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Properties of a $CaSO_4$: Mn Phosphor under Vacuum Ultraviolet Excitation

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The properties of a manganese-activated $CaSO_4$ phosphor were investigated in connection with its use as a detector of extreme ultraviolet solar radiation in upper atmosphere research. The luminescence of particular interest was a long-period phosphorescence which is excited by wavelengths in the range 1350A to gamma-rays. The energy stored in the phosphor after exposure to short ultraviolet was released by heating and measured by means of a photomultiplier. The stored energy was given by the integrated multiplier response and was independent of the form of the heating cycle. It was also nearly independent of the exposure temperature (-30 to $+70$°C) and humidity. There was a useful exposure range of 10^4 over which the stored energy was directly proportional to the exposure intensity and time; for higher exposures, saturation set in. The excitation spectrum of the stored energy was measured and the maximum quantum efficiency (5 to 10 percent) was found to lie at 1030A. At room temperature, the long-period phosphorescence decay was of the hyperbolic type. Fluorescence in addition to phosphorescence was excited by wavelengths shorter than 1350A, and an additional excitation band of fluorescence only was found in the region 1400–1600A. The emission spectrum extended from 4480 to 5790A.

INTRODUCTION

WIEDEMANN and Schmidt[1] observed that when a $CaSO_4$ phosphor activated with a few percent of $MnSO_4$ was exposed to a condensed spark in air at a distance of a few centimeters and then heated to about 200°C, a green thermoluminescence was given off. Since the interposition of a plate of fluorite prevented the effect, they concluded that the exitation of the phosphor was not due to the ultraviolet component of the spark but to a special radiation, which they named "Entladungsstrahlen." Hoffmann[2] continued the experiment but was not able to establish the nature of this radiation. Later, Laird[3] suggested that the effect was due to x-rays from the spark and not to ultraviolet rays of wavelength longer than 1000A. Lyman[4] prepared the phosphor by Hoffmann's method and showed that its spectral sensitivity began abruptly at 1300A and extended at least to 140A. He also demonstrated that it was radiation in the region of partial transparency of air, 100–1300A, that was Wiedemann's "Entladungsstrahlen." Recently, the phosphor was used by Purcell, Tousey, and Watanabe[5] to detect extreme ultraviolet and x-rays from the sun at high altitudes in the earth's atmosphere by mounting samples on V-2 rockets and exposing them to sunlight during flight.

PREPARATION OF SAMPLES

In our first experiments, the phosphor was prepared by the process described by Hoffmann.[2] A little $MnSO_4$ was mixed thoroughly with a paste of $CaSO_4$ (analytical reagent by Mallinckrodt) and water. The mixture was evaporated to dryness, heated to redness for several minutes, and ground to a fine powder after cooling. The most efficient phosphor was obtained by mixing the sulfates in dilute sulfuric acid, letting the mixture stand for a few hours, evaporating it to dryness, and heating the residue to redness. The powder thus obtained was very nearly white, and its sensitivity was five to ten times that of samples prepared by the method of Hoffmann. Lyman's observation[4] that the exact amount of manganous sulfate is not important was confirmed for samples containing from 0.2 to 17 percent $MnSO_4$. Phosphor strips were prepared by pressing the power into 100 mesh nickel screens.

APPARATUS AND EXPERIMENTAL CONDITIONS

The luminescence of the phosphor was measured with a 1P21 photomultiplier tube. The photocurrent was further amplified by an RCA Ultrasensitive Microammeter, type WV84A; and the amplified current was fed into a recorder. The total emission in arbitrary units was obtained by integrating the recorder trace. Usually, the phosphor strip was clamped between two electrodes at a fixed position 1.8 cm from the surface of the photomultiplier tube and heated by the current from a 2.5-volt filament transformer. The time of heating was between 2 and 5 minutes depending on the setting of a Variac connected to the transformer. For a strip 0.4 inch wide, a current of 8 amperes was required to heat the strip to about 200°C.

The sensitivity of the photomultiplier and amplifier system was checked periodically by use of a self-luminous radium phosphor button as a standard light source. Since each group of measurements extended over only a few days, possible deterioration of the button could be neglected. The sensitivity of the particular tube used when operated at 100 volts per dynode was 4.4×10^4 amp per watt at 5140A; and as ordinarily used, the photomultiplier current ranged from 10^{-5} to 10 microamperes.

For measuring the spectral response of the phosphor to extreme ultraviolet radiation, a vacuum grating

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[1] E. Wiedemann and G. C. Schmidt, Wied. Ann. **54**, 604 (1895).
[2] M. W. Hoffmann, Wied. Ann. **60**, 269 (1897).
[3] E. R. Laird, Phys. Rev. **30**, 293 (1910).
[4] T. Lyman, Phys. Rev. **48**, 149 (1935).
[5] Purcell, Tousey, and Watanabe, Phys. Rev. **76**, 165 (1949).

