

Thermoluminescence of ZnS Single Crystals

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The blue and green components of the glow of ZnS:Cu:Cl crystals were recorded separately. Thermoluminescence-excitation spectra taken for each of the components were found to be identical with the excitation spectra for the blue and green luminescence at steady excitation. Other measurements included the spectral distribution of the glow, saturation effects, effects of infrared radiation, and computation of activation energies. The activation energy for the blue peak was found to be about 0.14 eV, and that for the green—about 0.20 eV. From the shape of the peaks it was concluded that the recombination process is bimolecular in character.

Electrical glow curves were also recorded and were found to be similar to the green glow curves.

The results are discussed and an energy model is proposed.

INTRODUCTION

ZINC sulfide seems to have been investigated more than any other phosphor, and its properties as a phosphor are described in any book dealing with luminescence.¹ In spite of this, the processes involved in the emission of luminescence are yet not very clear.

The method of glow curves has been used extensively in the investigation of these phosphors.² In most of the earlier work, however, the blue and green components of the thermoluminescence were not separated, which might have introduced confusion in the results.

In the present work we concentrated the investigation on the thermoluminescence of ZnS single crystals activated by chlorine and traces of copper.

The blue and green peaks of the thermoluminescence were examined for: (1) spectral distribution, (2) saturation of the excited glow, (3) thermoluminescence-excitation spectra, (4) activation energies, and (5) effects of infrared radiation.

The results of these measurements were compared to those on the luminescence under steady excitation obtained previously³ for the same crystals.

In parallel with the optical measurements some of the crystals were examined for photoconductivity and electrical glow, in hope that correlation of all these properties might help to get a better view on the processes involved.

EXPERIMENTAL

Glow curves were recorded with the crystal mounted in a vacuum cryostat described elsewhere.⁴ A compact source Hg lamp (Mazda MD/E, 250W) in conjunction with a Hilger small quartz monochromator (D222) supplied the monochromatic light for exciting the crystals. In some of the measurements, the Hg lamp

was replaced by a Hanovia xenon compact arc lamp (Type 507c, 800 W).

The filters used for reducing the stray light in the monochromator and for separating the blue and green components in the glow were the same as in the previous work.³

The spectral distribution at various temperatures during the glow was measured with a liquid-air-cooled photomultiplier (IP 28) mounted in place of the light-source in a Beckman DU spectrophotometer equipped with a rapid scanning wavelength drive. The construction and the apparatus, and its amplification and recording devices, were described elsewhere.⁵

In some of the measurements, glow spectra were taken with a Beckman DK spectrophotometer, in which the crystal, in a suitable cryostat, was fitted in place of the light source (tungsten lamp) of the spectrophotometer.

Monochromatic infrared light, when used, was supplied through an extra quartz monochromator (Hilger D 246) with a zirconium arc or a xenon compact arc as light sources. A set of adjustable mirrors was used to direct the beam of light onto the crystal.

For photocurrent measurements and electrical glow curves the crystals were ground to make plates with two parallel faces. Stannum oxide films evaporated⁶ on the ground faces served as transparent conducting electrodes. A dry cell battery supplied the electric field (up to a few thousand volts/cm), and a Keithley micro-micro-ammeter was used to measure the current through the crystal. By this arrangement, current and luminescence glow curves could be taken simultaneously on separate recorders.

The rate of heating used in obtaining the glow curves was in most of the measurements about 0.5 deg/sec.

The ZnS crystals were the same as in the previous work.³ They contained about 100 parts per million of chlorine, and traces of copper. Spectroscopic check of

¹ See for example: P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., London, 1949); G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, New York, 1949).

² For a recent review and for references see: W. Hoogenstraaten, Philips Research Repts. 13, 515 (1958).

³ A. Halperin and H. Arbell, Phys. Rev. 113, 1216 (1959).

⁴ A. A. Braner and A. Halperin, Phys. Rev. 108, 932 (1957).

⁵ A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. 48, 996 (1958).

⁶ E. Alexander and I. T. Steinberger, J. Sci. Instr. 33, 320 (1956).

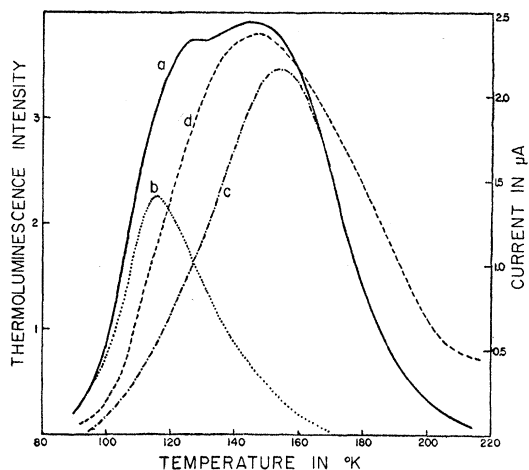


FIG. 1. Luminescence glow curves and electrical glow of a ZnS:Cu:Cl crystal. *a*—luminescence glow, unfiltered; *b*—blue glow; *c*—green glow; *d*—electrical glow.

some of the crystals showed their copper content to be less than 10 parts per million.

