TABLE III. Velocities of 10-Mc/sec transverse acoustic waves in ADP (m/sec).

Crystal	v_{zy}	v_{yz}
A	2186	2185
B	2179	2184

ments made in this way have a standard deviation of 0.2%. It is seen that the velocities v_{yz} and v_{zy} agree in both crystals within this precision. The small variations in velocity shown in Table III are also comparable with the variations to be expected from the known angular deviations mentioned above, but no correlation could be obtained with the specific values of misorientation determined by x-ray diffraction.

The fact that the observed pulse velocities are 0.2% lower than the velocities from resonance is not significant because no attempt was made in either case to put the measurements on an absolute basis.

All measurements were made at $25\pm2°C$.

CONCLUSIONS

Measurements of shear wave velocities by each of two simple methods show these velocities for the two waves involving shear between the Y and Z axes to be equal well within the experimental error limits. For the resonance method, which was carried to higher accuracy than the pulse-echo method, the probable error in the velocity difference is 0.05% of the velocity which corresponds to 0.1% for the difference between the Laval elastic constants c_{44} and c_{77}. Reported differences of 6% or more between these elastic constants must therefore be regarded as erroneous, or possibly arising in phenomena other than elasticity affecting the ultrasonic light diffraction method.

Behavior of Excited Electrons and Holes in Zinc Sulfide Phosphors*

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The luminescent properties of silver and copper activated ZnS phosphors have been investigated at room and liquid air temperatures using uv, blue light, and β-ray excitation. In many cases it was found that the deficiency area was considerably smaller than the glow curve area, especially for β-ray excitation of ZnS:Cu. This is explained by the hole production causing quenching during β-ray excitation, while during the glow curve the smaller amount of holes produced causes a much smaller amount of quenching. However, even with blue light where excitation does not directly produce holes, the deficiency area is smaller than the glow curve area. The effects of infrared radiation on the fluorescence, phosphorescence, and glow curve has been investigated, and the quenching and stimulation at room and liquid air temperature reported. For ZnS:Cu the long wavelength infrared band ($\sim$12 000 A) produces quenching at room temperature but only stimulation at low temperature. A determination of trap density from the glow curves shows $\sim10^{17}/cm^3$ for ZnS:Cu and $\sim10^{16}/cm^3$ for ZnS:Ag at liquid air temperatures. Finally, a theoretical discussion of the possible transition mechanisms giving rise to these effects is given.

1. INTRODUCTION

LUMINESCENT properties of zinc sulfide type phosphors have been extensively investigated by many workers in the field of solid-state luminescence.[1] However, it is not yet possible to explain completely the complicated phenomena associated with luminescence, that is, to describe the exact behavior of excited electrons and holes which participate in the excitation and emission processes in these phosphors. It is well known that the incorporation of small amounts of activators, especially copper and silver, into a zinc sulfide crystal creates impurity levels above the top of the valence band, although the exact nature of these levels is still under a discussion.[2,3] Luminescent emission has been attributed to an electron transition from the conduction band, or from an excited level located close to the

[1] Latest review articles of this field are: C. C. Klick and J. H. Schulman, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Vol. 5, p. 97; F. A. Kröger, Ergeb. exakt. Naturw. **24**, 61 (1956); W. W. Piper and F. E. Williams, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1958), Vol. 6, p. 95.

[2] F. A. Kröger, Suppl. Brit. J. Appl. Phys. No. 4 (1955).
[3] J. S. Prener and F. E. Williams, J. Electrochem. Soc. **103**, 342 (1956).

bottom of the conduction band[4] to the ground level of these impurities. It is further known that there are certain electron traps within the crystal which are responsible for the slow rise of fluorescence after the onset of excitation, for long phosphorescence, for the remarkably strong glow emission, for infrared stimulation, and probably for infrared and/or heat induced radiationless transitions. These traps originate from the incorporation of co-activators,[2,5] the presence of some particular impurities, or from crystal lattice imperfections.

This paper correlates the various processes which are involved in fluorescence, phosphorescence, glow emission, stimulation, and quenching. Comparison of the deficiency areas of the rise curves of fluorescence[6] with glow curve areas was carried out at various temperatures under various conditions of excitation. These measurements yielded new information on the behavior of electrons and holes in these phosphors. The results were corroborated by measurements of infrared quenching and stimulation, which also showed the important role played by holes in these processes. This is further supported by the change with temperature of fluorescence and phosphorescence efficiencies of phosphors with various activators.

Zinc sulfide phosphors show photoconductivity upon absorption of light in the activator levels as well as in the valence band[4,7]; this conductivity is due mostly to free electrons. It has been pointed out, however, that the creation and movement of not only free electrons but also of free positive holes plays an important role in the luminescent process.[8,9]

A knowledge of the number of traps in the crystal is also of importance in understanding luminescence phenomena.[6,10] An estimate of the number of traps will be derived from the results of the measurements presented.

2. EXPERIMENTAL PROCEDURES AND RESULTS

A. Samples

Commercial phosphor materials were used. Those most thoroughly investigated were a ZnS:Cu phosphor RCA (2040) and a ZnS:Ag phosphor RCA (2030). The ZnS:Cu phosphor has a bright yellow-green fluorescence and a persistent phosphorescence of the same color. These are characteristic of a copper-activated zinc sulfide. The ZnS:Ag phosphor has a bright blue fluorescence and a short phosphorescence.

[4] R. H. Bube, Phys. Rev. **90**, 70 (1953).
[5] W. Hoogenstraaten, J. Electrochem. Soc. **100**, 356 (1953).
[6] H. Kallmann and G. M. Spruch, Phys. Rev. **103**, 94 (1956).
[7] H. Kallmann and B. Kramer, Phys. Rev. **87**, 91 (1952).
[8] M. Schön, Z. Physik **119**, 463 (1942); Ann. Physik **3**, 333 (1948).
[9] H. A. Klasens and M. E. Wise, Nature **158**, 483 (1946); J. Opt. Soc. Am. **38**, 226 (1948).
[10] H. Kallmann and E. Sucov, Phys. Rev. **109**, 1473 (1958).

B. Apparatus

An apparatus was constructed which can keep samples at liquid nitrogen temperature (77°K) for rather long periods of time and can vary the sample temperature linearly with time from this low temperature to 200°C. The powder phosphor sample was deposited in a layer (thickness: from 2 to 10 mg/cm²). The plate was attached to the top of a copper rod. A copper-glass seal was attached to the middle of the rod, and its glass portion flared out to form a bowl-shaped container around the phosphor. The emitted light was observed through this glass wall. Infrared was applied to the phosphor at 90° with respect to this direction of observation. The top of the container was closed with a quartz plate used as a window to pass the exciting light. When a β-ray source was used for excitation, a thin Mylar film on a brass mesh through which β particles can pass was used instead of the quartz plate. The lower half of the copper rod was placed in a Dewar flask containing liquid nitrogen. A nichrome wire wound around this part of the copper rod heated the sample. The glass container was evacuated to prevent the deposition of condensed moisture. To measure the temperature a copper-constantan thermocouple was used; the junction was placed just below the sample plate.

The sources of photoirradiation were a 100-w Hanovia high-pressure mercury lamp for the 4360 and 3650 A lines and a 4-w General Electric low-pressure mercury lamp for the 2537 A line. These mercury lines were isolated with interference filters made by Farrand and by Axler Associates. The incident energies will be given in the discussion of the experiments. A 14-mC Sr⁹⁰-Y⁹⁰ β-ray source was also used, and it was placed about 6 cm from the phosphor. For infrared irradiation a Bausch and Lomb grating monochromator with a tungsten light source was used, from which monochromatic light from 7000 v to 14 000 A was obtained. Infrared radiation covering the entire region of $\lambda > 7000$ A was obtained from a tungsten lamp with a Corning 7-56 filter.

