

Decay of Luminescence and Light Absorption in Phosphorescent Materials

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Effect of continuous irradiation with α , β and γ -rays on the light absorption coefficient of certain phosphorescent materials. With continuous irradiation the light absorption coefficient of each sample reaches a characteristic saturation value which is a function of the intensity of the radiation and the temperature at which the irradiation takes place, but is independent of the variations in

the light emission of the material and also of the total amount of energy absorbed by it. The experimental curves of the rise and decay of phosphorescence and of the changes in light absorption coefficient of these materials cannot be explained by the generally accepted theories of these phenomena.

THEORIES of luminescence produced in certain materials by absorption of various forms of radiation can be classified in two groups: (1) the "excitation" theory which considers the emission of light as due to displacement of electrons and their subsequent return to normal energy levels without any permanent change in the material; and (2) the "destruction" theory which considers the emission of light as resulting from a chemical change and therefore gradual disappearance of luminescent centers in the material. The second theory was adopted to explain the decay of luminescence, in some cases, as a result of continuous irradiation.¹ In the case of scintillations produced by alpha-particles in phosphorescent zinc sulfide Rutherford's destruction theory seems to be generally accepted.² The theory postulates that each active center upon being hit by an alpha-particle is destroyed and emits a flash of light. Hence the brightness of the material, when bombarded by a constant source of alpha-particles, decays exponentially with time. This law of decay, however, is not verified experimentally.

In studying the decay of self-luminous zinc sulfide paints, extending over a period of ten years, Walsh came to the conclusion that the discrepancy between the destruction theory and his experimental curves could be explained if the

change in the light absorption coefficient of the material was taken into consideration. By making certain assumptions as to the nature of light absorption in an irradiated material he succeeded in deriving a theoretical formula which agrees with his curves within the limits of experimental error, thereby apparently confirming the original destruction theory of Rutherford.³

According to this modified theory the destruction of active centers which results in the emission of light, also results in increasing the light absorption coefficient of the material. This assumes a close relationship between the two phenomena, since both result from the destruction of the same active centers, the contribution of the non-active centers to this change being considered as negligible. Also, in correcting for the absorption of the glass containers, Walsh assumes the change in absorption coefficient of glass to follow a simple exponential curve of the type $\tau = \tau_0 e^{-pt}$, where τ is the transmission factor, p a constant depending upon the intensity of the radiation, and t the time.

In a previous paper⁴ attention has been drawn to the inadequacy of this modified destruction theory to explain luminescence phenomena in a number of materials, including zinc sulfide, and doubt was expressed as to the validity of the assumptions on which the theory is based. It will be shown further that the luminescence of these materials is of a complex nature and a simple ex-

¹ *Bulletin of Research Council*, No. 30, pp. 7-27, 1923.

² E. Rutherford, *Proc. Roy. Soc.* **A85**, 561 (1909-10); J. Charitan and C. A. Lea, *Proc. Roy. Soc.* **A122**, 335 (1929).

³ J. T. Walsh, *Proc. Phys. Soc. London* **38**, 318 (1926-27).

⁴ D. H. Kabakjian, *Phys. Rev.* **37**, 1120 (1931).

ponential decay curve cannot be expected except as an approximation.

The coloration of transparent substances resulting from irradiation has been extensively studied but there is no general agreement as to the nature of the phenomenon. In some luminescent substances this coloration is quite intense and would certainly affect the brightness of the samples. The variation of brightness due to this cause alone has never been studied to my knowledge. Therefore it was considered desirable to make an experimental study of this effect and of any relationship that might exist between the brightness decay and progressive changes in the absorption coefficient of a number of substances.

