wish to thank D. T. F. Marple for discussions concerning the values of several of the constants of ZnSe, C. K. Kim for the activation analysis for Cl,

<sup>1</sup>C. H. Henry and K. Nassau, Phys. Rev. B <u>2</u>, 997 (1970).

<sup>2</sup>K. Nassau, C. H. Henry, and J. W. Shiever, in *Proceedings of the Tenth International Conference of the Physics of Semiconductors, Cambridge, Mass.*, 1970, edited by S. P. Keller, J. C. Hensel, and F. Stern (National Bureau of Standards, Springfield, Va., 1970), p. 629.

 $^{3}\mathrm{C.}$  H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. B  $\underline{4},$  2453 (1971).

<sup>4</sup>C. H. Henry, K. Nassau, and J. W. Shiever, Phys. Rev. B 5, 458 (1972).

<sup>b</sup>P. J. Dean, J. D. Cuthbert, D. G. Thomas, and R. T. Lynch, Phys. Rev. Letters <u>18</u>, 122 (1967).

<sup>6</sup>D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. 174, 845 (1968).

<sup>7</sup>D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. <u>177</u>, 1161 (1969).

<sup>8</sup>D. C. Reynolds and T. C. Collins, Phys. Rev. <u>185</u>, 1099 (1969).

<sup>9</sup>H. Malm and R. R. Haering, Can. J. Phys. <u>49</u>, 2432 (1971); <u>49</u>, 2970 (1971).

<sup>10</sup>P. J. Dean and J. L. Merz, Phys. Rev. <u>178</u>, 1310 (1969).

<sup>11</sup>J. L. Merz, K. Nassau, and J. W. Shiever (unpublished).

 $^{12}$ K. Nassau and J. W. Shiever, J. Cryst. Growth  $\underline{13/14}$ ,

and E. A. Sadowski and A. M. Sergent for extremely competent technical assistance in all phases of the experiments.

375 (1972).

 $^{13}$ Operating at discharge currents between 30 and 35 A with uv reflectors, this laser emits two lines at 3511 and 3638 Å, with an intensity ratio of ~40:60.

<sup>14</sup>A. M. Sergent (private communication).

<sup>15</sup>D. T. F. Marple, J. Appl. Phys. <u>35</u>, 1879 (1964).

<sup>16</sup>S. Roberts and D. T. F. Marple (unpublished). Their result is quoted in Ref. 15.

<sup>17</sup>B. Segall and D. T. F. Marple, in *Physics and Chem*istry of II-VI Compounds, edited by M. Aven and J. S.

Prener (Wiley-Interscience, New York, 1967), p. 335.

<sup>18</sup>J. R. Haynes, Phys. Rev. Letters <u>4</u>, 361 (1960).

<sup>19</sup>A. Baldereschi, unpublished work in which the original estimates of exciton binding by J. J. Hopfield (Ref. 22) have been extended by including central-cell effects.

<sup>20</sup>J. J. Hopfield and D. G. Thomas, Phys. Rev. <u>122</u>, 35 (1961).

<sup>21</sup>M. Aven, D. T. F. Marple, and B. Segall, J. Appl. Phys. <u>32</u>, 2261 (1961).

<sup>22</sup>J. J. Hopfield, in Proceedings of Seventh International Conference on the Physics of Semiconductors, Paris, 1964, edited by M. Hulin (Dunod, Paris, 1964), p. 725. This work is systematically discussed by R. E. Halsted, in Ref. 17, Chap. 8, pp. 390-396.

 $^{23}\mathrm{T}.$  Skettrup, M. Suffczynski, and W. Gorzkowski, Phys. Rev. B  $\underline{4},$  512 (1971).

PHYSICAL REVIEW B

## VOLUME 6, NUMBER 2

15 JULY 1972

# Microwave Photoconductivity and Luminescence of ZnS and CdS Phosphors\*\*

Bernard Kramer, Samuel Gelfman, ‡ and Kalman Kalikstein

Department of Physics and Astronomy, Hunter College of the City University of New York,

New York, New York 10021

(Received 2 February 1972)

Using a microwave method for determining the true photoconductivity of ZnS and CdS powdered phosphors, and correlating these results with luminescence measurements, it is shown that the Schon-Klasens model does not hold under various conditions of excitation and additional infrared radiation. A modification of this model is proposed which takes into account the possibility that the luminescent centers have a range of differing transition probabilities. The modified model agrees with the experimental results reported here.

