

reported Q -values. For Be^9 only the one level at 2.57 Mev was observed. Levels higher than this might have been masked by a strong alpha-group appearing at ranges shorter than the proton group. The deuteron group from the $\text{Be}^9(p,d)\text{Be}^8$ reaction was observed between the inelastic and elastic proton groups with comparable intensity.

The C^{13} groups corresponding to reported levels at 3.10 and 3.70 Mev were observed but were very weak.

There were no groups in O^{16} for the energy region covered (to 4.6 Mev).

A new level at 3.90 Mev was found for fluorine in addition to the previously reported level at 1.4 Mev. This group appeared for both the BF_3 and CaF_2 targets.

Only natural neon gas was used, so the two observed levels were assigned to the most abundant isotope Ne^{20} (90 percent).

A Study of the Electron Traps in Zinc Sulfide Phosphor

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The thermoluminescence characteristics of a hexagonal zinc sulfide phosphor, copper activated, were measured as a function of the wavelength of the exciting light. The glow curve had maxima at 120, 220, and 280°K. It was found that the heights of these maxima at saturation varied with the wavelength of the exciting light, reaching the greatest values at 4270Å for the 120°K maximum, 4400Å for the 220°K maximum, and 4500Å for the 280°K maximum. When the sample was irradiated with 4400Å light for a definite time interval and then irradiated with monochromatic radiation of either shorter or longer wavelength for another time interval, it was found that the subsequently measured glow curve showed a decrease in the heights of the maxima from that with 4400Å light alone. Since the glow curve can be interpreted as a process of emptying electrons from traps, the above results are interpreted to mean that light which is capable of filling the traps is also capable of stimulating electrons out of the traps. There is a long wavelength limit beyond which irradiation does not affect electrons present in traps. It is 0.7 micron for the trap represented by the 280°K maximum.

INTRODUCTION

Thermoluminescence experiments have been used to characterize phosphors.¹⁻⁴ In these experiments a phosphor is excited with radiation for a definite period of time, the exciting light is removed, the material is heated at a constant rate, and the light output is measured as a function of the temperature of the phosphor. The glow curve so obtained is often characterized by the presence of peaks which can be interpreted in the following way: The position of the peaks on the temperature scale is a measure of the energy depth of trapped electrons in the solid, while the area under the peak often indicates the number of electrons transferred into these traps by the exciting light. It is the purpose of this investigation to study the process of the filling and the emptying of the electron traps in a hexagonal zinc sulfide, copper activated, as a function of the wavelength of the exciting light.

EXPERIMENTAL PROCEDURE

The phosphor used in these studies was a copper-activated hexagonal zinc sulfide obtained from Leverenz

of the RCA Laboratories. The phosphor was settled with ethanol in a layer about 1 mm thick on a flat-bottomed glass tube. This tube was suspended in a cavity in a copper cylinder which in turn was suspended in a Dewar flask. The phosphor could be maintained at the temperature of liquid air or heated at a rate of about 0.017°K. The temperature of the phosphor was measured by means of a chromel alumel thermocouple buried in the phosphor layer.

The phosphor was excited by monochromatic light either from a carbon arc, 100-candlepower Point-o-lite lamp or a globar. Either a Gaertner glass monochromator or a rock salt monochromator (Wadsworth mounting) was used to give monochromatic light. The current from the photomultiplier tube was amplified by means of a dc amplifier and recorded on a Brown potentiometer. No filter was used in measuring the light output of the phosphor since the emission band in the samples used was exclusively in the green region. Attempts to detect the blue band, which sometimes occurs in these phosphors, by spectral isolation with a 35D Wratten filter were unsuccessful.

RESULTS AND DISCUSSION

A typical glow curve for the phosphor sample used in these experiments is shown in Fig. 1. The important features are the three peaks at about 115°K, 225°K, and 280°K and the shoulder at about 180°K. Under

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¹ H. W. Leverenz, *An Introduction to Luminescence of Solids* (John Wiley & Sons, Inc., New York, 1950).

² G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, London, 1949).

³ J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 365 (1945).

⁴ F. Urbach, Wien. Ber. **11a**, 139, 363 (1930).

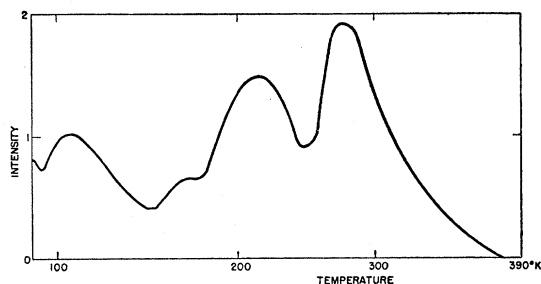


FIG. 1. Typical glow curve for ZnS:Cu.

different excitation conditions the positions of the peaks varied by as much as 20°K, but the reproducibility under the same condition was about 3°K.