MATERIALS AND METHODS OF PROCEDURE

Several types of glass, some of known composition, furnished by Corning Glass Company, were used for the absorption measurements. Data given in this paper refer to an ordinary microscope slide glass and to one containing 15 percent BaO, 25 percent K₂O, and 60 percent SiO₂ (Corning Glass No. 6). No luminescence measurements were made on these. Both luminescence and absorption measurements were made on crystals of fluorite, calcite, and anhydrous calcium sulfate activated with manganese. The latter was prepared by crystallizing calcium sulfate from a solution in concentrated sulfuric acid. These were cut into more or less transparent plates. Similar measurements were also made on thin films of crystalline powders of willemite and zinc sulfide. The powder was mixed with a dilute solution of Canada balsam and deposited on very thin glass or mica. The thickness of the ZnS films varied from 0.03 to 0.05 mm. Changes in absorption of very thin glass and a small thickness of balsam irradiated with α -rays was found to be negligible.

These materials were exposed to radiation of known intensity and changes in their brightness as well as in their absorption coefficients were made at various intervals of time.

The sources of radiation consisted of films of crystalline radium sulfate applied with a varnish on gold plates. The varnish was thin enough to absorb only a small part of the α -rays. Although there was a slight loss of emanation from the sur-

face, after equilibrium had been reached with the occluded emanation and the short-life products of radium these plates could be considered as constant sources of α , β and γ -rays. The radium contents mentioned in this paper refer to γ -ray determinations of radium C in the plates. For purely α -ray sources, polonium deposits on silver plates were used. A correction for the decay of polonium was made in the computations, by using 136 days as the half-life period of polonium.

Absorption measurements were made with an ordinary Lummer-Brodhun photometer. The transmission of each plate before irradiation and after measured intervals of irradiation were determined, and the absorption coefficient computed from the known thickness of the plates. In the case of powder films, these measurements do not give the absorption coefficient of the material of which the film is made but of the film itself. This was considered sufficient for the present purpose.

Luminosity measurements were made with a special type of photometer somewhat similar to the one described by Meacock and Lambert⁵ for the measurement of luminous paints, with, however, a Lummer-Brodhun cube for comparison of brightness. The photometer was calibrated with a Nutting polarization photometer. This calibration introduces an additional experimental error in the absolute values of the brightness of the samples. It does not affect, however, the relative values of brightness with which I was concerned. The experimental error in these measurements was about 5 percent.

RESULTS

Variation of absorption coefficient

Fig. 1 shows the effect of irradiating with different amounts of radium, ordinary microscope slide glass; Fig. 2, glass containing 15 percent BaO, 25 percent K₂O, and 60 percent SiO₂. It may be seen that in both cases the coefficient of absorption, μ , in cm⁻¹, defined by the relation $I/I_0 = e^{-\mu x}$ (where I/I_0 is the fraction of the light transmitted and x the thickness of the medium in cm), increases with time and approaches a saturation value. It is also quite evident that this

⁵ H. F. Meacock and G. E. V. Lambert, *J. Sci. Inst.* **8**, 214 (1913).

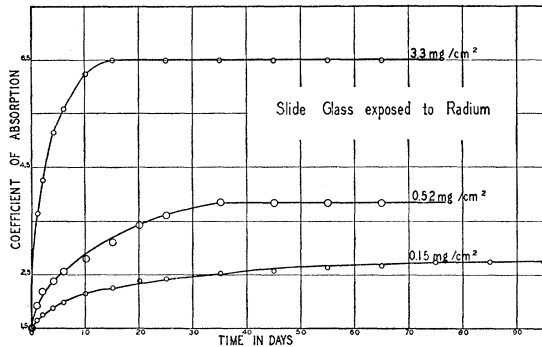


FIG. 1. Change in the coefficient of absorption for samples of ordinary microscope slide glass exposed to 3.3, 0.52, and 0.15 mg/cm² of radium.