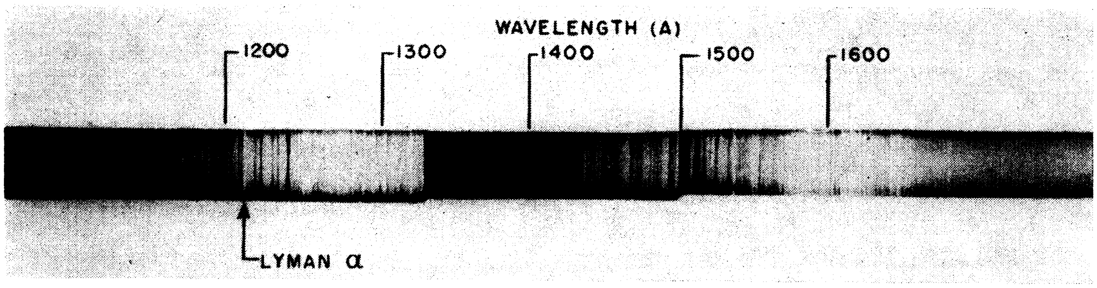

FIG. 1. Composite photograph of the hydrogen spectrum emitted by an Allen-type hydrogen arc with a LiF window. An exposure time of 16 sec was used for the region below 1330A and of one sec for the region above 1330A.

monochromator[6] and a high intensity hydrogen discharge tube source with open window were used. The radiation intensity emerging from the exit slit was known from measurements made with a thermocouple.[7] The wavelength range covered extended from 900 to 2500A.

The study of many of the optical properties of the phosphor did not require monochromatic radiation and was done in the open air with a hydrogen discharge tube with a LiF window. This was possible because of the transparency of air in the region of Lyman alpha, which was first pointed out by Hopfield[8] and later shown by Ladenburg, Van Voorhis, and Boyce[9] to extend from 1100 to 1300A.

The hydrogen discharge tube with a LiF window used as radiation source was of the type described by Allen and Franklin[10] and was constructed by Nestor of the Bartol Foundation. Figure 1 represents a spectrum of the radiation from this source obtained with a vacuum spectrograph. The many-lined spectrum of H_2 extends to 1630A, and the H_2 continuum continues from there to longer wavelengths. Because of the absorption of the LiF window, the intensity falls off rapidly below 1150A.

The region of the spectrum between 1100 and 1300A emerging from the window of the discharge tube penetrated several centimeters of laboratory air with sufficient intensity; however, it was necessary to know something about the dependence of intensity on the air path and on the composition of the air. The wavelengths of the main absorption bands of the common gases in air are fairly well known, but data on their absorption coefficients are meager or inaccurate. Preston[11] has obtained the following values of the absorption coefficients in cm^{-1} at 1216A: oxygen$=0.28$, nitrogen <0.0005, carbon dioxide$=2.01$, and water vapor about 390 (all values given in base e and reduced to NTP). These values appear to be the most reliable ones in this region.

The dependence of intensity on air path was investigated semiquantitatively in a simple manner. A phosphor sample was placed in front of the hydrogen discharge tube so that the air path between the strip and the window of the tube was x cm, and after a given exposure the stored energy E was measured. The light source within the tube was considered as a point, since its dimensions were small compared with its distance, D, from the phosphor strip. The departure from the inverse square law relation between E and x gave the attenuation of air. Data for air containing water vapor at 10.0–10.8 mm Hg partial pressure are shown in Fig. 2. The "effective absorption coefficients" obtained from the slope of this curve are about 4.2 and 1.8 cm^{-1} at $x=0$ and $x=2$ cm, respectively. Preston's value for the absorption coefficient of water vapor (at 1216A) gives 5.3 cm^{-1} as the absorption coefficient (at 1216A)