The luminescence measurements were made by a 1P21 photomultiplier adjacent to the window in the glass container. Appropriate filters were placed in front of the photomultiplier to exclude direct light from the excitation source. Its output was fed into a Raytheon 5886 electrometer tube. The plate current was amplified after compensation and recorded by a Sanborn No. 151 recorder so that the transient phenomena of luminescence (e.g., glow curves) were readily recorded.

In glow curve measurements, the Dewar flask containing liquid nitrogen was removed after the cessation of excitation, and the copper rod heated. A cam type program controller made by Minneapolis-Honeywell was used to obtain a constant heating rate (0.25°K/sec).

C. Deficiency Area and Glow Area

Glow curve measurements are a useful tool in investigating the number and distribution of electron traps in

crystals and in obtaining some information about their depth. Much work has been done on glow curves of zinc sulfide phosphors. Most of it concerns the theoretical analysis of glow curves and the trap depths derived therefrom,[11-13] or the relation between trap depth and chemical composition of phosphors.[5] The determination of deficiency areas[6] (the area above the rise curve and below the line through the equilibrium fluorescence intensity) is another method for the investigation of the number of trapped electrons. The first step of this study was to compare glow curve areas with deficiency areas at various temperatures.

Deficiency areas of the rise of fluorescence and glow curve areas were taken under various conditions for copper or silver activated zinc sulfide phosphors. Some of the results are described in Table I. The emission

TABLE I. Equilibrium intensities of fluorescent emission, deficiency areas of the rise of fluorescence and glow curve areas under various excitation conditions at low and room temperature for copper or silver activated zinc sulfide phosphors.[a]

(A) ZnS:Cu (RCA No. 2040) (Sample thickness: 6.1 mg/cm^2)

Excitation	L Def.[b]	L_r Def.	L_r/L	D Def. min	G Def. min
4360 A (20 μw/cm^2)	107	270	2.5	560	1300
2537 A (5 μw/cm^2)	76	130	1.7	480	2000
β ray (14 mC)	0.14	0.67	4.8	1.3	35

Excitation	G/D	D_r Def. min	G_r Def. min	G_r/D_r	D_r/D
4360 A (20 μw/cm^2)	2.3	120	140	1.2	0.21
2537 A (5 μw/cm^2)	4.2	80	60	0.75	0.17
β ray (14 mC)	27	5.2	2.9	0.55	4.0

(B) ZnS:Ag (RCA No. 2030) (Sample thickness: 3.5 mg/cm^2)

Excitation	L Def.	L_r Def.	L_r/L	D Def. min
3650 A (8 μw/cm^2)	95	50	0.53	93
2537 A (5 μw/cm^2)	36	22	0.59	23
β ray (14 mC)	0.87	0.49	0.56	25

Excitation	G Def. min	G/D	D_r Def.	D_r/D
3650 A (8 μw/cm^2)	85	0.92	4.5	0.049
2537 A (5 μw/cm^2)	53	2.3	2.6	0.12
β ray (14 mC)	62	2.4	2.0	0.11

[a] L, L_r: Equilibrium intensity of fluorescent emission at low (liquid nitrogen) and room temperature; D, D_r: Deficiency area obtained at low and room temperature; and G, G_r: Glow area obtained by heating from low and room temperature.

[b] The emission intensity is expressed by the deflection of the stylus of the recorder in an arbitrary unit.

[11] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 366, 390 (1945).
[12] G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, New York, 1949).
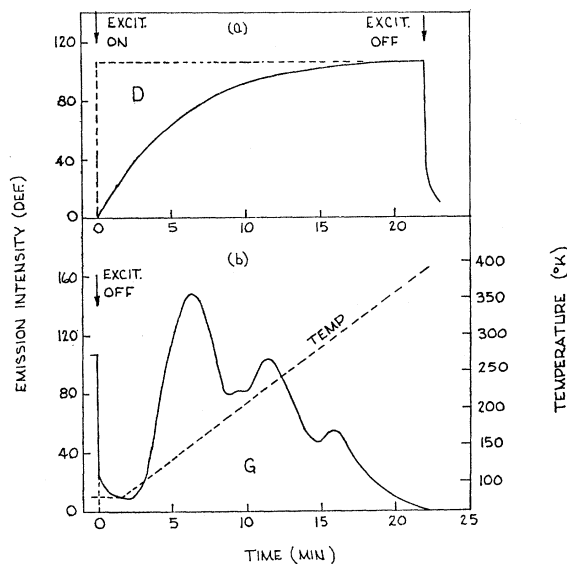[13] F. E. Williams and H. Eyring, J. Chem. Phys. 15, 289 (1947).

FIG. 1. Rise curve (a) at low temperature under the 4360 A (20 μw/cm^2) excitation and glow curve (b) obtained thereafter for ZnS:Cu.

intensities are expressed by the deflection of the stylus of the recorder in arbitrary units. Equilibrium intensities obtained for each radiation under various conditions were determined and are also given in the table. The copper activated phosphor was excited by 4360 A, which essentially excites the copper activators, 2537 A, and beta radiation. Both of the latter excite the phosphor in the valence band, but 2537 A excites the phosphor strongly in a very thin surface layer and the rest of the phosphor is excited by the fluorescence of this layer. For the silver activated phosphor 3650 A radiation instead of 4340 A was used to excite the activators. Rise and glow curve measurements were performed at liquid nitrogen and room temperatures. Before excitation, the samples were completely de-excited by means of infrared radiation and heating to 100–150°C. After cooling the rise curve was taken. When the equilibrium intensity had been reached, the excitation was stopped, and the sample was left in the dark for 1.5 min. The glow emission was then measured while the sample was heated at a rate of 0.25°K/sec. The heating rate was the same in all cases.

In the usual representation of glow curves, the glow emission intensity is plotted against temperature. Here, however, it is plotted against time in order to facilitate the determination of the glow area which is the area enclosed by the glow curve and the time axis. The magnitude of the deficiency areas and of the glow areas for ZnS:Cu and ZnS:Ag are given in the table. The exact shape of the rise and the glow curve of ZnS:Cu are given in Fig. 1 for excitation by 4360 A.

An important result of these measurements is the fact that at low temperature the deficiency areas D are smaller than the respective glow areas G, in all but one
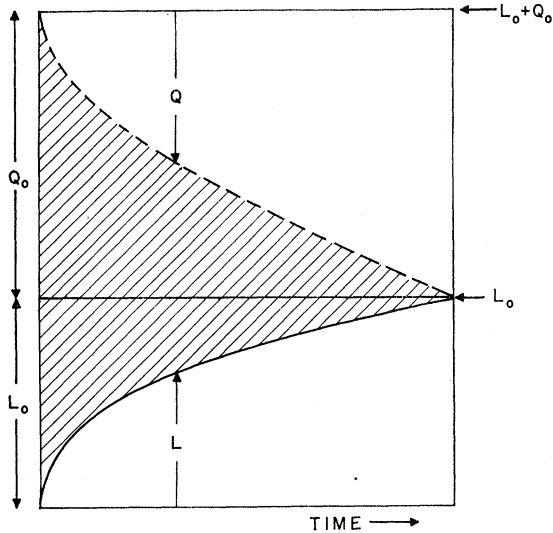
FIG. 2. Light emission (solid line), quenching (dashed line), and trapping (shaded area) as a function of time.

case, namely that of ZnS:Ag excited by 3650 A. At room temperatures for ZnS:Cu these areas are either almost equal, or the deficiency areas are larger than the glow areas, and for ZnS:Ag, G_r is almost zero under every type of excitation and is not given in the table. The ratio G/D is especially large for beta excitation of ZnS:Cu. These ratios are relatively smaller for the silver activated phosphors, and even for beta excitation the ratio is not as large as that of the copper activated phosphor. Luminescence under light excitation always starts with practically zero intensity, whereas beta excitation curves start with a finite intensity.[14] The glow curves of the copper activated phosphor after beta excitation and light excitation are quite different from one another. The maxima occurring at low glow temperatures are much weaker after beta excitation than after light excitation, and the total area is smaller by a factor of about forty. With the silver activated phosphors, there is not such a marked difference in these areas.