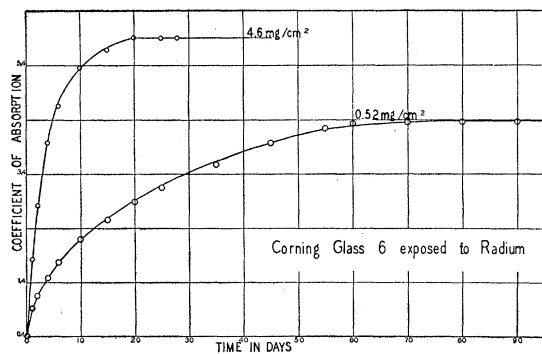


FIG. 2. Change in coefficient of absorption for samples of glass containing 60 percent SiO₂, 25 percent K₂O, and 15 percent BaO when exposed to 4.6 and 0.52 mg/cm² of radium.

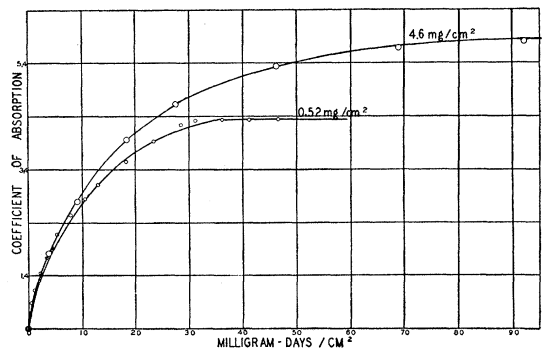


FIG. 3. Same samples as in Fig. 1. Coefficient of absorption plotted against the energy absorbed, the energy being expressed in milligram-days per square centimeter.

saturation value is a function of the intensity of the radiation rather than of the amount of energy absorbed by the material. In Fig. 3 the variation of μ is plotted against the energy absorbed in milligram-days/cm² for one of these samples.

Variation of absorption coefficient of strongly luminescent materials was quite similar to that observed in glass, with different constants characteristic of each material. There was always an initial rapid rise with an approach to a saturation value. An absorption curve for zinc sulfide is shown in Fig. 7.

The effect of temperature

The maximum value of μ in irradiated glass is fairly constant at ordinary room temperature. If, however, the temperature is raised the value of μ decreases reaching different constant values for different temperatures, until at a critical temperature the effect of irradiation completely disappears. Irradiating glass at this temperature does not produce any coloration. Fig. 4A shows

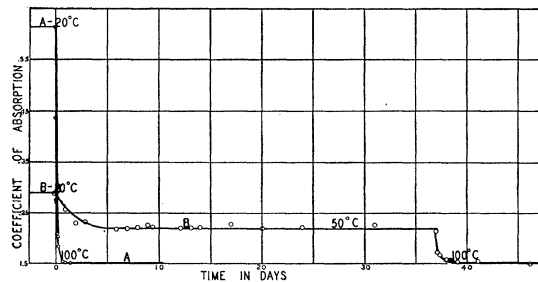


FIG. 4. Effect of temperature on the coloration for two samples of ordinary microscope slide glass. Both were irradiated at 20°C. Before irradiation μ was 1.5. Temperature of sample A was raised to 100°C and kept constant; that of sample B was first 50°C and later 100°C.

the recovery at 100°C and B the recovery first at 50°C and later at 100°C of the transmission of glass which had been irradiated at 20°C. It is seen that both glasses have completely recovered their original transmission. No attempt was made to determine the critical temperature at which complete recovery takes place. Qualitative observations indicate, however, that the critical temperature for recovery is different for different materials and for glasses of different composition.

Brightness decay and light absorption

Simultaneous determinations of change in brightness and in absorption coefficient on the same samples show that these two phenomena are not directly related to each other. In Fig. 5 is

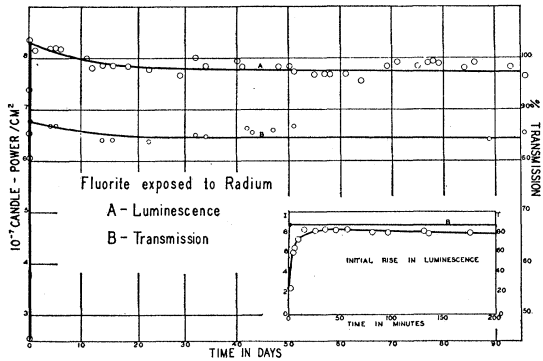


FIG. 5. Luminescence and transmission of a sample of fluorite 0.09 cm thick exposed to 11.7 mg/cm² of radium.

shown the change in luminescence and in transmission for a clear plate of fluorite exposed to radium. There is a very large initial rise in brightness with no corresponding change in the transmission. Fig. 6 shows the rise of brightness in calcite followed by a gradual decay. There was no measurable change in transmission in this case.