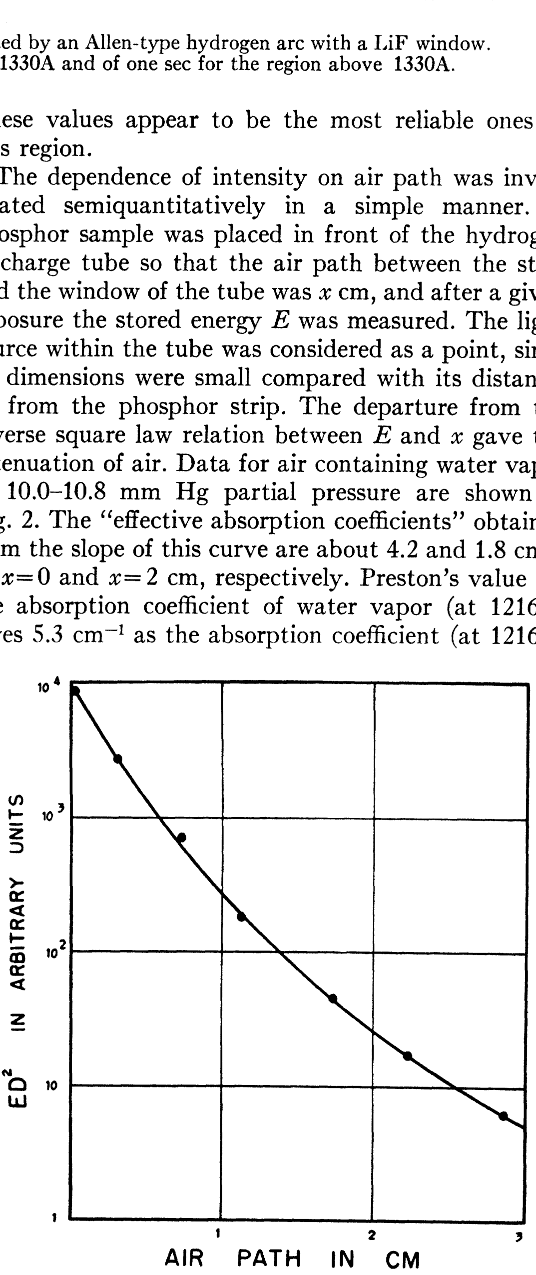

FIG. 2. Attenuation by air of the radiation in the Lyman alpha-region emitted by the Allen-type source. E is the radiation intensity at the phosphor surface, and D is the distance between the "point" source and the phosphor surface.

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[6] Tousey, Johnson, Richardson, and Toran, J. Opt. Soc. Am. **40**, 264 (1950).

[7] D. M. Packer and C. Lock, J. Opt. Soc. Am. **40**, 264 (1950).

[8] J. J. Hopfield, Phys. Rev. **20**, 587 (1922).

[9] Ladenburg, Van Voorhis, and Boyce, Phys. Rev. **40**, 1018 (1932).

[10] A. J. Allen and R. G. Franklin, J. Opt. Soc. Am. **29**, 453 (1939).

[11] W. M. Preston, Phys. Rev. **57**, 887 (1940).

of air containing water vapor whose partial pressure is 10 mm Hg. Since other wavelengths were included in the experimental measurement, the agreement was considered good. Similar experiments showed that, when a 2 cm air path was used, the response of the phosphor varied by as much as a factor of two under seemingly identical conditions but at different times. This can be accounted for by variation in absolute humidity. However, by placing the phosphor strip directly in contact with the window during exposure, it was possible to minimize the effect of water vapor.

PROPERTIES OF THE PHOSPHOR

(a) Spectral Sensitivity

To determine the spectral region to which the calcium sulfate phosphor is sensitive, Lyman placed a copper strip coated with the phosphor in a vacuum spectrograph in the place usually occupied by a photographic plate and exposed it to the spectrum from a hydrogen discharge tube for about eight hours. The strip was withdrawn, placed a mm in front of a photographic plate, and heated. The resulting thermoluminescence was thus recorded on the photographic plate. From this experiment and by visual observations, he found that the sensitivity of the phosphor began quite abruptly at 1300A. In order to determine whether our phosphor had the same long wavelength limit of sensitivity, Lyman's experiment was repeated. In addition to the spectrum from 1100 to 1300A, there appeared a trace of response in the region near 1600A. Thus, the phosphor as prepared by us was not completely insensitive to radiation of wavelengths longer than 1300A, but the sensitivity was very low and was estimated at about 10^{-3} of that in the region 1100–1300A.

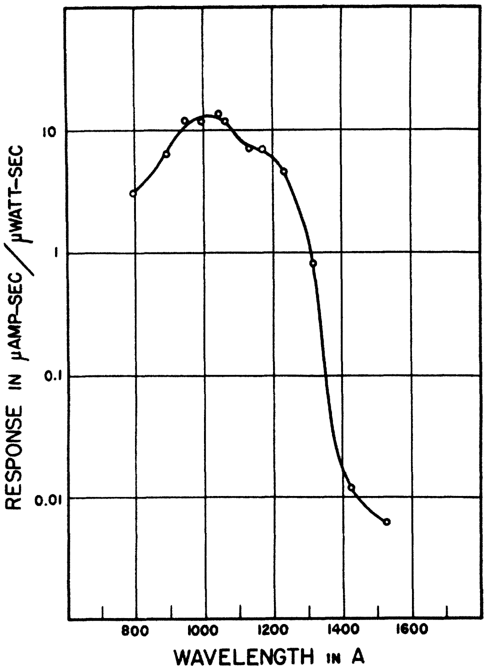

FIG. 3. Spectral sensitivity of the $CaSO_4$:Mn phosphor with respect to thermoluminescent energy. The spectral energy of the radiation producing excitation of the phosphor was measured in microwatt-sec by a thermocouple, and the stored energy was given by the integrated output of a photomultiplier in microamp-sec.