## I. INTRODUCTION

In a previous investigation, <sup>1</sup> a microwave method was described for measuring the photoconductivity of phosphor powders. The advantage of this method consists of the elimination of polarization effects (which are a source of error in dc and lowfrequency ac measurements) and surface effects introduced by electrodes. Using this possibility of making reliable photoconductivity measurements on powders, light emission and photoconductivity were measured simultaneously in order to facilitate the interpretation of the experimental data in terms of a suitable model. $^{2-6}$ 

The experimental results, all at room temperature, will be described in three parts. The first will deal with the determination of the photoconductivity-light-intensity relationship and the calculation of the corresponding electron densities. The second will treat the effects obtained with simultaneous application of uv and ir radiation after equilibrium is reached. The last part will report on measurements of the rise and decay of luminescence and conductivity due to uv excita-



FIG. 1. Diagram of microwave bridge.

tion.

The most important results of this investigation are the following: (a) The photoconductivity of ZnS phosphors activated with Cu and Cl or Cu and Al (green emission) shows a very weak dependence on the exciting intensity. Using the relationship  $\Delta \sigma \sim I^n$ , *n* is found to vary between 0.23 and 0.36 over a wide range of exciting intensities. (b) For all phosphors measured, the ir quenching of the photoconductivity is greater than or equal to the quenching of the luminescence. (c) Rise and decay times of the photoconductivity are considerably greater than corresponding times for the luminescence.

It is shown that these results are in disagreement with the Schon-Klasens model, but can be understood if this model is revised to take into account the fact that a range of luminescent centers may exist having varying transition probabilities.

#### **II. APPARATUS**

Figure 1 is a block diagram of the apparatus employed in the experiment. The reflection bridge used in determining the induced conductivity was described previously.<sup>1</sup> In the present work, frequency stabilization of the klystron oscillator has proven to be a very desirable refinement in stabilizing and balancing the bridge.

The luminescence was measured with a 1P21 photomultiplier, a dc amplifier, and a recorder.

For all powders, except R-134 and R-305, Corning filter 4-105, which transmits a green band with maximum at 5100 Å, was placed between the photomultiplier and phosphor to pass only the visible light emission and cut out the exciting uv light and the near-ir radiation. For R-134 and R-305, Corning filter 5-74 which passes a band centered at about 4400 Å was used.

A high-pressure xenon arc lamp with a Corning 7-83 filter served as the source of the uv excitation radiation centered at 3660 Å. Wratten neutral-density filters and a combination of wire meshes were employed to reduce the excitation by known amounts. For the quenching (and stimulation) measurements requiring ir radiation, a 750-W projection lamp was employed with a Bausch and Lomb monochromator. For high-intensity ir radiation, two 7-69 Corning filters plus a 25cm water cell were used. In this case the intensity was controlled by varying the voltage of the source.

The phosphors used, the percent concentrations of activators and coactivators, and the maximum wavelength of luminescent emission are listed in Table I.

### **III. EXPERIMENTAL RESULTS**

## A. Photoconductivity at Various Excitation Levels

To determine the photoconductivity as a function of the excitation intensity, the microwave

557

TABLE I. Phosphor composition. (After the activators were added to the purified, nonluminescent sulfide, the material was heated in  $N_2$  for 2 h at 1150 °C.)

Phosphor	Туре	Max luminescence wavelength emission (Å)	Activator (wt.%)	Coactivator (wt.%)
J-7	ZnS	5300	0.005 Cu	1 Cl
J-27 <sup>a</sup>	ZnS	5300	0.005 Cu	1 Cl
R-130	ZnS	5200	0.1 Cu	1 Cl
R-134	ZnS	4700	Self-	Activated
R-153	CdS	Not measured	0.005 Cu	0.1 Cl
R-210	ZnS	5300	0.005 Cu	0.1 Al
R-305	ZnS	4700	0.005 Ag	1 Cl
LG-2150	ZnS	5300	0,003 Cu,	Cl <sup>b</sup>
			0.04 Pb	

 $^{a}$ J-7 and J-27 have the came composition, but were prepared at different times.