RESULTS

(1) Thermoluminescence and Electrical Glow Curves

The glow curve of a crystal which exhibits both blue and green thermoluminescence is shown in Fig. 1, curve *a*. Two poorly resolved peaks appear in the glow curve. Using suitable filters they were separated into a blue peak at about 115°K, and a green one at 156°K (curves *b* and *c* of Fig. 1, respectively). No correction was made in the intensities of the various curves to allow for the variation with wavelength in the sensitivity of the photomultiplier.

The electrical glow curve for the same crystal is given in Fig. 1, curve *d*. Only one peak at about 150°K appears in this case.

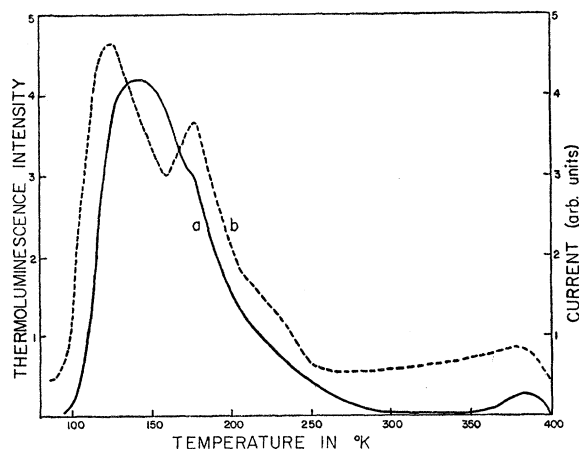


FIG. 2. As in Fig. 1 for another crystal. *a*—green glow; *b*—electrical glow.

Though the given glow curves are typical, the distribution of the peaks in the glow curves varied somewhat from one crystal to another, even of the same batch. An example is given in Fig. 2. This crystal showed only green thermoluminescence (curve *a*). The main peak appears now at 145°K and in addition there is a shoulder at 170°K and another weak peak at 375°K. The electrical glow for the same crystal is shown in curve *b* (Fig. 2). Here the first peak appears at about 125°K, the next at 170 with a shoulder at about 200°K, and at higher temperatures there is again a peak at 375°K.

There is, in addition, a glow peak just below 80°K, which on starting at liquid-air temperature can be noticed only by the strong decay in the phosphorescence at liquid-air temperature immediately after stopping the excitation. This peak was obtained more clearly on exciting the crystal at 70°K, a temperature achieved by evaporating the liquid-air in the cryostat with a fast vacuum pump.

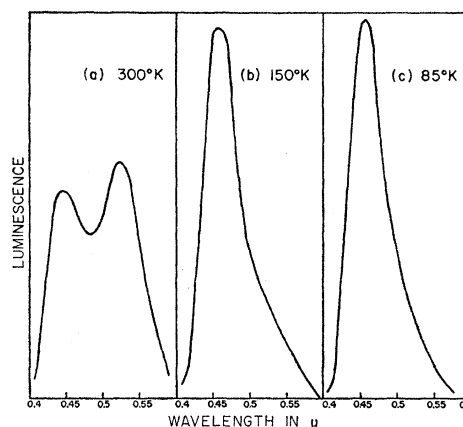


FIG. 3. Effect of temperature on the spectrum of the steady luminescence of a ZnS crystal.

(2) Luminescence and Thermoluminescence Spectra

Crystals which up to above room-temperature emitted only blue luminescence at steady excitation showed only blue thermoluminescence (at about 115°K). If, however, any green luminescence could be noticed on excitation with uv (0.36μ), the thermoluminescence obtained after excitation to saturation with the same wavelength was mainly green. This is demonstrated in Figs. 3 and 4, which show the luminescence and thermoluminescence spectra, respectively, for such a crystal. The green luminescence band (at 0.525μ) appears quite strong at 300°K [Fig. 3(a)], but is very weak at 150°K (curve *b*), and hardly noticeable at 85°K (curve *c*). In the glow, on the other hand, the green band is much stronger compared to the blue one (slightly below 0.46μ). Even at 120°K [Fig. 4(a)], where the blue peak is about at its maximum, there is

already a strong green component. At 135°K (curve *b*) the green band is already stronger than the blue one at its maximum, and it is much stronger at 150°K (curve *c*) where it nears its maximum.

This effect was observed in all the examined crystals; whenever a crystal exhibited traces of green luminescence, its glow showed a strong green peak, which was mostly the dominating one in the glow curve.