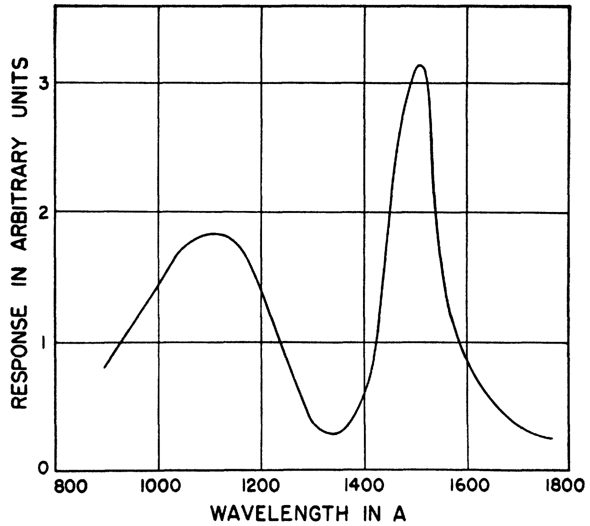

FIG. 4. Response of the $CaSO_4$:Mn phsphor with respect to fluorescence as a function of excitation wavelength.

A direct measurement of the absolute spectral response of the phosphor was made from 900 to 2500A by means of the vacuum monochromator and the high intensity hydrogen discharge tube. The phosphor sample was mounted in vacuum about two millimeters behind the exit slit and exposed to a band width of 14A for 5 to 90 sec, keeping the exposure within the linear portion of the stored energy curve. The exposed strip was removed, and its total thermoluminescence was measured with the photomultiplier-recorder system. The responses of the phosphor for several wavelengths were then compared with the values of the absolute spectral intensity measured by Packer and Lock.[7] Since the energy available below 900A was too small to be measured with the thermocouple, a value for 800A was estimated from the response of a photomultiplier coated with anthracene, making use of the fact that anthracene exhibits constant quantum efficiency[12] at least down to 900A.

The spectral response for one sample is shown in Fig. 3 and is expressed in microamp-sec of integrated photomultiplier current per microwatt-sec of incident radiation. There is a maximum in response at about 1030A and the response drops to 10^{-3} of the peak value at 1422A. The variation in sensitivity at 1050A for five different samples was 13 percent. The quantum efficiency of the phosphor at the peak was estimated to be about 5–10 percent.

An intense fluorescence was emitted by the phosphor

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[12] Watanabe, Johnson, and Tousey, Phys. Rev. **79**, 217 (1950).

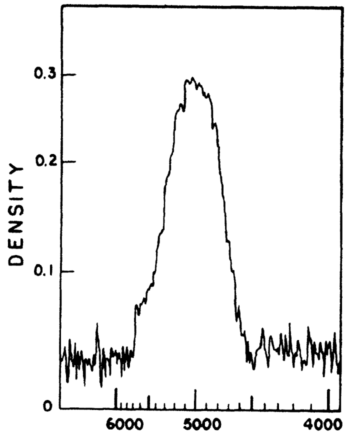

FIG. 5. Microphotometer trace of the emission (thermoluminescence) spectrum of $CaSO_4$:Mn phosphor after extreme-UV excitation.

while it was being exposed to the extreme ultraviolet. To study the dependence of fluorescence on wavelength, a 1P21 coated with the phosphor was placed about an inch behind the exit slit of the monochromator and the spectrum was scanned at the rate of 100A per minute. It was found that the fluorescence was so much stronger than the phosphorescence that the latter could be neglected for the scanning speed used.

Figure 4 represents the relative quantum efficiency of fluorescence response as a function of wavelength. The band at the shorter wavelength is broader than the corresponding thermoluminescence band of Fig. 3 and is displaced a little from it. There is, in addition, a strong excitation band centered at 1500A, and this has not been reported previously.

Laird,[3] and Wick and Slattery[13] have studied the $CaSO_4$:Mn phosphor under x-ray excitation. Preliminary experiments by us indicated that an x-ray tube with a beryllium window using 30 milliamperes at 3 kilovolts was about as effective as the Allen-type hydrogen discharge tube operating at 1.2 amp. It was also found that a one-minute exposure to gamma-rays from a 5-mg radium source at 3 cm produced a barely observable thermoluminescence.

