed cannot be reformed and since the number of such centers hit by an alpha-ray would be proportional to the number present at any time, the brightness of the compound for a given steady source of radiation should decay in accordance with a simple exponential law.

Chemically pure zinc sulphide does not exhibit this phenomenon to any great extent. The presence of a small quantity of some foreign element such as copper or manganese seems necessary to obtain a maximum effect. This fact lends force to the active center theory since the molecules of foreign matter might act as nuclei for such aggregations.

---

[1] E. Rutherford, Proc. Roy. Soc. **83A**, 561 (1909–10).

The theory has the virtue of extreme simplicity but none of the subsequent investigators have been able to obtain a simple exponential decay curve of brightness in such compounds, especially when the measurements extended over a considerable period of time. Therefore various modifications have been suggested, from time to time, to make the original theory conform to the observed facts.

Patterson, Walsh and Higgins[2] found that the theory in its simple form did not agree with their measurements of brightness of luminous paints extending over 450 days. There was a distinct slowing up of the rate of decay as time went on, which could be explained if it was assumed that the active centers were capable of recovery in accordance with an exponential law.

In a more recent article Walsh[3] gives additional data on the decay of brightness of luminous paints. The paints consisted of mixtures of zinc sulphide and radium bromide. Measurements of brightness extended over 4000 days.

In this article Walsh, after reviewing various theories advanced on the subject, comes to the conclusion that Rutherford's original theory agrees with his and others' results if the absorption of light by the luminous material itself is taken into consideration.

It is a well-known fact that many transparent substances are colored by the rays from radium. Zinc sulphide used in luminous paints is also colored gradually and its absorption for light progressively increased.

In combining this factor of light absorption with Rutherford's simple theory, Walsh finds, however, that the observed values of brightness agree better with the modified theory if the change in transmission constant of the material due to ionization of inactive centers be put equal to zero; i.e., if the increased absorption be considered as resulting from the destruction of active centers only.

This conclusion can not be justified unless it can be shown that the transmission constant of nonluminescent (inactive) zinc sulphide remains unchanged by the passage through it of ionizing rays. This, however, is not the case. A qualitative test made in this laboratory showed that a film of chemically pure zinc sulphide, exposed to alpha-rays from radium for a short time, is distinctly colored with resulting increase in absorption constant, although practically nonluminescent. Therefore even if in a luminescent compound the ratio of inactive molecules to active ones may be considered small at the start, evidently this ratio is constantly increasing due to the transformation of active molecules to inactive ones as required by the theory. And since these undergo a similar change in transmission constant, their effect on the decay of brightness cannot be neglected in the final analysis.

A number of researches on luminescence due to radio-activity have been carried on in this laboratory. An attempt to explain the results of these observations on the active center theory, with such modifications as have been suggested, was unsuccessful.

---

[2] Patterson, Walsh and Higgins, Proc. Phys. Soc. Lond. **19**, 215 (1916–7).

[3] J. T. Walsh, Proc. Phys. Soc. Lond. **39**, 318 (1926–27).

Karrer and Kabakjian[4] showed that mixtures of radium bromide and barium bromide acquired the property of luminescing with an intense bluish light by simply heating the compounds to a suitable temperature and then cooling. The luminescence decayed in time but could be completely regenerated by heating the compound to the original temperature. Addition of foreign substances was not necessary in this case. In fact addition of minute quantities of copper or manganese seemed to reduce the brightness.

Rodman[5] investigated the decay of brightness of pure radium bromide, and also of some mixtures of radium bromide and barium bromide. Two points were brought out in her paper. First that the decay of brightness did not conform to a simple exponential law. Second, that although the decay was very rapid at the start, the curve representing the brightness became finally parallel to the time axis, giving a constant value of brightness which was not zero. Both of these facts are at variance with the active center theory.

For example, the brightness of pure radium bromide decayed to about one percent of its initial value in 24 hours. It reached a constant value in about 300 hours and did not show a measurable variation in the following 200 hours.

Smith[6] investigated the luminescence of pure barium bromide exposed to alpha, beta and gamma-rays. In his case the source of the rays and the luminescent material were kept separate so that it was possible to observe the variation of brightness from the start. Smith's results showed an initial rise in brightness of barium bromide on exposure to the rays from radium. This rise continued for several hours reaching a maximum value and then decaying to a final constant value.

It is quite evident that Smith's results cannot be explained by the active center theory which fails to account for the initial rise in brightness. The final approach of brightness to a constant value instead of zero is also in agreement with Rodman's results.

Since the original active center theory was formulated by Rutherford to explain the decay of luminescence in zinc sulphide, it was considered desirable to investigate this compound by a similar method.