(3) Saturation of the Luminescence and Thermoluminescence

On exposing the unexcited crystal to uv light, its luminescence rises steeply at the beginning, and tends to saturation after a period which, for a given crystal, depends on the intensity of the exciting light. The blue luminescence was found to saturate much quicker than the green band. This is shown in Fig. 5. The blue band (curve *a*) reaches, in this case, about 90% of its saturation value in about 10 sec, while with the same

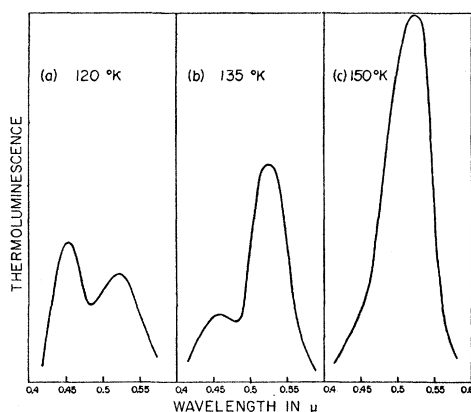


FIG. 4. The spectral distribution of the glow of a ZnS crystal at various temperatures.

intensity of exciting light this takes about 100 sec for the green luminescence (curve *b*). It follows that energy storage takes place mainly in the traps connected with the emission of green luminescence. This fits well the observations described in paragraph 2, according to which the green component is the dominant one in the thermoluminescence. The stored light sums (the areas between the curves and their saturation lines) were found, in fact, to be nearly equal to the light sums of the corresponding emitted glow peaks, both for the blue and green components.

Saturation curves for the thermoluminescence were obtained similarly. These are shown in Fig. 5, curves *c* and *d*, in which the intensity of thermoluminescence *versus* the time of previous excitation is given for the blue and green components, respectively. The blue thermoluminescence saturates in parallel with the blue luminescence, while the green component seems to saturate somewhat slower than the green luminescence. It is of interest that in the first few seconds, when the

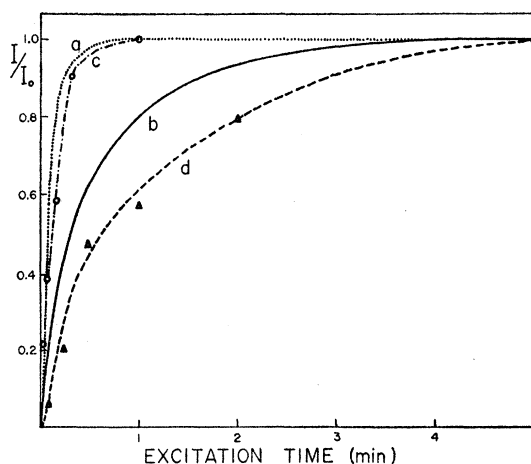


FIG. 5. Saturation curves for: *a*—blue luminescence; *b*—green luminescence; *c*—blue glow; *d*—green glow. The intensities are normalized to the saturation values (I_0).

blue peak rises steeply, the green one remains weak, and starts to rise faster only when the blue peak nears saturation. The “blue traps” seem to be filled first, and filling up of the “green traps” takes place after the blue ones are already full.

Similar measurements carried out on a crystal with transparent conducting electrodes enabled comparison of the saturation of the photoconductivity and electrical glow curves. The photoconductivity was found to saturate much slower than the green luminescence. The electrical glow peaks, however, seem at least at short excitation times to rise in parallel with the green thermoluminescence.

The peak temperature of the blue glow did not depend appreciably on the degree of saturation, and remained almost unchanged on varying the time of excitation. The peak temperature of the green component, however, varied in some crystals with the degree of saturation. For example, in one crystal it was 132°K at low excitation and moved to 142°K at saturation. In another crystal the green peak did not change, while the electrical glow peak of the same crystal moved from 130° at low excitation to 156°K at saturation.

(4) Thermoluminescence Excitation Spectra

The excitation spectrum for thermoluminescence gives a measure of the relative effectiveness of various wavelengths in exciting the thermoluminescence. To obtain an excitation spectrum, a series of glow curves was recorded, each excited with monochromatic light differing in wavelength, but with the same light sum ($It = \text{const}$). Care has been taken in these measurements not to near saturation, even with the most efficient wavelength of exciting light. The excitation spectra for the blue and green peaks of the thermoluminescence are represented in Fig. 6 by the circles and triangles, respectively. They fit well the excitation spectra for