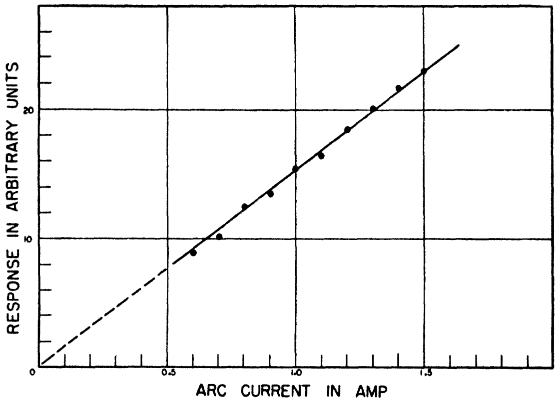

FIG. 6. Total energy stored in the $CaSO_4$:Mn phosphor after a one-minute exposure to the hydrogen arc as a function of the arc current. The intensity of the arc spectrum was known to vary directly with the arc current.

(b) Emission Spectrum

The emission spectrum of the calcium sulfate phosphor excited by wavelengths 1100–1300A was photographed with a Gaertner quartz spectrograph by charging a sample and discharging it thirty times in front of the slit, which was 0.1 mm wide. The band extended over the range 4480 to 5790A, and the microphotometer trace (see Fig. 5) placed the maximum at 5020A.

The emission spectrum of $CaSO_4$ and 0.1 percent $MnSO_4$ excited by cathode rays was studied by Tanaka,[14] who used a Hilger spectrophotometer; and the maximum emission was found to lie at 5050A. Also using cathode-ray excitation, Randall[15] found the maximum at 4975A for the emission band which extended from 4600 to 5800A. A comparison of his microphotometer trace and the one shown in Fig. 5 indicated that the spectral distribution of the band does not appear to vary radically with the mode of excitation.

(c) Thermoluminescence Independent of Heating Cycle

It was hoped that the area under the luminescence trace drawn by the recording photometer would not depend greatly on the way the phosphor was heated and so could be taken as a simple measure of the total ultraviolet energy absorbed by the phosphor. To investigate this, a phosphor strip was given a 30-second exposure to the hydrogen arc, and the thermoluminescence released by heating was measured one minute after exposure. This was repeated with the heating cycle changed in a variety of ways. The area under the recorder trace was found to be constant to within 5 percent of the mean value for 20 different heating cycles.

(d) Dependence of Stored Energy on Exposure Intensity and Time

Several methods were available for reducing the intensity of radiation falling on the phosphor strip: (1) the phosphor could be placed at different distances from the source; (2) plates of LiF with ground surfaces and aluminum foils with many uniformly distributed pinholes could be sandwiched between the window of the discharge tube and the phosphor, leaving no air space; and (3) the arc current could be reduced. Method (1) would require a vacuum. The second method is a very convenient one to use when it is not necessary to know exactly the factor by which the intensity is reduced. The reproducibility of results justified the use of this simple arrangement. The third method was made

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[13] F. G. Wick and M. K. Slattery, J. Opt. Soc. Am. **14**, 125 (1927); **16**, 398 (1928).

[14] T. Tanaka, J. Opt. Soc. Am. **8**, 287 (1924).

[15] J. T. Randall, Proc. Roy. Soc. (London) **A170**, 272 (1938).

possible by the fact that thermocouple measurements showed that the radiation intensity in the region 1100–1300A was directly proportional to the arc current. By this method, the intensity could be varied by an accurately known factor up to 3 and the combination of methods (2) and (3) permitted covering a wide range of radiation intensity.

The dependence of the phosphor response on intensity was measured by reducing the intensity by method (3) and is shown in Fig. 6. The intensity level was kept below the point at which saturation was found to commence (30 units—Fig. 6). It is reasonable to believe that linearity is maintained at intensities lower than those used. This could not be checked by this method because the arc became unstable for current less than 0.5 amp.

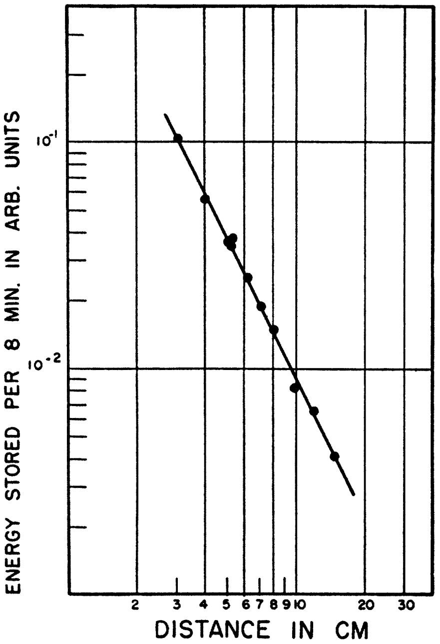

FIG. 7. Linearity of the total stored energy under gamma-ray excitation. The slope of the straight line is -2 in agreement with the intensity reduction according to the inverse square of the distance.