Before giving a detailed discussion of these results we would like to give a theoretical explanation of these effects, especially of the large difference between the beta deficiency areas and the respective glow areas. If it is assumed that the glow emission is due to a release of trapped electrons and their subsequent radiative transitions to the ground state of the activators, then it might be expected that the light emitted during the glow periods is just that which is lacking during the rise period if the efficiencies of light emission in fluorescence and in glow are equal. This would imply an equality of the deficiency area and the glow area. Here the efficiency of glow emission means the probability that elec-

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[14] H. Kallmann and J. Dresner, Phys. Rev. **114**, 71 (1959).

trons stored in traps return to the empty activators radiatively.

The general equation for the light emission during excitation can be written as follows:

$$\alpha I = L + Q + dn_t/dt + dn_c/dt. \qquad (1)$$

The notations are: I = excitation intensity, αI = the number of electrons/cm³ excited per second, L = the number of electrons/cm³ recombining per second radiatively, Q = the number of electrons/cm³ recombining per second nonradiatively, n_t = the number of electrons/cm³ in traps, n_c = the number of electrons/cm³ in the conduction band. At equilibrium

$$\alpha I = L_0 + Q_0. \qquad (2)$$

If the quantum efficiency of fluorescence η is used,

$$L_0 = \eta \alpha I, \qquad (3)$$

and

$$Q_0 = (1-\eta)\alpha I = [(1-\eta)/\eta]L_0. \qquad (4)$$

Equation (1) is multiplied by dt and integrated up to an arbitrary time τ during the rise, and one obtains

$$\alpha I \tau = \int_0^\tau L\,dt + \int_0^\tau Q\,dt + n_t(\tau) \qquad (5)$$

for $n_t \gg n_c$. Inserting Eq. (2) into (5)

$$L_0\tau - \int_0^\tau L\,dt + Q_0\tau - \int_0^\tau Q\,dt = n_t(\tau). \qquad (6)$$

Under the assumption that the efficiency of glow emission is high, it can be roughly assumed that $n_t(\tau)$ is proportional to the glow area obtained after an excitation of duration τ. That is

$$n_t(\tau) = C \cdot G(\tau). \qquad (7)$$

The measured deficiency area is given by

$$C \cdot D(\tau) = L_0\tau - \int_0^\tau L\,dt, \qquad (8)$$

where the constants in (7) and (8) are the same. Inserting (7) and (8) into Eq. (6) the following equation is obtained.

$$C \cdot D(\tau) - C \cdot G(\tau) + Q_0\tau - \int_0^\tau Q\,dt = 0, \qquad (9)$$

which enables one to determine the quenching up to a time τ. We will see below that for certain cases $[G(\tau)/D(\tau)]$ = constant. Then it follows from (9) that

$$\frac{Q_0\tau - \int_0^\tau Q\,dt}{L_0\tau - \int_0^\tau L\,dt} \simeq \text{const} = \frac{1-\eta}{\eta}. \qquad (10)$$

Thus the number of electrons recombining nonradiatively is proportional to the number of those recombining radiatively at any instant during the rise of fluorescence. In other words, if the quenching of excitation energy were plotted as a function of time it would be similar to the rise curve.

One can represent this situation with the schematic diagram of Fig. 2. The abscissa represents the time axis. The true observed light emission is represented by the solid curve. After the equilibrium intensity L_0 is reached, the number of electrons excited into the conduction band per second is larger than the number of quanta emitted per second corresponding to L_0. The parallel solid line at the L_0+Q_0 level represents the number of electrons created per unit time. The difference between the broken line and L_0+Q_0 represents the number of nonradiative transitions at any moment. The shaded area thus represents the number of trapped electrons as given by Eq. (6) and should be equal to the glow area. This figure clearly shows that when quenching occurs the number of trapped electrons is larger than the normal deficiency area above the rise curve, that is, the area between the light curve and the line parallel to the time axis through L_0, and thus is smaller than the total shaded area.

Most of our results can be explained by the assumption that considerable quenching occurs during the rise of fluorescence at low temperature but not during glow emission.

As can be seen from the glow areas in Table I, copper activated phosphors contain more traps than silver activated phosphors. This is based on the assumption that in both phosphors the efficiency of light emission during the glow is close to one. Therefore the quenching in copper activated phosphors may be expected to be larger than in silver activated phosphors if it is due to a radiationless recombination of free holes with trapped electrons. One would further expect this quenching to be especially large with beta excitation, which produces more holes than activator excitation. The experimental results bear out both expectations. The agreement between expectation and experiment is only qualitative, however, and there are observations which do not seem to fit completely into the scheme. A detailed analysis, therefore, is given below.

One might expect that excitation by 2537 A would give results similar to excitation by beta rays, since in both cases the excitation occurs in the valence band, but apparently this is not the case. The probable explanation is that this wavelength excites only a very thin layer of the phosphor and the bulk of the material is excited by the fluorescent radiation, which, for the most part, excites the activator levels and does not produce free holes directly. Then the question arises as to why the glow areas are larger than the deficiency areas with 4360 A excitation if one assumes that holes are responsible for the quenching, since holes are not created directly by this radiation. Therefore, to understand the
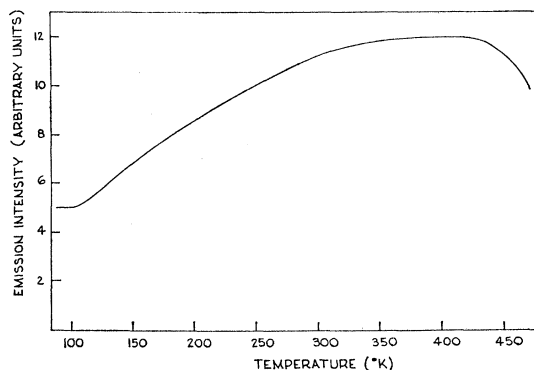

FIG. 3. The variation of the fluorescent intensity with temperature for ZnS:Cu under the 4360 A excitation (200 μw/cm^2).

fact that the ratio G/D is of the order of 2, one must introduce an additional assumption, that perhaps the external exciting light and/or the fluorescent radiation partially excites electrons from the valence band into ionized activator levels (transition δ_A in Fig. 7). This will be discussed below.

That with this exciting radiation quenching indeed occurs is borne out by measuring the quantum efficiency of fluorescence with this radiation at various temperatures. Figure 3 shows the variation of the fluorescent intensity with temperature for ZnS:Cu under excitation provided by the 4360 A line (200 μw/cm^2). The results indicate that the intensity decreases with a decrease in temperature, and the ratio of the intensity at room temperature to that at low temperature is 2.3. This value is 2.5 under weaker excitation intensities such as that in Fig. 1. Thus, the quantum efficiency decreases by a factor of about 2.5 when the temperature decreases from room to liquid nitrogen temperature. This, according to our viewpoint, is due to the larger number of traps filled at low temperature, which increases the possibility of radiationless recombination of trapped electrons with holes.