<sup>b</sup>Percentage unknown.

bridge was first balanced with the sample in the dark (or quenched by the infrared radiation). Maximum excitation was then applied and the deflection due to the unbalance noted; the bridge was then rebalanced. The change in conductivity  $(\Delta \sigma)$  is then obtained by using the relationship<sup>1</sup>

$$\sigma - \sigma_0 = \Delta \sigma = e \,\mu \,\Delta n_c = \frac{2 \pi a \Delta h (L + x)}{8.68 L^2 \lambda_{so} t \,\omega \mu_0} , \qquad (1)$$

where  $\sigma_0$  is the dark conductivity, e is the electron charge,  $\mu$  is the mobility, a is the wide dimension of waveguide,  $\Delta h$  is the dB change in attenuation setting when light is added, L is the length of sample,  $\lambda_{go}$  is the guide wavelength,  $\omega$  is the angular frequency of microwave signal,  $\mu_0$ 

is the permeability of vacuum, t is the thickness of sample,  $\Delta n_c$  is the change in the density of free carriers upon illumination, and x is the shortcircuit change.

To determine if the measured  $\Delta\sigma$  is independent of frequency, the most sensitive phosphor (R-153) was fully excited at both 8 and 12 GHz. It was found that the ratio  $\Delta h/\omega$  was constant. This indicates that no dispersion effects occur in this frequency range; at low ac frequencies such dispersion effects are observed.

To obtain the conductivity change at lower excitation levels, the unbalanced bridge deflections were compared to the deflection caused by the maximum excitation. Since these deflections (output power) are proportional to the square of the conductivity change,<sup>1</sup> the dependence of the conductivity change on the intensity could be obtained for each sample.

An attempt was made to measure the dark conductivity by first balancing the bridge, and then depositing the powder on its glass support in the waveguide. Unbalanced deflections observed were in the noise range of the equipment and corresponded to values of  $\Delta \sigma \leq 10^{-4}$  mho/m. This value is therefore an upper limit to the dark conductivity, and corresponds to an electron density of ~10<sup>11</sup>/cm<sup>3</sup>.

Figure 2 shows the values of the conductivity change as a function of uv exciting intensity (3660 Å) for six different ZnS phosphors, two of which were measured for two different sample thickness. The slopes range from n=0.23 to n=0.83 (where  $\Delta\sigma \sim I_{uv}^n$ ) and except for R-305, the samples with the smallest photoconductive response show the great-



FIG. 2. Photoconductivity vs uv intensity for ZnS phosphors.



FIG. 3. Photoconductivity vs exciting intensity at different wavelengths for a CdS phosphor (R-153).

est slopes. The exponent n in the conductivity-excitation relationship has previously been found to vary between 0.5 and 1, except for a superlinear relationship (n > 1) over a limited range of intensity.<sup>7</sup> The values of n less than 0.5 reported here for the copper-activated phosphors are quite unusual.

The ZnS samples showing the greatest photoconductivity are copper activated: R-210, J-7, and J-27. However, when a considerably greater amount of copper is added (R-130), the photoconductivity is reduced by at least one order of magnitude. Self-activated and silver-activated samples show intermediate photoconductive responses. For samples R-210 and J-7 the curves for the thicker samples are shifted to the right; that is, a higher intensity is required to obtain the same value of  $\Delta \sigma$ . This indicates that the sample, at least to some extent, is not uniformly excited.

Phosphor R-210 was excited by various wavelengths (all on the long-wavelength side of the absorption edge)  $\lambda = 3650$ , 3900, and 4350 Å. It was found that the slope was independent of the excitation wavelength.

Similar conductivity measurements were made on a CdS powder (R-153); in this case again three different excitation wavelengths were used. The first was weakly absorbed ( $\lambda = 5500$  Å), the second was at the absorption edge ( $\lambda = 5150$  Å), and the third was strongly absorbed ( $\lambda = 4800$  Å). The variation of the conductivity change with excitation intensity is shown for each wavelength in Fig. 3. The response is strongest at the absorption edge, but it is remarkable that for all three types of excitations the slope is not very different (0.  $68 \le n \le 0.84$ ), with the longest wavelength resulting in the highest slope.

The relation between the luminescence and exciting intensity for the ZnS samples was measured in this range of excitation; it is linear for each of these materials.

Table II summarizes the photoconductivity of the powders measured. Since the electron mobility of these materials is ~100 cm<sup>2</sup>/V sec, <sup>8</sup> the induced change in the density of the free electrons can be obtained and is given in column 5. To compare the CdS results with those of the ZnS materials only the long-wavelength excitation of the former ( $\lambda = 5500$  Å) should be considered. The photoconductive response of R-153 (CdS) and J-7 and R-210 (ZnS) are then seen to be approximately equal.