As an additional check, the dependence of response on intensity was investigated using a gamma-ray source consisting of 5 mg of radium placed in a Lucite cylinder. A phosphor sample was placed at distances varying between 3 and 15 cm from the source and the thermoluminescence was measured after an 8 minute exposure. Figure 7 shows that the points fall on a straight line of slope -2, and it was concluded that the stored energy was directly proportional to the intensity over a range of at least 25 for gamma-rays.

To study the amount of stored energy as a function of exposure time, a phosphor sample was pressed against the window of the discharge tube and given different exposures. As summarized in Fig. 8, the total stored energy, as measured by the total thermoluminescent emission, at first increased linearly with time and then gradually approached saturation when subjected to constant intensity of radiation. Curve V represents the case when no intensity reducer was used, and for the other curves filters of increasing opacity were interposed. For upper-atmosphere solar-radiation measurements, energies of the order one to two decades less than the lowest value in Fig. 8 were involved. At such low levels, there was no question of saturation effects and the response was strictly linear with exposure time.

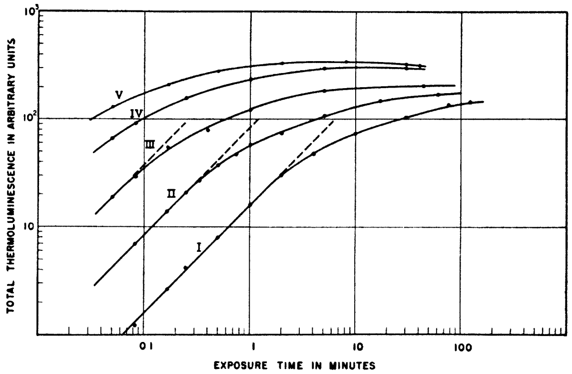

FIG. 8. Total energy stored in the CaSO₄:Mn phosphor as a function of exposure time for different exposure intensities. The broken lines have unit slopes.

(e) Sensitivity Independent of Exposure Temperature and Humidity

A phosphor strip, to which a copper-constantan thermocouple was attached, was pressed against the window of the hydrogen arc and the intensity of radiation was reduced by method 2. To lower the temperature, dry ice was used; and to raise it, electrical current was passed through the strip, which was padded sufficiently to prevent air circulation. When the temperature became constant, the strip received an exposure of one minute, was quickly brought to room temperature, and the thermoluminescence was measured one minute

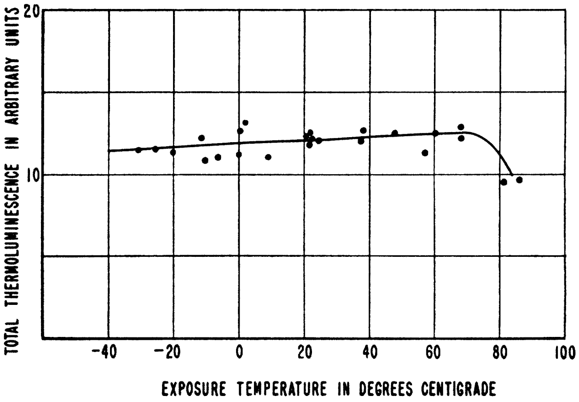

FIG. 9. Sensitivity of the CaSO₄:Mn phosphor as a function of the temperature during exposure.

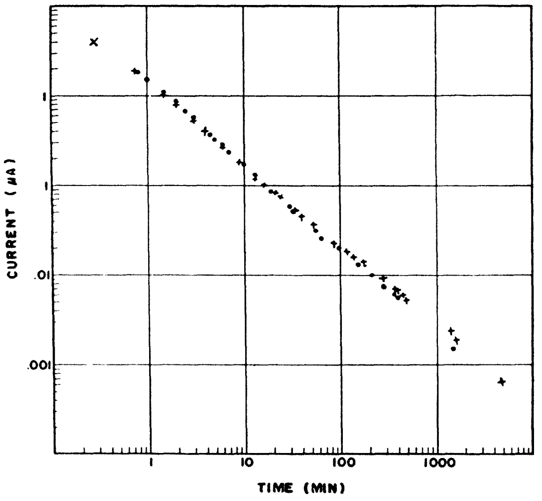

FIG. 10. Decay of phosphorescence of the $CaSO_4$:Mn phosphor at 25°C after extreme-UV excitation.

after exposure. For several reasons, the error was somewhat high; however, the experimental values were consistent and are shown in Fig. 9.