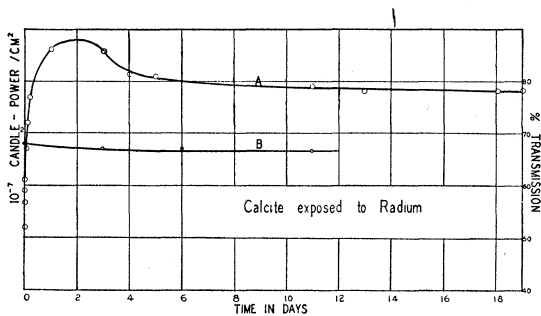


FIG. 6. Luminescence and transmission for a sample of calcite exposed to 11.7 mg/cm² of radium.

Because of the photosensitivity of zinc sulfide, brightness and absorption measurements could not be made on the same plate, as in the case of fluorite and calcite. They were made on two similar plates prepared from the same material and irradiated with approximately equal quantities of polonium. In Fig. 7, curve A represents the

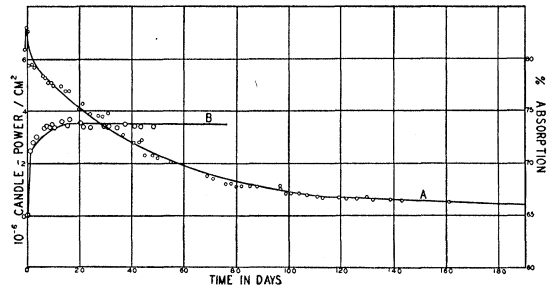


FIG. 7. Luminescence and absorption for a crystalline deposit of ZnS 0.005 cm thick, exposed to polonium.

rise and decay of brightness in zinc sulfide and curve B the increase in its absorption. It is seen that the absorption has reached a saturation value in about 8 days while the decay of luminescence continues over 100 days. Therefore the relationship between the decay of brightness and light absorption assumed by Walsh for this material is not borne out by these observations.

It is possible to check the modified destruction theory in another way. From the curve B, Fig. 7, and the known thickness of the film of zinc sulfide the value of the absorption coefficient for each point on curve A can be determined. It is now possible to plot a luminous flux-time curve, eliminating the effect of absorption. Since the brightness I is given by the relation

$$I = (F/4\pi\mu)(1 - e^{-\mu x}),$$

where F is the flux in lumens per cc, x the thickness, and μ the coefficient of absorption, then

$$F = 4\pi\mu I / (1 - e^{-\mu x}).$$

The variation of flux in time is represented in Fig. 8. This is not a simple exponential curve as required by the destruction theory.

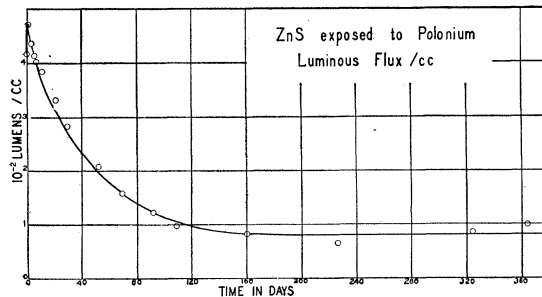


FIG. 8. Same material as Fig. 7. Luminous flux/cc.