Gessner[7] undertook this investigation by means of an improved type of apparatus. The constant source of rays was well separated from the luminescent material and the apparatus so arranged that readings of brightness could be taken within two minutes after the exposure.

The results obtained by Gessner were similar to those of Smith. In every case there was an initial rise in brightness, followed by a decay which was not exponential. Neither did any part of the curves conform to the modified theory developed by Walsh.

This initial rise in brightness of zinc sulphide was also observed by Marsden for beta-ray excitation, but no attempt was made to explain this fact in formulating the active center theory.

[4] E. Karrer and D. H. Kabakjian, Jour. Frank. Inst. **186**, 317 (1918).

[5] J. Rodman, Phys. Rev. **23**, 478 (1924).

[6] L. E. Smith, Phys. Rev. **28**, 431 (1926).

[7] G. S. Gessner, Phys. Rev. **36**, 207 (1930).

Since the alpha-rays produce individual scintillations, while the beta-rays produce more or less diffuse illumination, it may be assumed that the mechanism of light emission is different for the two rays. Chariton and Lea[8] have found, however, that scintillations similar to those produced by alpha-rays can be obtained from beta-rays under favorable conditions, showing clearly that the only difference between the two types of excitations is the energy carried by the individual rays.

That the rise observed in Gessner's samples was not due to beta-rays was evidenced by the fact that a polonium plate used to excite the compound gave the same type of brightness curve.

In attempting to check Walsh's latest explanation on the decay of zinc sulphide paints, Gessner had used thin films of zinc sulphide and a more intense source of radiation, hoping thereby to accelerate the rate of decay. The brightness of his samples were uniformly greater than those of Walsh. If the emission of light results from destruction of active centers, evidently these were being destroyed at a greater rate, and since the volume of the material used, and presumably the initial number of active centers was very small, one would expect the brightness of these samples to decay much faster than those of Walsh. The results were quite the opposite. Walsh's brightest sample (Sample *H*, initial brightness 0.28 candles per square meter) shows a decay of over 85 percent in 400 days whereas one of Gessner's samples (Sample 4, Maximum brightness 0.4 candles per square meter) shows a decay of less than 50 percent for the same interval. This disagreement with the theory can hardly be explained by possible differences in the materials used by the two investigators.

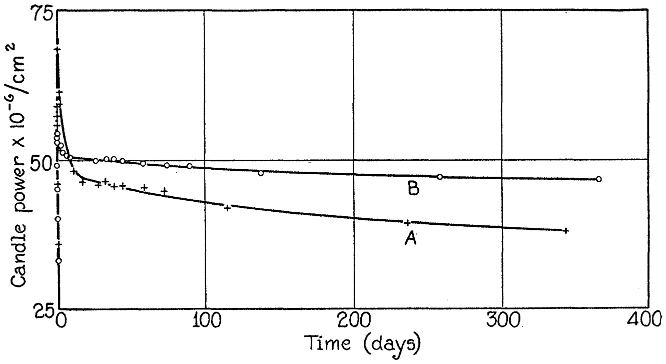

Fig. 1. Curves showing the decay of brightness in zinc sulphide. *A*, alpha, beta and gamma-rays from radium. *B*, beta and gamma-rays. Thickness of material, 0.022 cm.

It was also found that in the same material of approximately the same thickness the rate of decay was not in direct proportion to the rate of emission of light but depended on the nature of exiciting rays.

Fig. 1* illustrates this point. Although the total amount of light emitted

---

[8] J. Chariton and C. A. Lea, Proc. Roy. Soc. **A122,** 335 (1929).

* Curves represented in Fig. 1 and Fig. 2 were obtained by Mr. Gessner. For apparatus and the method of measurement, refer to his article, Phys. Rev. **36,** 207 (1930).

by sample B, due chiefly to beta-ray excitation is greater than that from sample A where alpha-ray excitation predominates, the rate of decay of brightness is in the reverse order. Assuming that the mechanism of light emission is the same for the two types of radiation this difference in the rates of decay of the two samples cannot be explained on the active center theory.

Another check on the theory could be obtained by estimating the number of active centers in zinc sulphide from the data given in Fig. 1, on the assumptions made by Walsh in estimating the number of active centers in his samples.

By integrating the area under curve A, the total amount of luminous flux produced in a quantity of zinc sulphide having a thickness of 0.022 cm and an area of one square cm can be computed from the formula

$$F = \frac{4\pi a I}{1 - e^{-0.022a}}$$

where F is flux in lumens; I is brightness in candles/cm^2; and a is the coefficient of absorption of freshly prepared zinc sulphide.