The usual hexagonal form of zinc sulfide is characterized by two glow peaks, one in the region 120–160°K and the other in the region 210–240°K.^{2,3} An additional peak in the region 280–320°K is found when copper is added as an activator. The glow curves obtained in this investigation is therefore very similar to that obtained by previous workers.

Urbach⁴ and Randall and Wilkins³ have worked out the relationships between the temperature of the glow peak and the energy of the corresponding electron trap. These relationships depend on whether a first- or second-order decay law is followed. In the sample studied the decay order was intermediated between first and second order. Since the variation in peak position under different excitation conditions is as great as the variation in the different formulas, the approximate Randall Wilkins formula was used: $E = T/500$, where E is the energy depth of the trap in electron volts and T is the temperature of the glow peak in degrees Kelvin. The energy depths of the traps are found to be 0.2–0.3 ev, 0.42–0.46 ev, and 0.54–0.60 ev.

The area under the glow curve is a measure of the number of electrons that left the traps by a radiative process. The number of electrons that were actually in traps may be greater than this because nonradiative transitions are possible. Since the breadth of the peaks is constant, the value of the height can be used as a measure of the area under the peaks. This can be used as an approximation to the number of electrons excited into the traps under different conditions, if one assumes the ratio of radiative to nonradiative transitions on emptying the traps is independent of the number of electrons in traps.

The effect of the wavelength of the exciting light on the position of the glow peaks on the temperature scale and their heights is given in Fig. 2. The phosphor was excited through a Gaertner monochromator with the carbon arc. The mean band width of the exciting light was 200Å. The excitation time was such that a longer time of excitation made no difference in the glow curves for exciting light of wavelengths less than 5100Å. For these wavelengths the time ranged from one-half to two hours. For excitation with wavelengths greater

than 5100Å, a four-hour exposure was used. Decreasing the intensity of the exciting light (4500Å) by a factor of four only affected the glow curve slightly in the vicinity of the 120°K peak. This effect is due to thermal stimulation during excitation at 90°K competing with photostimulation. The saturation of the deeper traps is not affected by intensity of illumination in the range of light intensities used in our experiments. Thermal stimulation affects only the shallow traps, for the glow curve of a phosphor, left for two hours at liquid air temperature after irradiation, was appreciably lower only in the 120°K range. The position of the 220°K peak is definitely affected by the wavelength of light used for excitation (Fig. 2, upper section). This is interpreted to indicate that there is a number of traps associated with the 220°K peak, and these are populated in different ways depending on conditions of excitation. The dependence of the position of the 280°K peak is less marked while the position of the 120°K peak could not be measured with sufficient accuracy to determine its wavelength variation. On the other hand, the heights of the three glow peaks at saturation are markedly affected by the wavelengths of the exciting light (Fig. 2, lower section). For wavelengths greater than 5000Å the heights of these glow peaks at saturation are very small. As one decreases the wavelength, the heights pass through a maximum and attain at 4000Å a value two-thirds of the maximum. The peak height for the three different peaks has a slightly different wavelength dependence in that the 280°K peak has maximum height at saturation for 4500Å, the 220°K peak at 4400Å, and 120°K peak at 4300Å. These results can be interpreted in two ways. There may be a slightly different absorp-

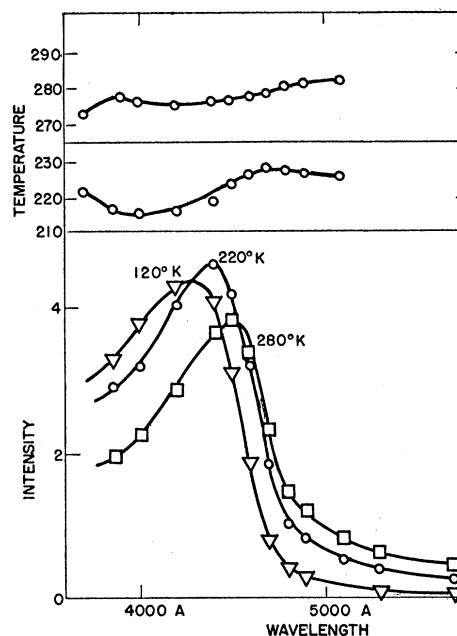


FIG. 2. Intensity and temperature of glow peaks at saturation versus wavelength of exciting light.

tion band associated with each peak in the glow curve, and this absorption band determines how many electrons get into the particular trap and consequently how many come out in a radiative process. The other possibility is that the exciting light both sends electrons into and spills them out of traps and that the wavelength efficiency of either or both of these processes varies from trap to trap.