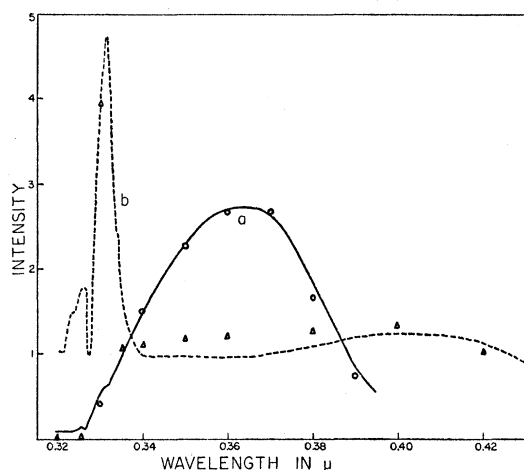


FIG. 6. Excitation spectra for the luminescence and thermoluminescence of a ZnS crystal. *a*—blue luminescence; *b*—green luminescence. The circles correspond to the blue, and the triangles to the green, thermoluminescence.

the blue and green luminescence for the same crystal (curves *a* and *b*, respectively).

(5) Thermal Activation Energies—The Method of Initial Rise

Activation energies of the traps are most directly measured from the initial rise of the glow.⁷ This method is based on the fact that the thermoluminescence intensity of a single glow peak can be expressed by $I = f \exp(-E/kT)$, where E is the activation energy, k —Boltzmann's constant, T —the absolute temperature, and f is a function of the number of full traps and of the number of empty centers, but can be taken as a constant for the initial part of the glow peak. Plotting $\ln I$ versus $1/T$ should then give a straight line from the slope of which the activation energy E is easily obtained.

High sensitivity of the amplification system and high speed of the recorder chart were used in these measurements, which enabled accurate determination of temperatures and thermoluminescence intensities. In some of the measurements, a whole set of "initial rise" curves was taken on one glow peak. The procedure was to warm up the excited crystal until the first initial rise curve was recorded, when the crystal was allowed to cool back. The remainder of the glow, which quite often contained some 80–90% of the light sum of the whole glow, was then treated again in the same way. Successive cycles of this type resulted in a series of "initial rise" curves, and activation energies could be computed from each curve. This procedure was carried out for the blue glow, for the green one, and also for the electrical glow peaks.

Only two or three such cycles could be taken in a series of "initial rise" measurements on the comparatively weak blue peak. The derived activation energies

showed a tendency to increase slightly on passing from the first initial rise to successive cycles. For one specimen a value of 0.13 ev was obtained in the first cycle, 0.15 ev in the second after which about 20% of the total glow remained, and 0.16 ev for the last portion of the glow. For another crystal the values were 0.14 ev in the first cycle, and 0.17 in the third. In other measurements the values ranged between 0.10 and 0.15 ev.

In the green glow peak, the high intensity allowed seven or eight "initial rise" curves to be recorded from a single glow curve. For some crystals a nearly constant activation energy (0.20–0.22 ev) was obtained from all the segments. In others it changed appreciably as shown in Table I, which represents an extreme case. In this case the activation energy changed from 0.13 to 0.30 ev. Mostly, however, the values obtained did not exceed 0.22 ev, and values below 0.18 ev were obtained only for the very initial part of the glow, which comprised only a few percent of the total light sum of the glow peak.

It should be noted that in cases in which the activation energies varied appreciably within the same glow peak, the $\ln I$ versus $1/T$ plots did not form straight lines when taken from the beginning of the glow up to about one-third of the maximum. This indicates again

TABLE I. Activation energies obtained at various portions of one green glow peak by the method of initial rise.

Cycle No.	1	2	3	4	5	6	7
Remaining glow (% of total light sum)	100	83	68	53	37	21	7.5
E ev	0.13	0.16	0.20	0.25	0.25	0.27	0.30

that the peak is not a simple one, but is rather composed of more than one component.

Similar measurements were carried out on the electric glow curves. For the peak at about 150°K, the values obtained for the activation energy ranged between 0.11 and 0.16 ev. In this case, however, no regularity was noticed in the way the E values changed. For example the values 0.126, 0.116, 0.138, 0.112, and 0.114 ev were obtained in a series of successive "initial rise" curves. The mean value is about 0.12 ev in this case, and the scattering seems to be due to experimental error.

(6) Thermal Activation Energies Computed from the Symmetry of the Glow Peak

In the method described in the last paragraph, use was made of the fact that the initial rise of the glow peak is independent of the type of the kinetics involved in the process.

The shape of the glow peak, on the other hand, depends on the kinetics of the process of recombination of the trapped electrons with the empty centers. Halperin and Braner⁸ made use of this dependence and

⁷ See reference 2, p. 545.