LG-2150 (ZnS: Cu, Pb, Cl) does not show any measurable photoconductivity at microwave frequencies. The ac measurements done at low frequency (100-10000 Hz) show a measurable response,<sup>9</sup> indicating that at low frequencies the trapped electrons have sufficient time to evaporate and follow the field but that the actual equilibrium number of free electrons is very small in the fieldfree situation.

Theoretical calculations leading to values of n < 0.5 have previously been reported. Rose<sup>10</sup> finds that if the insulator or semiconductor has been highly sensitized by the addition of more than one class of discrete states, the conductivity-intensity curve is likely to have a slope n < 0.5. Klasens<sup>7</sup> obtains the condition  $n = \frac{1}{3}$  only when the light emission  $L \propto I_{uv}^{2/3}$ ; certainly this is not the case

Phosphor	Powder density mg/cm²	Excitation wavelength (Å)	Incident intensity $\mu W/cm^2$	Change in electron density <sup>a</sup> $(10^{12}/\text{cm}^3)$	Slope (n)
J-7	9.8	3660	140	30	0.29
J-7	30	3660	140	17	0.32
J-7	16	3660	150	10	0,36
R-130	12	3660	150	2	0.83
<b>R-134</b>	18	3660	280	9	0.72
<b>R-210</b>	6.5	3660	140	36	0.23
R-210	21	3660	140	23	0.24
R-305	22	3660	275	6	0.52
LG-2150	20	3660	280	< 0.5	Not measurable
R-153	14	. 4800	125	26	0.68
<b>R-15</b> 3	14	5150	125	100	0.78
R-153	14	5500	125	35	0.84

FABLE II.	Photoconductivity	∕ of	various	ZnS	and	CdS	samples.
-----------	-------------------	------	---------	-----	-----	-----	----------

<sup>a</sup>The change in the electron density was obtained from the conductivity by assuming that the mobility  $\mu = 100 \text{ cm}^2/\text{V}$  sec.

with these measurements.  $Moss^{11}$  derives a onethird power law assuming highly absorbed excitation; it is doubtful that this condition is fulfilled when ZnS is excited by  $\lambda = 3660$  Å. Kallmann and Kramer<sup>12</sup> show that a dependence  $n = \frac{1}{3}$  is obtained when the number of traps is comparable to or less than the number of conduction electrons. Since the former is at least of the order of  $10^{16}$ /cm<sup>3</sup>, this condition does not hold in the experiments reported here.

## B. Simultaneous uv and ir Radiation

It is known<sup>13</sup> that in the steady state, additional ir radiation reduces the induced light emission and conductivity in many ZnCdS materials. According to the Schon-Klasens model, this ir-radiation quenching is due to the release of positive holes trapped at activator sites and their subsequent recombination (partly nonradiative) with trapped or conduction electrons. A direct comparison of the ir-radiation quenching on luminescence and photoconductivity could lead to some conclusions on the transitions involved, but previous methods of photoconductivity measurements are subject to the errors discussed in Sec. I. At microwave frequencies, these difficulties are eliminated.

It was found in the experiments reported here that ir radiation alone (in the range of 7000-8000 Å) induces a measurable, nontransient photoconductivity for ZnS: Cu, Cl. Although this induced conductivity is relatively small compared to that induced by uv excitation of the same incident intensity, a correction is required in the usual quenching expression. It is assumed that this correction is independent of the uv excitation in the following results.

Table III gives the quenching of both luminescence and photoconductivity when ir radiation (two 7-69 Corning filters;  $\lambda = 8000$  Å; 6.6 mW/cm<sup>2</sup>) is added to various levels of uv excitation for five phosphors. With ZnS activated with copper, the quenching of the photoconductivity is greater than the quenching of the luminescence; for the self-activated (R-134) phosphor no conductivity quenching

TABLE III.	Quenching <sup>a</sup> of lumines	cence $(Q_L)$ and photocoultraviolet (36)	pnductivity ( $Q_o$ ) by infrare 60 Å) intensities.	d (8000 Å, 6.6 mW	/cm²) at various
N	ZnS:Cu, Cl	ZnS:Cu, Al	ZnS:Cu, Cl	ZnS	ZnS:Ag, Cl