Complexity of light emission

It has been observed by several investigators that the light emitted by phosphorescent materials consists of fluorescence and often more than one type of phosphorescence. This in itself precludes the possibility of observing a simple exponential decay curve of brightness. A quantitative determination of the relative importance of these factors in zinc sulfide is rather difficult. A more suitable substance for this purpose is the anhydrous calcium sulfate described above. Fairly transparent plates cut from crystals of this substance when irradiated with rays from radium show fluorescence and phosphorescence to about equal degrees.

A plate of this material was exposed to 4.6 mg/cm² of radium and its brightness measured at successive short intervals. After each measurement the radium was removed and the residual brightness measured immediately. The first set of measurements gives the combined fluorescence and phosphorescence while the second set gives the phosphorescence alone. The difference between the two readings gives the fluorescence. A small correction was necessary for the decay of phosphorescence between the removal of the radium and the measurement of the residual brightness, an interval of about 30 seconds.

In Fig. 9, curve *A* gives the luminescence of such a sample, *B* its phosphorescence, and *C*, which is obtained by subtracting the ordinates of *B* from those of *A*, its fluorescence. The luminescence curve, then, is a composite of a decaying

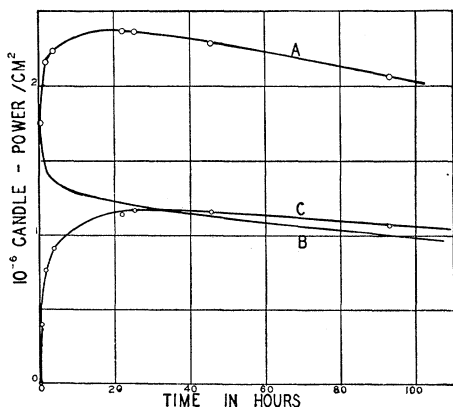


FIG. 9. Plate cut from a crystal of anhydrous calcium sulfate exposed to 4.6 mg/cm² of radium: *A*, luminescence; *B*, fluorescence; *C*, phosphorescence.

fluorescence and a rising phosphorescence curve, both modified by an increase in the absorption coefficient of the material. The luminescence curves shown in Figs. 5–8 are all of the same type with variations which must be attributed to the relative intensities of their fluorescence and phosphorescence factors.

DISCUSSION

Light emission

It has been shown that a simple destruction theory of light emission is inadequate to explain the brightness decay of the materials discussed in this paper even when the change in the absorption coefficient of the material is taken into consideration. Light emission in phosphorescent materials by α , β and γ -rays must therefore be considered as due to excitation. The nature of this excitation is not clear. The curves 5–8 show, however, that the process of light emission does not result in permanent changes such as coloration.

It has been shown in the previous paper⁴ that if each active center cannot be excited more than once, the number of such centers necessary to account for the luminous energy obtainable from a given quantity of zinc sulfide is greater than the number of molecules in the material. The conclusion to be reached is that the emission of light does not destroy the luminescent centers. This conclusion is in agreement with the findings of Wolf and Riehl⁶ that each luminescent center may be excited 1000 to 2000 times before being destroyed.

The curves 5–8 also show that coloration alone does not account for the decay of brightness as was previously suggested by the present writer. A chemical decomposition, not necessarily connected with the process of light emission might be assumed to account for the destruction of the luminescent centers. It has been shown that the coloration reaches a saturation value. Chemical decomposition produced by the rays may be considered a process of the same type and therefore reach sooner or later an equilibrium value. Since these two factors determine the brightness of a continuously irradiated material, its final bright-

⁶ Wolf and Riehl, *Ann. d. Physik* **11**, 103–112 (1931).

ness would not necessarily be zero but would reach a constant value determined by the extent of its coloration and its degree of decomposition. This is in agreement with the experimental observations on a number of materials where complete extinction of brightness was never observed even when the time was made very large.⁷

Light absorption

Examination of absorption curves in Figs. 1-3 shows that no simple explanation such as destruction of molecules of glass or of a limited number of centers due to impurities dissolved in it, is adequate to explain the phenomenon. The first is eliminated by the fact that the curves are not simple exponentials, and the second by the failure of the samples to attain the same saturation value of absorption with different intensities of radiation.