⁸ A. Halperin and A. A. Braner, Phys. Rev. (to be published).

developed a theory in which the activation energies were computed from the symmetry about the maximum of the glow peak. Formulas of the form $E_s = qkT_g^2/\delta$ were obtained, in which E_s is the activation energy obtained by this method, k —Boltzmann's constant, T_g —the peak temperature, δ —the half-width towards the falloff of the peak, and q —a factor which can be computed from the shape of the glow peak. A symmetry factor μ_g was defined by the ratio $\mu_g = \delta/W$, W being the half intensity width of the peak.

It came out that for monomolecular processes $\mu_g \leq e^{-1}(1+\Delta)$ with $\Delta = 2kT_g/E_s$ whereas for processes of bimolecular character⁹ larger μ_g values should be obtained: $e^{-1}(1+\Delta) < \mu_g \leq 0.5(1+\Delta)$.

The symmetry of the glow peaks of the ZnS crystals considered in the present work indicated a bimolecular process for both the blue and green components. We used therefore the approximate formula corresponding to this process⁸:

$$E_s = qkT_g^2/\delta, \quad \text{with} \quad q = [2\mu_g/(1-\mu_g)](1-2\Delta).$$

TABLE II. Activation energies for the blue and green glow peaks as computed from the symmetry of the peaks (E_s). Values obtained by the method of initial rise (E_i) are given for comparison. For the meaning of the other parameters see text.

Serial number	Color	Cleaning temp. in °K	T_g in °K	δ	μ_g	Δ	q	E_s in ev	E_i in ev	Crystal
1	blue	...	120	15	0.53	0.13	1.7	0.14	0.16	VIII
2	blue	...	121	14	0.56	0.13	1.9	0.17	0.16	VIII
3	blue	112	127	18	0.60	0.13	2.2	0.17	0.17	VIII
4	blue	100	122	13	0.54	0.17	1.6	0.15	0.12	VI
5	blue	100	124	21	0.62	0.18	2.1	0.13	0.10	VI
6	blue	100	122	17	0.56	0.18	1.6	0.12	0.11	VI
7	green	...	156	23	0.48	0.12	1.4	0.16	~0.2	VI
8	green	117	156	22	0.52	0.12	1.6	0.16	~0.2	VI
9	green	...	141	18	0.45	0.11	1.3	0.12	~0.2	VIII
10	green	103	145	19	0.51	0.12	1.6	0.15	~0.2	VIII
11	green	118	147	18	0.54	0.12	1.8	0.18	~0.2	VIII

This formula was derived for an isolated peak. The green glow peak, however, was shown not to fulfill this condition. To eliminate the disturbance, the excited crystals were kept for some time just below the peak temperature of the measured glow peak. This treatment cleaned away the components at lower temperatures, so that nearly a single glow peak remained.

It should be noted that weak shoulders at the falloff of the main glow peak do not change appreciably the computed E_s values. It happens that the increase in the q value is in such cases just compensated by a similar increase in the measured value of δ .

Typical values of E_s obtained by this method are given in Table II for the blue and green glow peaks. Values obtained for the same glow peaks (from the same curves) by the method of initial rise are given for comparison in the last column of Table II (under E_i).

Examples 1–3 in Table II belong to the blue peak of

a crystal which gave by the method of initial rise almost a constant activation energy throughout the whole glow peak. For this crystal there was no need to clean away the lower temperature part of the glow. This is shown in examples 1–3, where the E_s values fit well the E_i ones though they were both obtained without any cleaning.

Results for the blue peak of another crystal are given in examples 4–6. For this crystal the E_i values were 0.1 ev in the beginning of the glow and 0.16 ev for the final part of the glow. This might explain the higher values of E_s compared to the E_i values obtained in this case.

The green glow at about 150°K has already been shown to be composed of more than one peak. This appears now again. Examples 7 and 8 belong to a crystal which by the method of initial rise gave a spread in activation energies from 0.14 to 0.22 ev. Without any cleaning we get now (example 7) 0.13 ev for E_s , while after cleaning away a part of the glow (by warming the excited crystal to 117°K and recooling) $E_s = 0.16$ ev is obtained. This is still more pronounced in examples 9–11, which correspond to the green peak of another crystal. In this case E_i was nearly constant throughout the whole glow (0.18–0.22 ev), nevertheless, the peak seems to be complex. In example 9, without any cleaning the value for E_s was 0.12 ev; after cleaning at 103°K, it rose to 0.15 ev; and cleaning at 118°K resulted in a value of 0.18 ev. The low values of E_s obtained without cleaning away the low-temperature components of the glow seem to be caused by a reduction in the μ_g values which results in low values for E_s . That this is the case can be seen in a check of the variation in μ_g which follows the cleaning treatment. The μ_g values increase from 0.45 in example 9 to 0.51 in example 10 up to 0.54 in 11.

In general all μ_g values obtained after cleaning were larger than 0.5, which indicates the bimolecular character of the process.