	ZnS:C	Cu, Cl	ZnS: C	Cu, Al	ZnS:C	Cu, Cl	Z	nS	ZnS:	Ag, Cl
<sup>I</sup> uv 2	J-	27	R-	210	R-	130	п-	134	R-0	300
µW/cm²	$Q_L$	Qσ	$Q_L$	Qσ	$Q_L$	Qo	$Q_L$	Qo	$Q_L$	Qσ
155	7.9	27	16	30	1.8	2.0	0	0	11	11
45	18	37	25	37	3.2	7.3	0	0	19	<b>22</b>
10	22	48	40	49	5.9	24	4.0	· · . <sup>b</sup>	35	• • •
4.0	31	59	47	с	12	30	8.0	•••	46	• • •
1.0	42	60	61	64	16	• • •	9.0	• • •	59	• • •
0.3	64	75	76	•••	39	• • •	• • •	• • •	• • •	• • •

 ${}^{a}Q_{L} = 100 \ (L_{uv} - L_{uv*ir})/L_{uv}$  with a similar expression for  $Q_{\sigma}$ .

<sup>b</sup>Dots (···) indicate not measurable. <sup>c</sup>No measurement made.

TABLE IV.	J-7 (9.8	mg/cm²	) quenchin	g at various	ir
wavel	engths,	ir intens	ity 0.47 m	$W/cm^2$ .	

Iuv	7500	)Å	100	00 Å	12	:000 Å
$\mu W/cm^2$	$Q_L$	$Q_{\sigma}$	$Q_L$	$Q_{\sigma}$	$Q_L$	Qσ
67	0.2	17	0	3.6	0	6.5
45	0.5	19	а	a	1.2	6.0
12	4.5	30	0.4	10	1.2	9.8
1.7	11	41	3.2	12	3.2	17
0.45	22	42	6.3	15	8.8	23

<sup>a</sup>No measurement made.

is observed although some luminescence quenching is noted at low exciting intensities. For the silver-activated sample (R-305), the quenching for both is roughly the same in the intensity range where  $Q_{\sigma}$  can be measured. These results indicate that a model valid for one type of activator may not hold for another, a result also indicated by polarization studies of luminescence.<sup>14</sup> It was noted that for all phosphors except R-134, the quenching of the luminescence as a function of the uv excitation can be approximated by  $Q = (1 + \alpha I_{uv}^{1/2})^{-1}$ .

J-27 and R-210 contain the same amount of copper activation but different coactivators and are remarkably similar as regards luminescence and conductivity quenching. R-130, which has a larger copper concentration, has a smaller quenching effect in both luminescence and conductivity, contrary to the results of Meijer<sup>15</sup> in which increased luminescent quenching occurred with higher copper content.

To examine the light and conductivity quenching at different wavelengths, a monochromator was used resulting in a lower ir-radiation intensity. Tables IV and V give the results of the quenching for two Cu-activated ZnS phosphors, J-7 and R-210, at wavelengths of 7500, 10 000, and 12 000 Å over a range of uv intensities. For both phosphors, the quenching of both luminescence ( $Q_L$ ) and conductivity ( $Q_{\sigma}$ ) is larger for 7500 and 12 000 Å and smaller for 10 000 Å as has previously been reported.<sup>16</sup> The conductivity quenching is greater than that of the luminescence for all wavelengths, and the quenching increases with decreasing uv excitation.

TABLE V. R-210 (21  $mg/cm^2$ ) quenching at various ir wavelengths, ir intensity 0.3  $mW/cm^2$ .

 	7500	) Å	10.0	00 Å	12 00	 00 Å
$(\mu W/cm^2)$	$Q_L$	$Q_{\sigma}$	$Q_L$	$Q_{\sigma}$	$Q_L$	$Q_{\sigma}$
145	3.4	17	1.7	3.9	1.7	4.4
40	5.0	22	1.8	7.7	2.2	9.8
10	9.7	31	3.4	14	6.2	16
4.3	14	37	3.7	17	7.2	25
1.8	22	41	6.0	22	9.0	25
0.34	29	54	17	20	20	33

TABLE VI. Light and conductivity quenching of J-7 (30 and 9.8 mg/cm<sup>2</sup>), ir intensity  $0.45 \text{ mW/cm}^2$ .

	J-7:30 and	d 9.8 mg/cm <sup>2</sup>	a	
$I_{uv} (7-83) \ \mu W/cm^2$	<i>Q</i> 7500 Å	8500 Å	ې 7500 Å	8500 Å
140	· · · (2.0) <sup>b</sup>	••• (1.0)	9.0 (9.0)	7.9 (7.5)
39	1.5 (3.0)	1.5 (1.5)	16 (14)	16 (12)
9.0	2.7 (5.0)	2.7 (4.7)	27 (22)	23 (18)
3.4	5.3 (9.0)	5.3 (6.0)	30 (26)	24 (21)
1.3	12 (14)	10 (11)	30 (30)	27 (22)
0.30	30 (27)	20 (21)	34 (37)	32 (28)

<sup>a</sup>Latter in parentheses.