The quantum efficiency of fluorescence for ZnS:Cu under near ultraviolet excitation at room temperature is known to be quite high, i.e., 80–90%.[15,16] If one assumes it to be 85%, the efficiency at low temperature will be 34%. Then the result that G/D at low temperature for 4360 A excitation is 2.3 can be easily understood. The result that G_r/D_r is nearly equal to one is reasonable, since the quantum efficiency is 85% at room temperature. In the case of 2537 A excitation the quantum efficiency will not be as high as for 4360 A excitation; therefore a value of G/D is expected which is larger than that for 4360 A excitation. The energy efficiency of fluorescence under high-energy excitation β-rays[17] at room temperature is between 10 and 20% for zinc sulfide phosphors,[18] which is much lower than

[15] J. Tregellas-Williams, J. Electrochem. Soc. **105**, 173 (1958).
[16] Gy. Gergely, Z. physik Chem. **207**, 81 (1957).
[17] Energy emitted as light per absorbed energy.
[18] M. Furst and H. Kallmann, Phys. Rev. **91**, 766 (1953).

that under ultraviolet excitation. The high value of G/D obtained for β excitation indicates that a very large fraction of the excited electrons return to their ground state via nonradiative transitions. This is probably due to the large number of holes created by this type of excitation.

The variation of the fluorescent intensity with temperature for ZnS:Ag is quite different from that for ZnS:Cu. Under $8 \mu\mathrm{w}/\mathrm{cm}^2$ of 3650 A excitation the intensity increases rather rapidly when the temperature is lowered from room temperature, passes a small maximum at 250°K, decreases a bit, and then stays constant until liquid nitrogen temperature. This indicates that the quenching of fluorescence at low temperature does not occur, which is different from the case of ZnS:Cu, but that some quenching, probably temperature quenching, does take place even at room temperature. Therefore the results that the G/D values for ZnS:Ag are smaller than those for ZnS:Cu under every type of excitation and that the values of G_r are almost zero can be understood.

Before we give a more detailed discussion of these results we will discuss several other experiments, which will provide a clearer view of the underlying processes. The full discussion is given in Sec. 3.

D. Filling of Traps

The magnitude of the glow area may be dependent on the excitation intensity. It is generally assumed that with higher excitation intensities all the traps are filled to saturation, and that the glow area reaches a saturation value. With lower intensities, however, the traps may not be filled to saturation. This seems to be true for the special case of activator excitation, but it is not generally true at low temperature, as will be shown in Sec. 3.

Figure 4 shows the relation between the glow area and the intensity at low temperature (4360 A). The fluorescent intensity, L at low temperature and the G/D values are also shown. The glow area becomes saturated and the G/D value remains constant with intensities above $3 \mu\mathrm{w}/\mathrm{cm}^2$. In this intensity region the
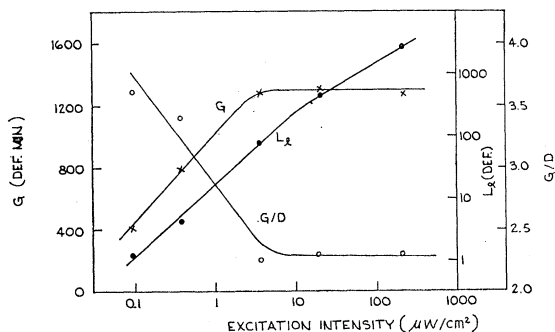

FIG. 4. The relations of the fluorescent intensity (L), glow area (G), and G/D value against the intensity of the 4360 A excitation at low temperature for ZnS:Cu.

TABLE II. Incomplete deficiency and glow area under 4360 A excitation of 20 $\mu\mathrm{w}/\mathrm{cm}$ for ZnS:Cu.

Time of excitation given (min)	Emission intensity (def.)	Incomplete deficiency area D_i (def. min)	Incomplete glow area G_i (def. min)	Ratio of glow peak heights[a]	G_i/D_i
1	16	100	120	1/2.4/2.1	1.2
3	45	250	470	1/1.48/1.0	1.9
6	72	390	780	1/0.86/0.50	2.0
9	87	470	890	1/0.83/0.40	1.9
13.5	99	530	1010	1/0.80/0.40	1.9
20 (full excit.)	107	560 $(=D)$	1300 $(=G)$	1/0.70/0.37	2.3

[a] Listed from low temperature to high temperature.

shape of the glow curve is just the same as that shown in Fig. 1, and the deficiency area does not change.

When excitation intensities below $3 \mu\mathrm{w}/\mathrm{cm}^2$ are used, the glow and deficiency areas decrease and the shape of the glow curve changes. D decreases more rapidly than G since G/D increases with decreasing intensity. This indicates an increase in quenching with decreasing intensity which is not yet understood completely, but may be due to the existence of killer impurities. The heights of the glow peaks at the low-temperature side decrease more than those at higher temperature side. The ratio of the heights of the three glow peaks in the higher intensity region is 1/0.70/0.37 (counted from the low-temperature side) as shown in Fig. 1. The values of this ratio with intensities of 0.37 and 0.094 $\mu\mathrm{w}/\mathrm{cm}^2$ are 1/1.03/0.68 and 1/2.1/2.0, respectively. This could be interpreted to mean that deep traps are filled more than shallow traps. However, if the effect of the retrapping of the thermally released electrons during the glow curve is taken into consideration, another interpretation is possible. If all the traps are uniformly filled but not to saturation, and are equally quenched during excitation, then after termination of excitation many deeper lying trapping sites are not occupied. If electrons are released during the glow, those released first are those from the shallow traps. But instead of emitting light most of them fall into deeper traps and contribute to the light emission only at higher temperatures when they are released from the deep traps. Retrapping thus makes the peak of the glow curve for the shallow traps smaller than it should if it corresponded to the actual number of electrons in these traps at the beginning of the glow emission, and it makes the peaks of the deep traps higher. Thus when the traps are only partially occupied, it may not be possible to determine the exact distribution of the electron population in each trap at the beginning of the glow curve.

The glow area obtained after β-ray excitation of ZnS:Cu at low temperature is smaller than that obtained with high intensities of 4360 and 2537 radiation. One would be inclined to attribute this decreased trap filling to the small excitation intensity obtained with

our β source. This may not be correct as will be discussed in Sec. 3.

E. Quenching at Low Temperature

As was mentioned above, the fluorescence efficiency at low temperature of the copper activated phosphor is not as high as at room temperature because of increased nonradiative recombinations of excited electrons at low temperature. The following experiment was carried out in order to investigate the nature of this quenching.

During a rise curve measurement the excitation was removed before the fluorescence intensity reached an equilibrium value, and a glow curve taken. This was repeated for various cutoff times; the results are given in Table II. It can be seen that the G_i/D_i values are approximately constant during the rise of fluorescence although they are somewhat low in the beginning and a little higher in the final stage of the rise. Further one sees that the peak corresponding to the shallow traps is again relatively low for incomplete trap filling and reaches its full value only when trap saturation has been accomplished.

The near constancy of $G_i/D_i = 1/\eta$ can be used to determine the quenching Q. Introducing this in Eq. (10) the following formula is obtained

$$Q = [(1-\eta)/\eta]L. \qquad (11)$$

From these relations, the following equations are also derived.

$$C \cdot D(\tau) = \eta \cdot n_t(\tau), \quad D_\tau \text{ deficiency area after time } \tau.$$
$$C \cdot D = \eta \cdot n_t^*, \quad D \text{ final deficiency area.} \qquad (12)$$

Thus, the total number of trapped electrons n_t^* or the ideal deficiency area can be calculated.