Since calcium sulfate is hygroscopic, tests were also made to study the effect of moisture on its sensitivity. A few samples were dipped in water after they had been irradiated with extreme ultraviolet radiation and allowed to dry at room temperature. Other samples were dipped in water, left standing at room temperature until they appeared dry, and then irradiated. Both sets of samples when discharged showed no appreciable reduction in their sensitivity.

(f) Decay

The energy stored by the phosphor is emitted as visible luminescence at a rate which depends on the temperature. The rate at 0°C is so low as to be unimportant, but at 20°C it is no longer negligible. At 250°C the energy is entirely emitted in two or three minutes under the usual conditions of measurement.

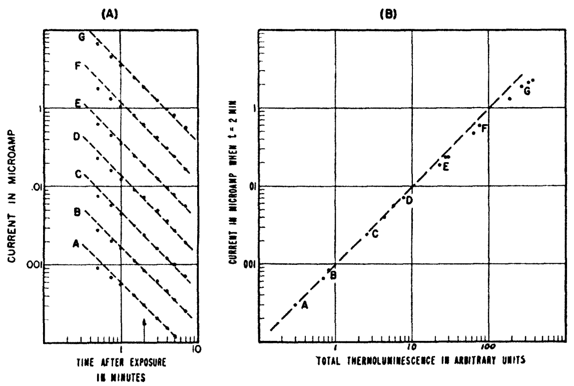

FIG. 11. (A) Decay of phosphorescence for different initially-stored energy, E_0. Slopes of the broken lines are -1. (B) Linearity of brightness of phosphorescence with E_0. The abscissa is E_0 and the ordinate is the brightness as measured by a photomultiplier.

The intensity of phosphorescence at room temperature (25°±1.5°C) as a function of time after exposure is shown in Fig. 10 for two runs with the same sample. It can be seen that the slope of the curve is very nearly minus one for times from 1 to 60 min. The average for eight decay curves was -1.01. For times greater than one hour the absolute value of the slope diminishes gradually.

A portion of the decay curve was studied for different intensities in order to determine whether the slope of the decay curve depended on the total exposure. The arc current, exposure time, and filters were varied so as to subject a given sample to a wide range of exposure intensity. The decay at room temperature during the first eight minutes was recorded, and immediately thereafter the remaining thermoluminescent energy was discharged by heating and was likewise recorded. Figure 11(A), in which the luminescence at room temperature is plotted against time, shows that the slope of the decay curve during the first eight minutes is independent of the exposure. Other experiments showed that this conclusion holds for times considerably greater than eight minutes.

The next question investigated was whether or not the intensity at any point on the decay curve was proportional to the initially stored energy, E_0. The energy E_0 was calculated by integration of the luminescence curves from $t=0$ to $t=8$ min and addition of the total thermoluminescent energies measured directly at $t=8$ by heating the phosphor. These data are plotted in Fig. 11(B) with the intensity of luminescence, I, at $t=2$ min as ordinates. The points lettered A, B, C, etc., refer to the respective curves of Fig. 11(A). The broken line has unit slope and corresponds to direct proportionality between I and E_0. Over most of the range I is directly proportional to E_0, but for large exposures there is a departure.

As a result of these data, it is possible to describe the decay approximately by the empirical equation,

$$I=E_0F(T)/(a+t), \tag{1}$$

where I is the intensity of phosphorescence, E_0 is the total emission (or exposure), $F(T)$ is an unknown function of phosphor temperature during decay, t is the time in minutes after exposure, and a is a constant introduced to fit the decay curve for $t<2$ min and is about 0.22 min.

Equation (1) was found to agree with the individual measurements to within 5 percent for t between 10 sec and 10 min; no measurements were made for $t<10$ sec. Additional data will be required to specialize the form of the function $F(T)$; qualitative experiments showed that $F(T)$ varies faster than T.

The phosphorescence decay law derived theoretically for a uniform electron trap distribution is given by[16] the equation

$$I = nkT/t(1-e^{-st}), \tag{2}$$

where I = intensity of emission, n = total number of electrons in the trap, k = Boltzmann's constant, T = temperature in degrees Kelvin, t = time in sec, and s is the frequency factor in sec^{-1}. This equation was found unsatisfactory, since constant a is not negligible and $F(T)$ does not appear proportional to T.

The residual thermoluminescent energy E was given approximately by the equation

$$E = E_0 - \int_0^t I dt, \tag{3}$$

provided T was constant during the experiment. This is exemplified by the upper curve in Fig. 12, in which E is plotted against t. That Eq. (3) is true was proved by the fact that the negative slope of the upper curve of Fig. 12, when plotted against time, gave a decay curve (I *versus* t) similar to that plotted in Fig. 10.