<sup>b</sup>Dots (···) indicate not measurable.

No conductivity quenching was observed for R-134 (self-activated) or R-305 (Ag, Cl) at any of these wavelengths.

To determine the effect of the sample thickness on conductivity quenching, measurements were made with a 30- and a 9.8-mg/cm<sup>2</sup> sample of J-7 under various levels of uv excitation using 7500and 8500-Åir irradiation. Table VI shows that the effect of ir radiation on these two samples is approximately the same even though one is three times thicker than the other. This indicates that a thickness difference does not induce appreciable errors in the quenching measurements.

Table VII gives the quenching for phosphor J-7 as a function of the ir-radiation intensity with the excitation level remaining constant  $(I_{\mu\nu} = 2.5 \mu W)$  $cm^2$ ). The quenching increases with increasing ir intensity but not at a linear rate. Thus, when the ir-radiation intensity increases from 30 to 260  $\mu$ W/cm<sup>2</sup>,  $Q_L$  increases by a factor of 2.5 and  $Q_{n}$  by a factor of 2.0. With a further tenfold increase of ir-radiation intensity (to 2700  $\mu$ W/cm<sup>2</sup>),  $Q_L$  increases by a factor of 3.4 and  $Q_\sigma$  by a factor of about 2.0. This is in rough agreement with previous measurements<sup>17</sup> which indicate that the quenching reaches a maximum value less than 100%. The conductivity quenching is again greater than the luminescent quenching at all ir-radiation values with the ratio  $Q_{\sigma}/Q_{L}$  decreasing with increasing ir-radiation intensity.

TABLE VII. Conductivity and luminescence quenching of J-7 (30 mg/cm<sup>2</sup>) as a function of ir intensity (two 7-69 filters plus 25 cm of water),  $I_{uv}=2.5 \ \mu W/cm^2$ .

ir intensity μW/cm²	$Q_L$	$Q_{\sigma}$	$Q_{o}/Q_{L}$
30	4.0	11	2.7
115	7.1	14	2.0
260	10	21	2.1
520	16	25	1.6
1400	27	34	1.3
2700	34	40	1.2
4500	40	55	1.4



FIG. 4. Rise and decay of photoconductivity and luminescence of a ZnS phosphor (J-7); excitation at 4400 Å, 7.3  $\mu$ W/cm<sup>2</sup>.

### C. Rise and Decay of Conductivity and Luminescence

The transient behavior of the conductivity and luminescence was observed using the equipment described in Sec. II and a recorder to display the information. Figure 4 shows the rise and decay for J-7 using visible excitation ( $\lambda = 4400$  Å) of 7  $\mu$ W/cm<sup>2</sup>. The conductivity rise and decay times are considerably longer than those of the luminescence. Thirty minutes after excitation is removed, the luminescence is less than 0.1% of the equilibrium value while the conductivity is about 30% of the equilibrium value. This is not due to any drift in the microwave apparatus since the addition of ir radiation brings the conductivity back to the zero level.

Table VIII summarizes the rise and decay times observed with the various samples. It is clear that the rise and decay time of the conductivity is larger than that of the luminescence for all the phosphors measured.

The most extensive series of measurements were made with J-7 and the table shows that (a) decreasing the excitation intensity increases both rise times ( $\tau_L$  and  $\tau_\sigma$ ), (b) increasing the thickness increases both rise times, and (c) increasing the excitation wavelength increases both rise times.

These results are not unexpected, since (a), (b), and (c) all effectively result in a decreased absorbed energy, so that a longer period of excitation time is requires to bring the sample to its equilibrium value.

For J-7, the rise time of the luminescence  $(\tau_L)$  is much more dependent on the exciting intensity than  $\tau_{\sigma}$ . Thus, for the 14 mg/cm<sup>2</sup> sample, a decrease in uv excitation by a factor greater than 10 increases  $\tau_L$  by a factor of about 3, but  $\tau_{\sigma}$  increases only by 40%. A similar effect is seen for the thicker sample (line 4 and 5) and for excitation with blue light (lines 6 and 7).