(7) Effect of Infrared on the Glow

In these experiments the crystals were excited (0.366 μ) to saturation at liquid-air temperature. They were then exposed to infrared radiation before the glow curve was taken. This was repeated for various wavelengths of infrared, but with the total infrared energy (It) made constant for all wavelengths. Figure 7 shows the effect of infrared on the blue peak (curve *a*) and on the green one (curve *b*). Care has been taken in these measurements to keep the exposures to infrared short enough (small It values), in order to avoid saturation effects which tend to equalize the effects of different wavelengths. With this precaution, the blue band was found to show the most effective quenching on irradiation with 0.8 μ . The green band was found to be quenched by shorter wavelengths, and to be enhanced by wavelengths around 1.2 μ .

⁹ The term monomolecular is used here for processes of the first order, and second order processes are termed bimolecular.

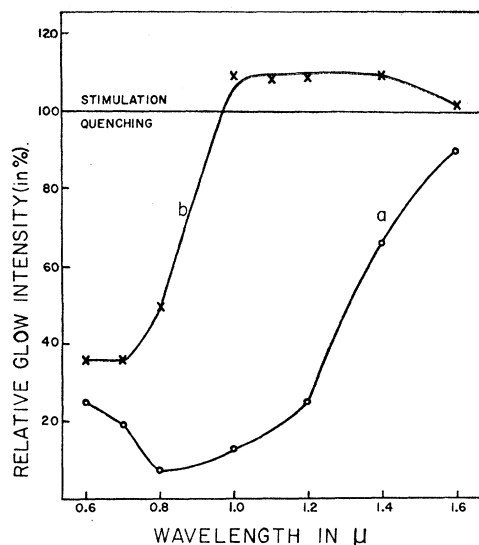


FIG. 7. Effect of various wavelengths of infrared on the blue (a) and green (b) glow peaks. The 100% line corresponds to the glow intensity without infrared radiation.

This effect seems to go in parallel with the effect of infrared on the steady excitation luminescence at liquid-air temperature, which in the case of the green band showed enhancement with a maximum at 1.2μ , and quenching for wavelengths below 1.0μ . In other crystals the enhancement was completely suppressed by the quenching effect, which takes place to some extent even at wavelengths above 1μ .

DISCUSSION

The experimental results described in the present work provide information, which might help to establish a model for the transitions involved in the process of luminescence in ZnS crystals.

We start with the excitation spectra. In the case of steady luminescence the traps are in equilibrium when the luminescence becomes saturated, and so they do not affect any more the luminescence intensity. The influence of the wavelength of exciting light on the relative intensities of the blue and green luminescence bands should therefore be attributed only to differences in emptying the blue and green centers by different exciting wavelengths. On the other hand, the thermoluminescence excitation spectrum was shown to be almost identical with that at steady luminescence (see Fig. 6). This seems to imply that also in the case of thermoluminescence the effect of wavelength of exciting light on the relative intensities of the blue and green glow peaks is due to differences in the emptying of the various centers. This implication seems still more convincing remembering that the excitation spectrum at steady luminescence was obtained with constant energy for all wavelengths (using the Beckman DK) and at saturation, while that for thermoluminescence

was obtained with constant light sum and far from saturation.

We have, therefore, to assume the existence of separate "blue" and "green" centers, which can be emptied independently. Browne¹⁰ has suggested that the blue and green luminescence arise both from the same center. According to Browne there are two levels in each center, and blue luminescence is obtained only when both levels are empty, while only the green band is emitted when one level is empty. This seems to contradict our results. For, according to Browne's model, the number of centers having both levels empty should be very small on starting the excitation, so that mainly green luminescence should be expected in the beginning. It has been shown, however, in the present work (paragraph 3) that the blue band rises much faster than the green one on starting the excitation.

Another conclusion from the similarity of the luminescence- and thermoluminescence-excitation spectra is that the transitions between the blue and green centers should be negligible. Otherwise the thermoluminescence excitation spectrum would change with the time between excitation and measurement of the glow, which was not found to be the case.

We conclude further that the traps are also separate for the blue and green bands. This is indicated by the different activation energies, and is further supported by our results on the light sum of the glow, which was found to equal the missing area in the luminescence saturation curves, separately for the blue and green bands. The comparatively large missing area in the saturation curve for the green luminescence indicates that more energy is stored in the "green" traps compared to that in the blue; in other words, it indicates a higher concentration of green traps in the examined crystals.

The conclusion that the blue and green bands arise from two independent sets of traps and centers limits considerably the possible energy models.