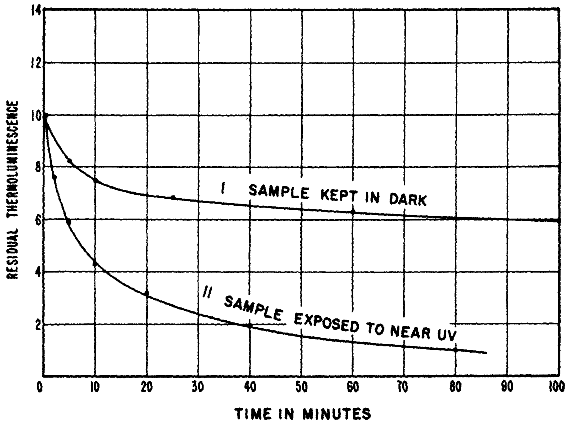

FIG. 12. Effect of near-UV radiation on the decay of energy stored in the CaSO$_4$:Mn phosphor. Both curves were obtained with the same phosphor sample.

(g) Stimulation by Near Ultraviolet

Wiedemann and Schmidt[1] found that the thermoluminescence of the calcium sulfate phosphor, when excited by cathode rays, was "quenched" by exposure to ordinary light and concluded that this was due to infrared radiation. However, for a calcium sulfate phosphor irradiated by x-rays, Wick and Slattery[13] found that the "quenching" was due to the near ultraviolet rays 2000–2400A and not to infrared. According to present usage, the term quenching should be replaced by stimulation. Our experiments confirmed the results of Wick and Slattery.

The effect of stimulation by near ultraviolet is shown in Fig. 12. The residual thermoluminescent energy of a sample which was kept in the dark for different durations after it received a standard exposure from the hydrogen arc was measured and plotted as curve I. In the second run, the same sample and procedure were used except that the phosphor, instead of being kept in the dark after exposure, was allowed to receive the radiation from the hydrogen arc covered with a Corning filter number 791 transmitting no wavelengths below about 2200A. Thus stimulation by near ultraviolet radiation was quite effective (see curve II).

In Fig. 12, let E_0 be the initially stored energy, which is identical for curves I and II, E_1 be the residual energy at time t for curve I, and E_2 be the residual energy at the same t for curve II. Then the ratio $(E_0-E_2)/(E_0-E_1)$ was constant for all values of t within the range measured. For the case shown, the near ultraviolet stimulation hastened the rate of emission by a factor of 2.3.

(h) Effect of Impurities

The calcium sulfate used in preparing our phosphor contained possibly as much as 0.2 percent magnesium and alkali salts and less than 0.005 percent of heavier metals. In order to determine whether the impurities might be contributing to the thermoluminescent property of the material, phosphors of magnesium sulfate, sodium sulfate, and potassium sulfate activated with manganese were prepared and tested for spectral sensitivity and efficiency. Their sensitivity was found to extend to wavelengths longer than 1300A, and the long wavelength limits were in the neighborhood of 2000A. Their efficiencies were considerably less than that of calcium sulfate. The presence of these elements as impurities in the CaSO$_4$:Mn phosphor may account for its feeble response at wavelengths greater than 1300A.

CONCLUSION

The manganese-activated CaSO$_4$ phosphor can be used satisfactorily as a measuring device for extreme ultraviolet radiation. Its lack of sensitivity to radiation of wavelengths above 1350A makes it rather unique among radiation detectors. Its response is linear over a useful range of 10^4 in intensity. The use of the phosphor for measuring from a rocket the intensities in the extreme ultraviolet spectrum of sunlight has been successful and will be described in a later paper.

The author is indebted to Dr. Richard Tousey and Mr. J. D. Purcell for helpful discussions and to Mr. F. S. Johnson for the spectrum of the hydrogen discharge tube.

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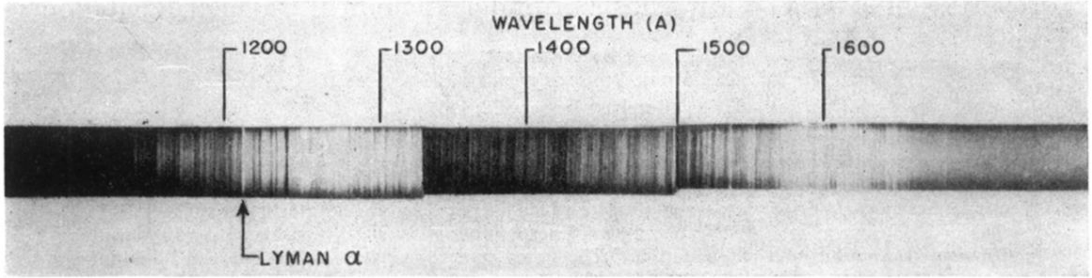
[16] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 390 (1945).



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