	Density		T	Bise (min)		Docory (min)	
Phosphor	mg/cm <sup>2</sup>	Filter <sup>a</sup>	$\mu W/cm^2$	$ au_L$	$\tau_{\sigma}$	$ au_L$	$\tau_{\sigma}$
J-7	14	7-83	1.35	0.6	4.0	b	b
J-7	14	7-83	0.11	2.0	5.5	~ 0.1	>40
J-7	30	7-83	29	< 0.5	2.0	< 0.1	0.5
J-7	30	7-83	0.93	1.0	7.7	b	b
J-7	30	7-83	0.20	4.5	11.5	b	b
J-7	14	5-74	7.3	< 0.2	27	~ 0.1	16
J-7	14	5-74	0.58	4.5	10.5	b	b
<b>R-134</b>	6.1	7-83	3.6	< 0.1	0.5	< 0.1	~ 0.3
R-305	21	7-83	42	< 0.1	< 0.1	< 0.1	~ 0.2
R-305	21	7-83	3.6	$\sim 0.1$	0.5	< 0.1	0.5

TABLE VIII. Rise time of photoconductivity  $(\tau_o)$  and luminescence  $(\tau_L)$  to reach 0.9 of the equilibrium value, and decaytime to decrease to 0.5 of the equilibrium value for various phosphors.

<sup>a</sup>7-83 passes 3660 Å; 5-74 passes 4400 Å.

<sup>b</sup>No measurement made.

## **IV. DISCUSSION OF RESULTS**

The use of microwave techniques in the investigation of the photoconductivity of ZnS phosphor powders in conjunction with luminescence measurements has resulted in a number of important observations:

(a) For the commonly investigated ZnS: Cu, Cl and ZnS: Cu, Al green-emitting phosphors, the photoconductivity shows only a weak dependence on the excitation over a wide range of incident intensities while the luminescence is linearly dependent. In the equation  $\Delta \sigma \propto I^n$ , *n* is experimentally found to vary between 0.23 and 0.36 (Table II). This is considerably below values to be expected from the Schon-Klasens model which lead to values 0.5 < *n* <1, depending on whether traps are saturated or not.

(b) For all the phosphors measured, the equilibrium quenching of the photoconductivity is greater or equal to the quenching of the luminescence. The Schon-Klasens model, where

$$L = \beta n_c P_t \tag{2}$$

(*L* the luminescence,  $\beta$  the transition probability,  $n_c$  the density of free electrons, and  $P_t$  the density of trapped holes) predicts that the luminescence will be reduced more than the photoconductivity because both  $n_c$  and  $P_t$  are reduced by the infrared.

(c) For all samples measured, a comparison of the rise and decay times of the luminescence and the photoconductivity shows that the former always has a shorter time constant as seen in Table VIII. Using the Schon-Klasens model, one can write

$$L/L_0 = n_c P_t / n_{c0} P_{t0}$$

where the zero subscript indicates the equilibrium value. During both the rise and decay  $L/L_0 < n_c/n_{c0}$  since  $P_t/P_{t0}$  is always less than 1. The expected luminescence rise and decay curve always falls below that of the photoconductivity curve (when both are normalized to their equilibrium values) and thus has a longer rise time and a faster decay time. Experimentally it is found that the time constant associated with the luminescence is faster than that associated with photoconductivity for both the rise and decay period.

It is clear that these experimental observations cannot be explained by the Schon-Klasens model. However, it is possible to modify this model and to account, at least in a qualitative way, for these discrepencies. This can be done by assuming that luminescent centers have a range of radiative recombination probabilities.<sup>5,18</sup> Thus, in Eq. (2) the recombination probability  $\beta$  is no longer a constant but depends on intensity, addition of ir radiation, and time after excitation or interruption of excitation.

If  $\beta$  depends on the excitation intensity, it should be larger for greater excitation intensities, since at these high intensities, more of the fast-recombination centers are operative. Thus, in Eq. (2) one can replace  $\beta$  by  $\overline{\beta}$ , where  $\overline{\beta}$  is some average recombination constant which increases with exciting intensity. In the range where traps are far from saturated this equation becomes<sup>12</sup> =  $KI_{uv}^{1/2}/\overline{\beta}$ . This causes the exponent *n* in the relationship  $\Delta \sigma$  $\propto I_{uv}^n$  to be lower than  $\frac{1}{2}$ ; the exact value determined by the dependence of  $\overline{\beta}$  on  $I_{uv}$ .