F. Efficiencies of Phosphorescence and Glow Emission

The efficiency of phosphorescence is defined in a manner similar to the efficiency of glow emission (see Sec. 2C). The following experiments were performed to estimate this value. After the equilibrium fluorescence intensity was reached at low temperature the excitation was removed, the phosphor was allowed to decay for some time, and then excitation was recommenced. The ratio of the phosphorescent area P to the deficiency area

TABLE III. Ratio of phosphorescent area of ZnS:Cu to corresponding deficiency area under 4360 A excitation of 20 μw/cm^2 at low temperature.

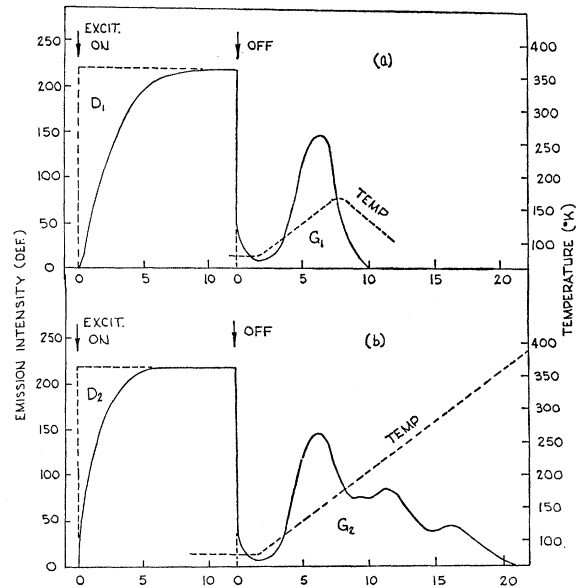| Time of decay (min)	1.2	3	10	30
P/D_p	1.3	1.2	1.1	1.0
D_p/D	0.047	0.073	0.12	0.18

FIG. 5. Experiment of the incomplete glow curve with the 4360 A excitation (40 μw/cm^2) for ZnS:Cu; (a) the regular (first) rise and incomplete glow curve, (b) the second rise and regular glow curve.

D_p (obtained during the rise following the decay) was determined. Results of a series of these experiments are summarized in Table III, where D is the deficiency area for the completely de-excited sample.

From these results it can be said that the efficiency of phosphorescence at low temperature is about 30% higher than that of fluorescence for a decay of 1.2 min, and that with increasing time it decreases and approaches the same value as that of fluorescence.

Similar experiments were done at room temperature. In this case the P/D_p values are nearly one, indicating that the efficiency of phosphorescence at room temperature is rather high. Analogous experiments using β-ray excitation at low temperature showed a P/D_p value of 11 at the beginning, which decreases and approaches three for longer decay times.

The decrease of the ratio P/D_p at low temperature with prolonged decay periods is probably due to the increase of quenching with decreasing trap occupation and the fact that the phosphorescence emission is not quenched as much as the fluorescence emission, especially at the beginning of decay.

The following experiments were carried out in order to investigate the efficiency of glow emission in more detail. After measuring the regular rise curve at low temperature, the excitation was removed, and the phosphor heated to a temperature T_1 so that only an incomplete glow curve (not all traps emptied) was obtained. The phosphor was then cooled to a low temperature, the excitation put on again, and a second rise curve taken. Finally a complete glow curve was measured. The light emission of ZnS:Cu obtained under 4360 A excitation of 40 μw/cm^2 is shown in Fig. 5.

The following values were obtained, where the notation is that indicated in the figure.

$$G_2/D_1 = 2.3,$$

$$G_1/D_2 = 1.9,$$

$$(G_2 - G_1)/(D_1 - D_2) = 2.7.$$

G_2/D_1 is the usual G/D. In taking the incomplete glow curve the temperature was raised until only the first glow peak appeared.

The G_1/D_2 value may be used to obtain the efficiency of the glow emission of the first peak. From Eq. (12) above, the number of electrons trapped during the rise curve is given by the deficiency area multiplied by the reciprocal of the quantum efficiency of fluorescence. This also holds for rise curve measurements for non-completely de-excited phosphors in which some traps are still filled. Therefore if the efficiency of fluorescence at low temperature is assumed to be 34% (see Sec. C), the efficiency corresponding to the first glow peak is calculated from the G_1/D_2 value to be 65% (34%×1.9). In the same way the efficiency for the second and third peak can be determined from the $(G_2 - G_1)/(D_1 - D_2)$ value to be 92%.

Another experiment of this kind was performed in which the first incomplete glow emission was not extended for as long as the case depicted in Fig. 5. In this case $G_1/D_2 = 1.4$. This means that the efficiency of the low-temperature side of the first glow peak is smaller than 65%. Similar results were obtained from an experiment carried out using 2537 A excitation.

To explore these processes further the phosphor was kept at low temperature for 240 min after the termination of 4360 A excitation (20 μw/cm²) and then a glow curve was taken. The phosphorescence area P for $t=0$ to 240 min was 130 def. min, and the successive glow area, G_d was 910 def. min, whereas the glow area obtained immediately after excitation (G) was 1300 def. min. Thus $(P+G_d)/G$ is 0.80 showing that about 20% of trapped electrons recombine nonradiatively during the long decay period, and that the efficiency of phosphorescence at low temperature is considerably less than the efficiency of glow emission. The peak heights in the glow curves after the long decay were 66, 82, and 85%, respectively, of those in the glow curve obtained from the regular heating schedule. Electrons responsible for the long decay at low temperature are for the most part released from the shallowest traps while electrons in deep traps, corresponding to the second and third peaks, are not readily released thermally. However, the heights of those peaks were decreased by 18% and 15% after the long decay. This indicates that electrons in deep traps also recombine nonradiatively without being raised to the conduction band. Thus, it may be concluded that every trapped electron can undergo non-radiative transitions at low temperature, probably by a recombination with holes (the formation of these holes is discussed in Sec. 3); that the efficiencies of phos-

phorescence and of glow emission at very low temperature are smaller than unity; and that these efficiencies increase with temperature and reach very high values in the range of 250–350°K. This temperature dependence of efficiency is similar to that of fluorescence intensity shown in Fig. 3. These facts suggest that the nonradiative recombination of excited electrons occurring during fluorescence, phosphorescence, and glow emission is caused by the same mechanism.

G. Influence of Infrared Radiation on Fluorescence, Phosphorescence, and Deficiency Areas

The influence of infrared irradiation on excited zinc sulfide phosphors has been considerably investigated.[19–22] Infrared irradiation during phosphorescence causes stimulation or quenching of the phosphorescence or both. Further, it was found recently that excited ZnS:Cu phosphors emit infrared fluorescence upon irradiation by long wavelength visible or infrared light.[23–25] It was suggested that this infrared emission is due to a transition between the ground state of the copper activator and the valence band. Therefore infrared irradiation of the excited phosphors may give rise not only to an optical release of trapped electrons producing conduction electrons, but also to an excitation of electrons from the valence band to the level of the ionized activators, thereby producing free holes in the valence band. That this process takes place also follows from conductivity measurements, which show tremendous quenching under infrared irradiation.[22,26]

Infrared stimulation and quenching were studied here in order to explore, particularly at low temperature, the mechanism of the quenching of fluorescence, phosphorescence, and glow emission. The following experiments were performed: after the fluorescent emission had reached equilibrium under 4360 A excitation (20 μw/cm²), the excitation was removed (at $t=0$ min), infrared light was put on at $t=0.5$ min, continued for 5 min, turned off, and 4360 A excitation was put on again at $t=6.0$ min, and the rise curve obtained. Monochromatic infrared light between 7000 and 14 000 A was used with an intensity of 1400 μw/cm² except at 7000 A where it was 1050 μw/cm². This was done at both low and room temperatures with ZnS:Cu.