Taking the value of a as 32 and the mechanical equivalent of light for the wave-length emitted as 660 lumens per watt, the amount of luminous energy radiated by this sample during the first 350 days is roughly equal to 1.5×10^{10} ergs.

If N is the number of active centers destroyed during this interval of time and if it be assumed that each active center emits, on destruction, one quantum of energy corresponding to a wave-length of 550mμ, the total amount of energy radiated by the destruction of N active centers will be equal to $N \cdot 3 \cdot 6 \times 10^{-12}$ ergs. Equating this with the above expression we have

$$N = \frac{1 \cdot 5 \times 10^{10}}{3 \cdot 6 \times 10^{-12}} = 4.16 \times 10^{21}.$$

But the number of molecules in this quantity of zinc sulphide is approximately 5.5×10^{20}. Therefore the number of active centers destroyed in this sample during the first 350 days comes out more than 7 times the number of molecules present. Since the brightness of the sample has decayed to 56 percent of its maximum value and the rate of decay has become very much slower it must be assumed that the original number of active centers present is many times the number of molecules present in the material if the active centers once destroyed cannot be regenerated.

The active center theory of luminescence, therefore, seems inadequate to explain, among other things:

(1) The initial rise in brightness of all the samples investigated;
(2) The difference in the rate of decay of brightness in luminescent material for alpha and beta-ray excitations;
(3) The general nature of brightness decay curves.

In view of these facts it seems more reasonable to assume that the passage of the rays through luminescent materials results, not in destruction of any hypothetical active centers, but rather in producing excited molecules which emit light on returning to their normal energy levels. As this is a reversible change this phenomenon can continue indefinitely.

The rays may also produce a certain amount of ionization or dissociation resulting in a more stable change such as coloration, due to the inability of the ions to recombine at ordinary room temperatures. The two phenomena are not strictly interdependent. It is possible to have coloration with very little luminescence and vice versa.

Light emission by excited molecules can take place in two distinct ways, giving rise to two types of luminescence. If the whole absorbed energy is re-emitted instantaneously, unaffected by the temperature of the absorbing material, the phenomenon is known as fluorescence. If, however, the absorbed energy is re-emitted gradually and the absorption and emission are more or less dependent on the temperature of the absorbing material, the phenomenon is known as phosphorescence. What is known as thermoluminescence is really phosphorescence at higher temperatures.

In this paper the term phosphorescence is used in a general sense without regard to the nature of the exciting rays. Its characteristic feature is the inability of the excited molecules to return at once to their normal state, consequently a phosphorescent material will continue emitting light after the exciting rays have been removed.

If the luminescence produced by alpha, beta and gamma-rays in the investigated materials is of the phosphorescent type, the initial rise in brightness of these samples could be explained. This would mean that all the energy absorbed from the rays is not radiated at once. It can be shown that this is generally true for the materials under discussion. Even in the case of alpha-ray excitation of zinc sulphide a diffuse radiation lasting several minutes follows each scintillation. This can easily be demonstrated by exposing a zinc sulphide screen to a strong source of alpha-rays for a few seconds. When the source is removed the screen will continue to glow in the dark for several minutes, its brightness gradually decaying to zero. It can also be shown that this is due to slow radiation of the energy absorbed from the alpha-rays and not to a possible absorption of its own luminous energy.

At ordinary room temperatures the ratio of energy radiated as diffuse light to that radiated as scintillations is small and has usually been overlooked, but this ratio is dependent on the temperature of the absorbing material. If a zinc sulphide screen in contact with a polonium plate is cooled to the temperature of liquid air its brightness is considerably diminished. When after a few minutes of exposure the polonium plate is removed and the screen is allowed to reach the room temperature, it glows much more brightly, showing that a larger percentage of the energy of the rays is absorbed and retained at the lower temperatures and released only with the aid of heat agitation of the molecules.

These experiments justify us in regarding the absorption and emission of energy by luminescent materials when excited by alpha, beta and gamma-rays, as essentially a phosphorescence phenomenon. If this view is correct then the brightness of these materials, when excited by a constant source of rays should rise to a maximum where the rate of absorption and emission balance each other, and if there is no physical or chemical change in the material, it should remain constant at this value indefinitely. But it is well known that the coefficient of light absorption of these materials increases as a result of irradiation, therefore the brightness must decay in time, not necessarily because of a decrease in the amount of light produced but due to the fact that more and more of it is absorbed by the material itself as time progresses.

Again if the coefficient of absorption never becomes infinite but tends to approach a constant as time approaches infinity, the brightness would never decay to zero.