When ir is added to uv excitation, there is an increase in the number of free holes<sup>8</sup> and a decrease in the luminescence and conductivity. It is assumed that these free holes are quickly trapped at fast-recombination centers; thus the effective  $\overline{\beta}$  is increased.<sup>14</sup> Examing the ratio of quenched to unquenched luminescence at equilibrium, the following is obtained:

$$\frac{L_{uv+ir}}{L_{uv}} = \frac{\overline{\beta}_{uv+ir}}{\overline{\beta}_{uv}} \frac{n_{uv+ir}}{n_{uv}} \frac{P_{tuv+ir}}{P_{tuv}}$$

For constant  $\overline{\beta}$ ,

$$L_{\rm uv+ir}/L_{\rm uv} \leq n_{\rm uv+ir}/n_{\rm uv}$$
,

since the ratio  $P_{tuv+ir}/P_{tuv}$  is always less than or equal to 1. However, if  $\overline{\beta}_{uv+ir}$  becomes considerably larger than  $\overline{\beta}_{uv}$  the luminescence quenching may become considerably less the current quenching, as observed in these experiments.

Finally, the rise and decay times will be discussed. As soon as excitation is applied, the fastrecombination centers play the dominant role, but as equilibrium is reached  $\overline{\beta}$  decreases since both types (fast and slow centers) are now involved. Thus, the luminescence curve may rise more quickly than that of the conductivity because of the larger initial values of  $\overline{\beta}$  as observed in Table VIII. In the decay, as observed above, the luminescence should decrease more rapidly than the conductivity even if  $\overline{\beta}$  remains constant. If  $\overline{\beta}$  decreases (since only the long-time centers remain active), the luminescence will decay even more rapidly than expected from the unmodified Schon-Klasens model.

For the experiments described in this paper, the modification of the Schon-Klasens model based on changes of  $\overline{\beta}$  (within a factor of 10) seems to be a possible explanation.

## ACKNOWLEDGMENT

The authors are greatly indebted to Paul Balkin for his technical help in designing and constructing the apparatus. <sup>\*</sup>Supported in part by a grant from the City University of New York Faculty Research Program.

<sup>†</sup>Part of dissertation submitted in partial fulfillment of the Ph.D. degree, City University of New York.

<sup>‡</sup>Also at the Cooper Union School of Engineering and Science, New York, N.Y.

<sup>1</sup>K. Kalikstein, B. Kramer, and S. Gelfman, J. Appl. Phys. <u>39</u>, 4252 (1968).

<sup>2</sup>M. Shon, Z. Physik <u>119</u>, 463 (1942).

<sup>3</sup>H. Klasens, Nature <u>158</u>, 306 (1946).

<sup>4</sup>J. Lambe and C. Klick, Phys. Rev. <u>98</u>, 909 (1955).

<sup>5</sup>J. S. Prener and F. E. Williams, J. Electrochem. Soc. <u>103</u>, 342 (1956).

<sup>6</sup>Ch. S. Kang, P. Beverley, P. Phipps, and R. H. Bube, Phys. Rev. <u>156</u>, 998 (1967).

<sup>7</sup>H. A. Klasens, J. Phys. Chem. Solids 7, 175 (1958).

<sup>8</sup>C. B. Burgett and C. Lin, J. Phys. Chem. Solids <u>31</u>, 1353 (1970).

 ${}^9A$ . N. Silverman, Ph.D. dissertation (New York University, 1969) (unpublished).

<sup>10</sup>A. Rose, Phys. Rev. <u>97</u>, 322 (1955).

<sup>11</sup>T. S. Moss, Optical Properties of Semi-Conductors (Academic, New York, 1959).

<sup>12</sup>H. Kallman and B. Kramer, Phys. Rev. <u>87</u>, 91 (1952).
<sup>13</sup>H. W. Leverenz, Introduction to Luminescence of

Solids (Wiley, New York, 1950).

<sup>14</sup>T. Koda and S. Shionoya, Phys. Rev. <u>136</u>, A541 (1964);
S. Shionoya, Y. Kobayashi, and T. Koda, J. Phys. Soc.

Japan 20, 2046 (1965).

<sup>15</sup>G. Meijer, J. Phys. Chem. Solids <u>7</u>, 153 (1958).

<sup>16</sup>N. J. Melamed, J. Electrochem. Soc. <u>97</u>, 33 (1950). <sup>17</sup>B. Kramer and A. Turner, J. Electrochem. Soc.

110, 366 (1963).

<sup>18</sup>D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. <u>140</u>, A202 (1965).

564