A sharp stimulation peak appears at the instant that infrared light of any wavelength is put on. In Fig. 6 (curve 3) the heights of these peaks are plotted against

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infrared wavelength for low temperatures. The height at 7000 A was multiplied by 1400/1050 in order to compare all values for the same incident energy, 1400 μw/cm². The peak heights at room temperature are quite low, of the order of 1 to 4 def. and could not be measured very accurately. A sudden decrease of the emission intensity always appears at the instant the infrared light is turned off. In the calculated values of $(S+P)/D$, S is the stimulation area, i.e., the area for $t=0.5$ to 5.5 min, P is the phosphorescence area, i.e., the sum of two areas, one for $t=0$ to 0.5 min and the other for $t=5.5$ to 6.0 min, and D is the deficiency area for the second rise curve. $(S+P)/D$ is plotted against wavelength for both low and room temperature (curves 1 and 2, Fig. 6).

The $(S+P)$ value should be proportional to the number of electrons which are released from traps either by radiation or thermally and which recombine radiatively with the ionized activators (probably via the conduction band); the D value multiplied by $1/\eta$ is equal to the total number of electrons which escape from traps and return to the ground state either radiatively or nonradiatively. In the infrared region of 7000 to 9000 A the $(S+P)/D$ value at low temperature is quite small and less than $1/\eta$. This means that irradiation with infrared of this wavelength region causes considerable nonradiative recombination of trapped electrons. Thus, the over-all effect of infrared is quenching of phosphorescence, although a stimulation peak is also observed. On the other hand, in the region of 11 000–14 000 A, the $(S+P)/D$ value at low temperature is rather high, and is largest at 12 000 A where the value is 1.64. It is suggested that when $(S+P)/D$ is larger than unity the over-all effect of infrared is stimulation. The following considerations show that electrons released from traps by infrared radiation undergo radiative recombination with high efficiency. The net stimulation area S^* is given by $[(S+P)-P']$ (where P' is the phosphorescence area for $t=0$ to 6.0 min in the case of no infrared irradiation) and is shown in Fig. 6. The deficiency area D_S which should be compared with S^* is given by $D-D'$, where D' is the respective deficiency area in the case of no infrared irradiation. Then the S^*/D_S value presents information about the efficiency of the emission stimulated by infrared. At 12 000 A S^*/D_S is 2.4, a value which is close to $1/\eta$. Therefore once electrons are released from the traps into the conduction band, they recombine radiatively with a very high efficiency even at low temperature. This fact is useful in discussing the mechanism of quenching at low temperature.

In any case, the effect of infrared on phosphorescence at low temperature is a superposition of stimulation and quenching. Infrared irradiation gives rise to stimulation throughout the entire wavelength region, since the sharp rise or fall of phosphorescence is observed at the instant the infrared is turned on or off for all wavelengths. The curve of stimulation peak heights vs wave-
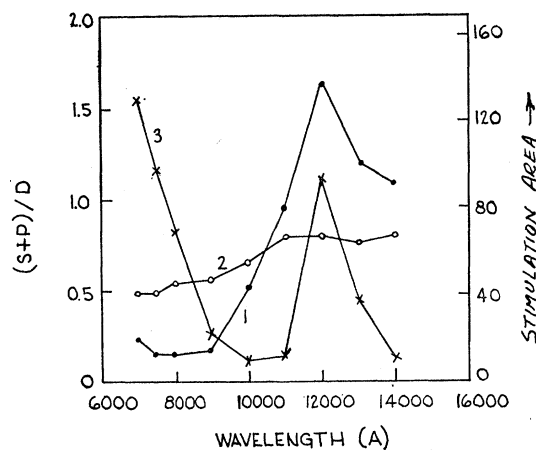

FIG. 6. The $(S+P)/D$ value for infrared stimulation and quenching and the stimulation peak height against infrared wavelength (1) $(S+P)/D$ at low temperature, (2) $(S+P)/D$ at room temperature, (3) Stimulation area at low temperature.

length seems to show two maxima, one at 7000 and one at 12 000 A. However, it follows from the curve of $(S+P)/D$ vs wavelength (Fig. 6, curve 1) that the quenching as a function of wavelength has only one maximum 8000 A and that infrared beyond 11 000 A does not give rise to quenching at low temperature but only to stimulation.

At room temperature the situation is different. The $(S+P)/D$ values are always less than unity, indicating that the over-all effect of infrared is that of quenching. A weak stimulation occurs at all wavelengths since an increase in light emission upon application of infrared is always observed. But quenching predominates over stimulation throughout, and this predominence is strongest in the region below 10 000 A. There are decided differences between the effects at low and room temperature. The irradiation with infrared of about 12 000 A induces stimulation at low temperature, but at room temperature there is both stimulation and quenching, the latter predominating. Thus infrared induces two different processes, one to the stimulation which may be caused by raising trapped electrons into the conduction band optically, and the other the quenching, which seems to be caused by some other transition.

The superposition of infrared and visible radiation in the steady state was also studied at low temperature. Superposition of 7500 A light (570 μw/cm²) causes a 45% decrease of fluorescence at equilibrium although it causes a sharp, short stimulation at the instant that the infrared is turned on. The slow rise in fluorescence after infrared has been turned off indicates that it had emptied many traps. These results show that the addition of 7500 A markedly accelerates the nonradiative recombination of trapped electrons. On the other hand, the addition of 12 000 A light with an intensity of 2400 μw/cm² causes a 5.3% enhancement at the equilibrium state, and the deficiency area of the

TABLE IV. Phosphorescence, stimulation, and glow area, P, S, and G for infrared irradiation during decay of ZnS:Cu.

Infrared wavelength	P $t=0$-0.5	P or S $t=0.5$-20.5	G $t>20.5$	Total area $t>0$
		Unit: def. min		
No infrared	15	63	1160	1230
7500 A	15	84	324	423
12 000 A	15	147	1140	1300

rise curve taken after the infrared has been removed is not so large. This shows that the 12 000 A radiation releases some of the trapped electrons thereby increasing the concentration of conduction electrons, but does not cause considerable nonradiative recombination. There is a sharp dip upon cessation of 12 000 A irradiation since the traps emptied by infrared must be refilled. These results are in agreement with those mentioned above, obtained from infrared stimulation and quenching.

H. Influence of Infrared on Glow Curve

Experiments similar to those described in Sec. 2G were carried out in investigating the influence of infrared on glow areas rather than on the deficiency areas. After equilibrium was reached with excitation of 4360 A (20 μw/cm^2), the excitation was removed ($t=0$ min). Infrared light was turned on at $t=0.5$, continued for 20 min, and turned off, the phosphor being kept at low temperature during this irradiation. The regular heating program was then started. The results are shown in Table IV, including the case of no infrared irradiation. Two infrared wavelengths, 7500 A (570 μw/cm^2) and 12 000 A (2400 μw/cm^2), were used. Phosphorescence, stimulation, and glow areas are listed. It is seen that infrared irradiation of 7500 A during the decay causes a strong decrease in the glow area, while that of 12 000 A does not change the flow area, although it causes considerable stimulation. This result agrees with that mentioned in Sec. 2G, and indicates that 12 000 A irradiation does not induce nonradiative recombination of trapped electrons at low temperature, but only promotes radiative transitions. It is noteworthy that despite the increase of light emission (stimulation) using 12 000 A the glow area is not changed and the total area is even larger than in the case of no infrared. This may indicate that, unlike fluorescence and phosphorescence, the stimulated light emission is not accompanied by nonradiative processes.