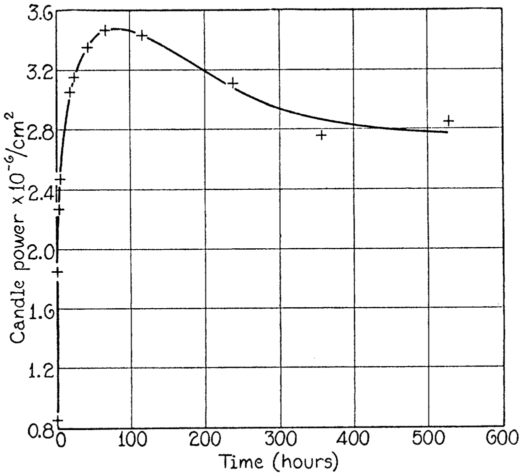

Fig. 2. Luminosity curve. Capsule *A*, beta, gamma-rays. Calcium sulphate Mn activated.

These conclusions are qualitatively in agreement with the observed facts on all materials investigated in this laboratory.

Fig. 2 represents the rise and decay in brightness of a typical thermoluminescent material which is also phosphorescent at ordinary room temperatures. The material consists of crystalline calcium sulphate activated by manganese. It will be noted that the brightness increases in time reaching a maximum in about 70 hours and then begins to decay. The decay curve is not a pure exponential and final brightness will never become zero. The similarity between the characteristics of this curve and those obtained by Smith and Gessner is quite apparent.

The factor controlling the decay of brightness seems to be the change in the transmission constant of the material. In pure barium bromide this change is small and its rate of decay is also small. The final constant value of brightness for samples investigated by Smith varied from 40 percent to 60 percent of their maximum. On the other hand in pure radium bromide, which becomes almost black, the rate of decay is very large and the final constant value of brightness is about 0.1 percent of its maximum. Both radium bromide and barium bromide completely recover their maximum brightness on heating to an adequate temperature. The heating results also in complete disappearance of any coloration.

According to this view luminous paints which have decayed should also regain their brightness if the coloration of the crystals is removed. This was attempted on some samples of zinc sulphide paints which had been allowed to decay for over eleven years in sealed tubes. The paints contained 50 and 100 micrograms of radium element, respectively, per gm of zinc sulphide. On heating the tubes over a bunsen burner the brightness was promptly restored but the degree of restoration could not be determined since no record of the initial brightness of the paint was available. The coloration of the samples disappeared at the same time and their photosensitiveness was also revived.

It is not claimed here that there is no chemical decomposition in the irradiated samples resulting in a decrease of light emission. But it has been shown that an attempt to explain the decay of luminescence as due to disappearance of active centers gives inconsistent results, and since it has been shown that the change in transmission constant plays such an important part in the apparent decay of brightness, a quantitative application of any theory of luminescence becomes difficult until the exact nature of this change is determined experimentally.

It has already been shown that the increase in absorption constant cannot be considered as due to the destruction of hypothetical active centers. On the other hand the curves representing the rise and decay of brightness do not furnish sufficient data to determine the nature of this change. Experiments are under way to determine directly the variation in the transmission constant of some of these materials as a result of irradiation, when a quantitative application of the assumptions made above to the experimental curves will become possible.

If the absorption coefficient a is defined by the expression $I_x/I = e^{-ax}$ where I_x/I is the fraction of light transmitted through thickness x of the absorbing material, it is quite evident that a is a variable quantity in this case, its value depending upon the nature and intensity of the radiation and the time.

$$a = f(R, t).$$

In correcting for the absorption of light by the walls of the glass containers Walsh assumes a transmission factor, due to the coloration of glass, of the form

$$T = e^{-pt}$$

where p is a constant for a given tube and t is the time. This is based on the assumption that the coloration of the glass is produced by the destruction of certain molecules in the glass. On this view the transmission should become zero when t is put equal to infinity. If, however, the coloration of transparent materials is due to ionization of the molecules, such ionization might have a saturation value, in which case the transmission factor would be represented by an expression of the form

$$T = a \cdot e^{-\beta(1-e^{-ct})}$$

where a, b and c are constants for a given material and a given intensity of radiation of one type. In this expression the value of T is never equal to zero. This is more in accordance with the experimental facts. However this may prove to be, it has been shown that experimental results recounted in this paper cannot be satisfactorily explained on the active center theory of luminescence without further modification.

The writer wishes to acknowledge his indebtedness to Mr. Gessner for the use of data obtained by him and to Dr. H. C. Richards and Dr. E. E. Witmer for many valuable suggestions and criticisms during the preparation of this paper.