Two such models are given in Figs. 8(a) and 8(b). In model *a* [Fig. 8(a)] the green glow peak is obtained when electrons in the green traps, with $E_g \sim 0.2$ eV, are released thermally into the conduction band and emit the green glow on recombining with the empty green centers (transition *G*). The blue traps, on the other hand, are described as having an excited state (with $E_b \sim 0.14$ eV) below the conduction band from which recombination with the blue centers occurs by a tunneling process (transition *B*). They contribute very little to the electrical glow because only a few of them reach the conduction band. This accounts for the resemblance between the green thermoluminescence and the electrical glow.

The assumption of a tunneling process presumes some sort of proximity between traps and centers, which may correspond to the model given by Prener and

¹⁰ P. E. Browne, J. Electronics 2, 154 (1956).

Williams.¹¹ The fact that the glow curves indicated a bimolecular process both for the green and blue peaks does not contradict this model. As pointed out by Halperin and Braner,⁸ the process will be bimolecular in character whenever the probability for retrapping of the excited electron is large compared to the probability for recombination.

Model *b* [Fig. 8(b)] assumes for the green glow the same process as in model *a*. A different transition, however, is assumed for the blue glow peak. In this case a hole transition is assumed between the hole-trap ($E_b \sim 0.14$ ev above the valence band), and the blue center (about 2.7 ev above the valence band). Here, excitation raises a hole from the center into the valence band, which may consequently be trapped in the hole-trap. The blue glow is produced by thermal release of the trapped holes into the valence band followed by recombination with the centers. The resemblance of the electrical glow curve to the green one is in this model explained by the fact that the current in the sulfide-phosphors is carried mainly by electrons.^{12,13}

Model *b*, as far as it concerns the blue glow, is the same as proposed by Lambe and Klick^{13,14} for CdS as well as for ZnS.

Hoogenstraaten¹⁵ obtained glow curves similar to ours, and using filters he separated the glow into the blue and green components. He rejected, however, the assumption of two species of traps for the blue and green peaks. Instead, he attributed the difference in the peak temperatures of the two components of the glow to the different temperature-dependence of the two emission bands. This explanation does not seem to us satisfactory, because we obtained the same separation of the two peaks even for crystals for which the luminescence intensity remained almost constant in the temperature range at which the blue peak is already on its falloff while the green one is still rising.

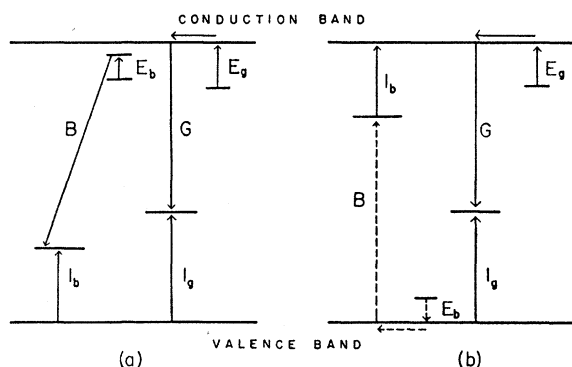


FIG. 8. Models for the transitions involved in the process of thermoluminescence. Dashed lines indicate hole transitions.

¹¹ J. S. Prener and F. E. Williams, *J. Electrochem. Soc.* **103**, 342 (1956).

¹² F. A. Kröger, *Physica* **22**, 637 (1956).

¹³ J. Lambe and C. C. Klick, *Phys. Rev.* **98**, 909 (1955).

¹⁴ J. Lambe and C. C. Klick, *J. phys. radium* **17**, 663 (1956).

¹⁵ See reference 2, p. 571.

Activation energies as computed in the present work show a distribution of trap depths, especially pronounced for the green peak. In our measurements, the distribution of activation energies for the green peak was in general much less than that given in Table I, which represented an extreme case. On the other hand, Hoogenstraaten¹⁶ has reported a still broader distribution of activation energies (0.008–0.3 ev). In this case, however, Hoogenstraaten did not separate the blue and green components, which might account for the wide distribution in the activation energies.

A point which remains unexplained is the low-activation energies obtained for the electrical glow. According to both our models these should be expected to equal the activation energies of the green peak. The discrepancy might arise from differences in the mechanism of the two phenomena not included in the models.

In connection with our results it is of interest to discuss shortly some results reported by Neumark¹⁷ on effects of an electric field on glow curves of electroluminescent ZnS crystals. The glow curves obtained by Neumark were similar to ours; i.e., they showed two peaks, one below 120°K, and another at about 160°K. Although the spectral distribution was not measured by Neumark, we identify the peaks with our blue and green ones. This is supported also by the fact that the electrical glow in Neumark's experiments followed exactly the luminescence glow peak at 160°K, which is again similar to our results.

Neumark, trying to explain this result, assumed that there is a change with temperature of the effectiveness of the released electrons as current carriers. One explanation given by Neumark for this dependence on temperature is that "the low temperature ($\sim 120^\circ\text{K}$) trap together with the activator form a localized center." This is in fact identical with our model *a*. More light, however, is thrown on this phenomenon taking in account the spectral differences between the two components of the glow curve, as obtained in the present work.