7500 A irradiation, on the other hand, accelerates nonradiative recombination of trapped electrons considerably, thereby reducing the glow area to 28% of that obtained without infrared, although this radiation also causes some stimulation. These results agree with those described in Sec. 2G. The shape of the glow curve after 7500 A irradiation is quite different; as in the case of weak excitation, the low-temperature peaks are reduced more.

I. Determination of Number of Traps per Unit Volume

An attempt was made to estimate the number of traps per unit volume by using the deficiency area[6,10] and glow area. The estimate can be made most accurately for the case of β-ray excitation, since in that case the amount of energy absorbed by the phosphor depends only on its mass and therefore can be calculated accurately. The mean energy of β particles from the Sr^{90}—Y^{90} is about 1 Mev and the mean energy loss is 1.5 Mev/(g/cm^2). The energy efficiency of fluorescence under β-ray excitation may be about 15%[18] at room temperature. Using these data and the deficiency area, the number of traps filled under β-ray excitation can be calculated, if it is assumed that the self-absorption of fluorescence is small.[6] The number of traps filled under ultraviolet excitation is calculated by comparing the deficiency or glow area under this excitation with that under β-ray excitation.

The number of electrons in each trap is obtained as follows: The total glow area is divided graphically into three parts, each corresponding to one of three traps. The efficiency of glow emission for each peak was estimated in Sec. 2F, i.e., 65% for the first glow peak and 92% for the second and third peaks. Therefore, the ideal glow area (by which is meant the area for the ideal case with 100% glow efficiency) can be calculated for each trap. Comparing these ideal glow areas with the deficiency area under β-ray excitation at room temperature, the number of each trap filled by strong ultraviolet excitation is obtained at low temperature and is shown in Table V. Of course these values are only approximate; probably they show only orders of magnitude.

The total number of traps corresponds to a mole fraction of about 10^{-5}, which is almost the same order of magnitude as that of the activator. These numbers would be larger if self-absorption took place, particularly at low temperature when the glow area is saturated. However, since the thickness of sample used was very small, the effect of self-absorption is not too large.

A similar determination was carried out using ZnS:Ag. In this case some of the glow area at the high-temperature side seems to be missing. This is seen from the appreciable deficiency area observed at room temperature, and may be due to a temperature quenching of glow emission. Therefore, in order to obtain the ideal

TABLE V. Number of traps filled under strong ultraviolet excitation at low temperature for ZnS:Cu.

Glow peak temperature (°K)	Number of traps filled (cm^{-3})
150	1.5$\times$10^{17}
225	8.5$\times$10^{16}
295	4.5$\times$10^{16}
Total	3 $\times$10^{17}

TABLE VI. Number of traps filled in ZnS:Ag under ultraviolet and β-ray excitation at low temperature.

Glow peak temperature (°K)	Number of traps filled (cm⁻³)
135	1.0×10^{16}
230	2.5×10^{16}
295	3.0×10^{15}
Total	4×10^{16}

glow area, the deficiency area at room temperature is added to the observed glow area. The results are given in Table VI.

This corresponds to a mole fraction of 1.5×10^{-6} and is about 10 times less than that for ZnS:Cu. The effect of self-absorption may be more than that for ZnS:Cu, because the excitation and emission spectra overlap appreciably in this case.

3. BEHAVIOR OF EXCITED ELECTRONS AND HOLES

The energy band model normally applied to these phosphors is depicted in Fig. 7. The band gap of ZnS is 3.6 ev. An excited state level of ionized copper activators may exist just below the conduction band. The decrease of ZnS:Cu photoconductivity by one order of magnitude at low temperature[27] could be explained by assuming a level of this kind. The kinds of electron traps indicated by the glow curves are shown as one in the figure. This simple model suffices to explain most of the phenomena described in this paper.

Of special importance are the quenching at low temperature of fluorescence, of phosphorescence, and of glow emission.

We will discuss three possibilities to explain such quenching:

1. There may be special activators which, when ionized, recombine nonradiatively with free electrons.

2. There may be nonradiative transition between conductivity electrons and free holes.

3. There may be nonradiative transitions between trapped electrons and free holes. This process was first proposed by M. Schön.

Possibility (1) can explain the fact that quenching occurs strongly only during excitation and not so strongly during the glow period, if one makes the assumption that these activators must be ionized (occupied by holes) in order to become quenching centers, since during the glow period only few holes are available. This also explains the observation that quenching is much stronger when excitation occurs in the valence band. It cannot, however, explain why the quenching is so strong at low temperatures and why it occurs so strongly with copper and not with silver activators. There is no other property of Cu activated

[27] P. Mark (private communication).

phosphors with which it can be correlated. It cannot be that the copper activator itself is affected, for then the quenching would occur also during the glow. Furthermore, assumption (1) cannot easily explain the relatively small trap occupation under electron excitation which is not wholly an intensity phenomenon.

We are thus inclined to set aside this explanation, although it must be kept in mind; perhaps with appropriate additional assumption it could explain some of the effects described.

Assumption (2) can be discarded since conductivity measurements show that the density of conductivity electrons is relatively small in copper activated phosphors at low temperature but is high in those activated with silver.[27]

It is process (3) which will be discussed in detail. It can explain the following features: Quenching is largest at low temperature because under these conditions most traps are filled; there is little quenching during the glow period because few free holes are then available. Irradiation with infrared after excitation causes quenching because free holes are created by excitation of electrons from the valence band into ionized activators (release of holes into the valence band indicated by δ_A in Fig. 7); δ_A also describes the probability of thermal release of holes from the activator. (Figure 6 shows that the maximum wavelength of infrared quenching is located at about 8000 A. Then it would seem that infrared of this wavelength induces the transition δ_A.) Finally, copper activated phosphors have more traps than those activated with silver. This could explain the most remarkable difference between the two phosphors.

There still are, however, several features which cannot easily be explained by this model without additional assumptions. How can quenching occur under activator excitation which should produce no holes? How can radiationless decay of the phosphor occur during the dark period after excitation as was shown in Sec. 2F? One could explain both features by the assumption that the process described by δ_A occurs thermally even at low
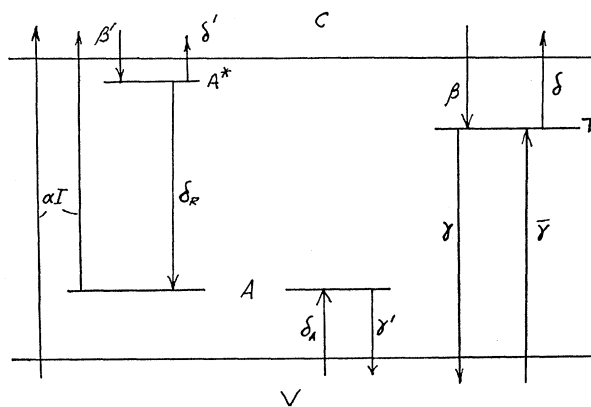

FIG. 7. Electronic transitions in ZnS type phosphor. A—Activator level, A^*—Excited state of activator, T—Electron traps, C—Conduction band, V—Valence band.

temperature. This is, however, theoretically unlikely. The energy difference, activator level-valence band is about 0.8 ev for thermal excitation in the case of ZnS:Cu.