To check this point the phosphor was irradiated with 4400A light until saturation, and this irradiation was followed by either a 3900A or a 4900A irradiation. As is seen from Fig. 3 re-irradiation at 3900A depresses the 280°K and 220°K peaks and leaves the height of the 120°K peak unchanged. On the other hand, if the phosphor after being saturated with 4400A light is re-irradiated with 4900A the whole glow curve drops. These experiments indicate that light can empty electrons from traps and that this process is wavelength dependent. Consequently, the variation of the "saturation" glow curve with wavelength is due to differences in the rate of filling and of emptying traps at different wavelengths.

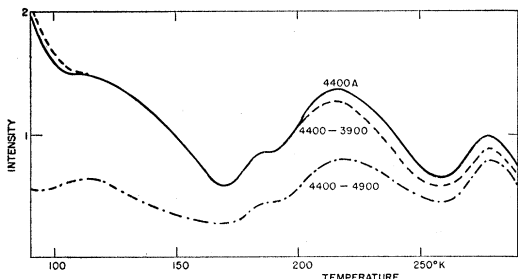


Fig. 3. Effect on the glow curve of irradiation with light of other wavelengths after 4400A light.

The wavelength dependence of the photoprocess of emptying electrons from traps was studied. The phosphor was irradiated with 4400A light for a half-hour at liquid air temperature thereby partially filling the traps with electrons. It was allowed to stand at liquid air temperature for half an hour, and a glow curve was obtained at standard conditions. This glow curve was taken as a standard curve and the results of subsequent experiments were standardized with respect to it. In these experiments designed to test the efficiency of light of various wavelengths in emptying trapped electrons, the phosphor after irradiation at liquid air for a half an hour with 4400A light was treated for an additional half-hour with light of various wavelengths from 5000 to 8000A. A glow curve was obtained and from it the heights of the three peaks were measured. The ratio of the peak heights after illumination with light of various wavelength to heights without subsequent irradiation are presented in Fig. 4. It should be pointed out that the process of removal of electrons from traps is a rate process, and the choice of half-hour time for determination of light efficiency is arbitrary. Furthermore, as one goes to longer wavelength the intensity

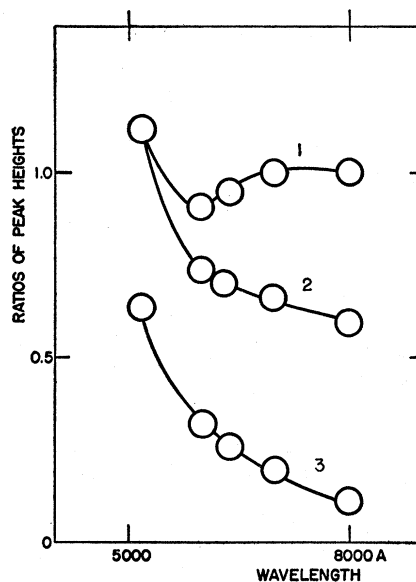


Fig. 4. Effect of subsequent radiation on glow curves of sample irradiated at 4400A. Ratios of glow peaks after second irradiation to those of a standard glow curve are plotted versus the wavelength of the second irradiation. Curve 1—280°K peak; curve 2—220°K peak; curve 3—120°K peak.

of the source (Point-o-light lamp with temperature 2920°K) increases so that there are more photons impinging on the solid at the longer wavelengths per unit time. Because of this the results are of qualitative nature. The 280°K peak decreases when irradiated with light of wavelength less than 7000A, and light of wavelength greater than 7000A though of greater intensity does not affect the 280°K peak. We can thus conclude that 7000A is a threshold of light energy necessary to remove electrons in the 0.6 electron volt trap. Both 220°K and 120°K peaks are diminished in height by subsequent radiation of wavelength greater than 5000A. The threshold for emptying electrons from traps by both radiative and nonradiative processes is beyond 8000A and was not determined. The threshold for emptying the traps by a radiative process (stimulation) was found to be 4 microns. The thresholds for two processes are not necessarily the same.

Mott and Gurney⁵ have discussed the relation between the optical absorption spectra due to an impurity center and the thermal activation energy of an electron in a center. Defining an optical activation energy as $E_0 = h\nu$, where ν is the minimum frequency of absorption, they estimate for alkali halides that the optical activation energy is of the order of two times the thermal activation energy. This is in agreement with the results found here in that the long wavelength of light capable of stimulating electrons from the 0.6 electron volt trap is 0.7 micron (1.7 electron volts) or almost three times the thermal activation energy.

⁵ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940).