If the coefficient of absorption is considered as proportional to the number N of absorbing centers, and the formation of these centers is similar to ionization and recombination of ions in air, then N would be given by the equation.

$$dN/dt = kR - \alpha N^2,$$

where R is the intensity of radiation and α is the recombination constant of the ions. The solution of this equation is

$$N = C(e^{2\alpha R t} - 1)/(e^{2\alpha R t} + 1).$$

C , the saturation value of the number of absorbing centers, is a function of the intensity of radiation. A theoretical curve from this equation does not agree very closely with the experimental curve. If a limited number of potential absorption centers be assumed to exist in the material, then

$$dN/dt = kR(m - N) - \alpha N^2,$$

where N can never be larger than m . The solution of this is of the form

$$N = C(e^{\beta t} - 1)/(e^{\beta t} + 1 - C/m)$$

where $\beta = [4\alpha kRm + (kR)^2]^{1/2}$. A theoretical curve obtained from this equation agrees well with the experimental curve of absorption. The constants

⁷ J. A. Rodman, Phys. Rev. 23, 4 (1925). Leon E. Smith, Phys. Rev. 28, 3 (1926). G. S. Gessner, Phys. Rev. 36, 2 (1930).

m and C , however, as determined from the curve give a value for C which is larger than m and therefore inconsistent with the original assumption. It is also very difficult to explain on the ionization theory the permanency of coloration in glass at ordinary room temperatures.

Decay of phosphorescence

Similar difficulties are encountered in explaining by some such simple theory the decay of phosphorescence in luminescent materials after the removal of the exciting source. In Fig. 10 the continuous curve represents the decay of phosphorescence in a calcium sulfate plate which had been previously irradiated with 4.6 mg/cm² of radium until maximum brightness was attained.

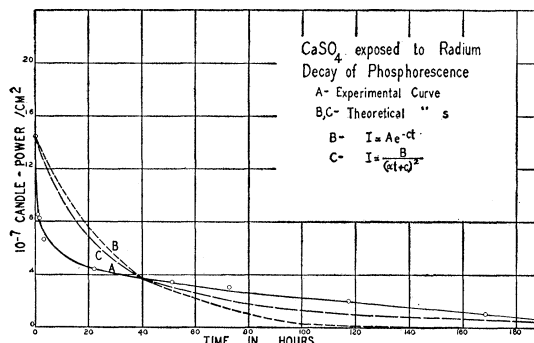


FIG. 10. Decay of phosphorescence for the same sample as in Fig. 9.

If the luminescence is due to excited electrons returning to their normal energy levels, as is usually assumed, the brightness should decay in accordance with the equation⁸ $I = Ae^{-ct}$, where I is the brightness, t the time, and A and c are constants for a given sample. If, however, luminescence results from the recombination of ions, the brightness should decay in accordance with the equation⁸ $I = B/(\alpha t + c)^2$, where B , α , and c are constants for the given sample. Curves corresponding to these two equations of decay are given in dotted lines in Fig. 10. Neither of these agrees even approximately with the experimental curve.

These experiments seem to indicate that in phosphorescent materials irradiated by α , β and γ -rays, light emission, coloration, and chem-

⁸ H. S. Allen, Photo-Electricity, p. 222, 1925.

ical decomposition take place more or less independently of each other and are not easily explainable as simple monomolecular transformations. A number of simple exponentials with different constants might be found to fit each experimental curve. Further investigation, however, seems necessary to determine these and their physical significance.

In conclusion, the author wishes to express his

indebtedness to Miss Sara H. Kehler who made the photometric measurements and to Dr. Horace C. Richards for assistance and criticism of the work, also to Corning Glass Company who furnished the glass specimens. This investigation was made possible by a special grant of the Faculty Research Committee of the University of Pennsylvania which is hereby gratefully acknowledged.