The number of free holes p released per second is

$$dp/dt = P_A s e^{-E_A/RT}. \tag{13}$$

P_A is the number of holes in activators ($\sim 10^{17}/\text{cm}^3$); s the well-known collision factor which is of the order of 10^{11}, and E_A is the energy difference between the activator level and the edge of the valence band; $e^{-E_A/RT}$ at low temperature is of the order of 10^{-50}. Thus, dp/dt is extremely small ($10^{-22}/\text{sec}$) instead of 10^{13} per sec, which would be required to explain the process observed. Furthermore, if this process were to occur, it would be stronger with silver (because of the smaller E_A). There is, however, no indication that this is so.

Another way of explaining the formation of holes during excitation with 4360 A is by assuming that the exciting radiation produces the transition $\bar{\gamma}$ of Fig. 7. This would mean absorption in the valence band bringing electrons into trap levels. This process would, however, produce most quenching at the beginning of the rise curve, and this would become small when all traps are filled. Our experiments (Sec. 2E) do not indicate this.

Positive holes would also be produced when the exciting light or the fluorescent light is absorbed in the valence band, bring an electron from this band into an ionized activator. The latter would mean self-absorption of the fluorescent radiation. We have tested whether quenching under 4340 A excitation depends upon the thickness of phosphor layer. The values of L_r/L_1 were measured using three kinds of sample plates with the following thicknesses: effectively infinite, 6.1, and 1.8 mg/cm². The corresponding L_r/L_1 were 2.8, 2.5 (shown in Table I), and 2.3, respectively. In the thinnest sample plate the phosphor layer consisted of single crystal grains. Thus, the ratio L_r/L_e is not strongly dependent on thickness, indicating that self-absorption is not the most important quenching process.

That self-absorption does, however, partially contribute to the creation of holes seems to be indicated by the quenching of the glow areas during long decay periods at low temperatures. If a noticeable amount of the phosphorescence radiation at low temperature were self-absorbed by the S_A transition, this self-absorption would lead to a radiationless transition and be lost for phosphorescence. Thus, the decrease of the glow areas would be larger than that of the light sum of the phosphorescence areas. This was found, as was mentioned in Sec. 2F. Whether this assumption can explain the observations quantitatively has not yet been established.

The processes at room temperature are easily explained with this model. Since the trap occupation is low, the quenching is low; self-absorption in the δ_A

process is low and the holes created recombine predominantly with activators. Only if they are repeatedly thermally released from ionized activators by δ_A does quenching occur. This is demonstrated by the nonexistence of any glow area above room temperature for ZnS:Ag.

But there are still processes at low temperatures which do not fit so easily into our picture. ZnS:Ag phosphors show much smaller differences between deficiency areas and glow areas than do ZnS:Cu phosphors. One would be inclined to explain this by the smaller number of trap levels available in ZnS:Ag. But this is not the case under electron excitation in ZnS:Cu. Here the number of actually trapped electrons is certainly not larger than that in the silver case, as is easily found by comparing Tables I, V, and VI, and yet the quenching is much larger for ZnS:Cu than for ZnS:Ag. One way out of this difficulty is to assume that γ' is larger for ZnS:Ag than for ZnS:Cu.

One can give theoretical arguments for this assumption. The energy freed by the transition:hole → activator is considerably smaller for Ag than for Cu. Now any energy releasing transition will in general be more probably when the energy release is small, because then the coupling with the lattice, which has to take over the energy, can be less. This may make the hole-activator transitions in Ag more probably than in Cu. We have, however, no other evidence that this is actually so.

Another point which will be discussed is the small trap filling in ZnS:Cu (3%) by β radiation compared to the strong filling in ZnS:Ag. It is mostly assumed that trap occupation depends upon excitation intensity. This is only correct when trapped electrons and holes are released during the excitation period in an amount comparable to the total number trapped. This is not the case in our low-temperature experiments as shown by the small phosphorescence over many hours. It was shown that about $\frac{3}{4}$ of the whole glow area persists for more than 4 hr. Thus these traps should be filled by prolonged β irradiation. We have found that no further trap filling occurs after equilibrium fluorescence is reached (about 90 min). Therefore, one must look for another reason for the small trap occupation observed.

Indeed one finds that under certain conditions, traps may not be filled to saturation quite independently of the intensity of excitation. If the number of electrons released from traps is negligible, trap filling reaches equilibrium when the number of electrons falling into traps equals the number of holes which recombine with traps. If free electrons and holes are produced in equal number, as the case under β excitation, one can derive the following equation (see Appendix):

$$\frac{\beta(n_0-n_t)}{\beta(n_0-n_t)+\beta^* n_t} = \frac{\gamma n_t}{\gamma n_t+\gamma' N}. \tag{14}$$

Equation (14) may be written in a more convenient

form:

$$\frac{n_0-n_t}{n_t}=\frac{\beta^*}{\beta}\cdot\frac{\gamma}{\gamma'}\cdot\frac{n_t}{N},$$

from which it is seen that when the right-hand side is larger than 1, the traps are not saturated while for the right-hand side smaller than 1, the traps are saturated. At low temperature β^* is approximately the same as β (see Appendix) and n_t/N may be of the order of 10^{-1}. Therefore if γ/γ' is larger than 10, the traps are not saturated. Thus, we may have the unexpected saturation of weak band to band excitation at low temperature not filling the traps.

If excitation is not by β radiation but rather by 4360 A, then fewer holes are produced. Thus, a hole is not created for each free electron produced, and the right side of (14) has to be multiplied by a factor $\Sigma < 1$. As a consequence of this trap filling is increased, explaining why traps are filled to saturation with activator excitation.

For Ag activated phosphors the situation is quite different. Here, apparently, γ/γ' is smaller and there is apparently no noticeable activator level close to the conductivity band, as shown by conductivity measurements which give as high a conductivity at low as at room temperatures. Thus, with ZnS:Ag, traps are always filled to saturation at low temperature.

The last point we wish to mention is the results obtained when these phosphors were iradiated by infrared at low temperatures. It is obvious that two stimulation maxima occur, but apparently they cannot be related to the various trap levels observed. It is very difficult to say why electrons from traps should be released with different wavelengths although these wavelengths apparently are not correlated to the energy levels of the traps involved. The other difficulty is that at room temperature both these maxima are accompanied by nonradiative transitions. At low temperatures only the maximum of short wavelengths is connected with quenching. We cannot offer an easy explanation for these findings. Perhaps it may be that infrared opens another way of light emission which is not based on a release of trapped electrons by the infrared radiation.

APPENDIX

The time rate of change of electrons and holes is given by the following equations (see Fig. 7):

$$dn_c/dt=\alpha I-\beta^* n_c P_A-\beta n(n_0-n_t), \tag{1}$$

$$dp/dt=\alpha I-\gamma' pN-\gamma p n_t, \tag{2}$$

where we have neglected δ_A and δ. At equilibrium we have

$$n_c=\frac{\alpha I}{\beta^* P_A+\beta(n_0-n_t)} \quad \text{and} \quad P=\frac{\alpha I}{\gamma'N+\gamma n_t}. \tag{3}$$

Also at equilibrium

$$\gamma n_t p=\beta n(n_0-n_t), \tag{4}$$

since we have assumed these are the predominant transitions in emptying and filling traps; substituting (3) in (4) we obtain Eq. (14) of page 35, assuming $P_A\simeq n_t$.

All these symbols are explained in Fig. 7 where it is seen that for the free electron → activator transition we may use the transition probability $\beta^*=\beta'\delta_R/(\delta_R+\delta')$. For $\delta_R\ll\delta'$, $\beta^*=\beta'\delta_R/\delta'\simeq10^{-4}\beta'=10^{-4}\beta$, while for $\delta_R\gg\delta'$, $\beta^*=\beta'$. Since δ_R is not temperature dependent while δ' is, we find β^* approaching β' at low temperatures.