An interesting implication is that although the crystals treated by Neumark were all *blue*-electroluminescent, the electrical field enhanced the *green* component of the glow only. This fact may bear importance in any theory trying to explain the mechanism of electroluminescence in crystals.

Turning back to our energy models, we take the band gap to be about 3.8 ev. This leaves in both models about 1.5 ev between the green center and the valence band. Absorption of a photon of 1.5 ev ($\sim 0.8 \mu$) by an excited crystal may then raise an electron from the valence band into the green center (transition I_g). Such a transition should result in quenching of the green thermoluminescence. Similarly, we obtain for model *a* that 1 ev ($\sim 1.2 \mu$) radiation should quench

¹⁶ See reference 2, p. 547.

¹⁷ G. F. Neumark, *Phys. Rev.* **103**, 41 (1956).

the blue thermoluminescence. To some extent, the more energetic 1.5-ev photons may affect also the I_b transition, and thus give also quenching of the blue band, which is in accordance with our results (see Fig. 7).

The stimulation of the green glow peak by 1.2μ seems difficult to explain by model *a*. Model *b*, however, can account for the stimulation of the green band as well as for the quenching effects. In this case irradiation by 1 ev (1.2μ) raises electrons from the blue centers up into the conduction band. Part of these electrons may then be trapped in the green traps and thus enhance the green glow as shown in Fig. 7. On irradiation with shorter wavelengths the transitions I_g enter, and cause quenching of the green peak as described above. As stated above, the more energetic photons may to some extent affect also the transition I_b and thus cause also quenching of the blue peak. The free

holes created by transition I_g seem to favor recombination with electrons in the blue centers rather than further filling up of the almost full blue traps, which again causes a reduction in the blue glow.

In some crystals no enhancement of the green glow peak was observed on irradiation with 1.2μ . Such crystals usually exhibited a very weak blue component in the glow which further supports our model.

The results seem, therefore, to be better explained by model *b*. More experimental work seems, however, to be needed before final decision about the correct model is made.

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Measurements of Equilibrium Vacancy Concentrations in Aluminum*

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Measurements of change in length and change in lattice parameter were made at identical temperatures on 99.995% aluminum in the temperature range 229 to 656°C. Length changes, ΔL , were measured on an unconstrained horizontal bar sample using a rigid pair of filar micrometer microscopes. X-ray lattice parameter changes, Δa , were observed using a high-angle, back-reflection, rotating-single-crystal technique. The measurements are compared to earlier work. The relative expansions $\Delta L/L$ and $\Delta a/a$ were equal within about $1:10^5$ from 229 to 415°C. At higher temperatures additional atomic sites were found to be generated: the difference between the two expansions could be represented by $3(\Delta L/L - \Delta a/a) = \exp(2.4) \exp(-0.76 \text{ ev}/kT)$. At the melting point (660°C) the equilibrium concentration of additional sites is $3(\Delta L/L - \Delta a/a) = 9.4 \times 10^{-4}$. This result is independent of the detailed

nature of the defects, for example, the lattice relaxation or degree of association. The nature of the defects is considered and it is concluded that they are predominantly lattice vacancies; it is estimated that the divacancy contribution at the melting point may well be less than about 15%, corresponding to a divacancy binding energy ≤ 0.25 ev. The observed formation energy agrees with the values obtained by quenching techniques and by interpretation of the high-temperature electrical resistivity of identical material by Simmons and Balluffi. The present work is the first direct measurement of formation entropy; the value is near that expected from theoretical considerations. The contribution of the thermally generated defects to other physical properties at high temperatures is considered briefly.

I. INTRODUCTION

THE experimental determination of the predominant atomic defects present in thermal equilibrium in metals has proven to be a difficult problem. Even though the general thermodynamic theory of point defects is well developed, experiment has not yet established the nature and concentrations of the defects in a completely satisfactory way.^{1,2} The expected equilibrium atomic fraction of the j th type

of atomic defect may be written as

$$c = g_j \exp(-G_j^f/kT) = g_j \exp(S_j^f/k) \exp(-E_j^f/kT), \quad (1)$$

where G_j^f , S_j^f and E_j^f are, respectively, the free energy of formation, the entropy of formation, both exclusive of the configurational entropy, and the energy of formation. g_j is a constant geometrical factor which depends upon the number of ways that the defect can be orientated in the lattice. Theoretical estimates of S_j^f and E_j^f for various defects indicate that vacant lattice sites are probably the predominant defects present in close-packed metals, with concentrations in the range 10^{-8} to 10^{-4} at temperatures near the melting point.³

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¹ See the review papers in: *Impurities and Imperfections* (American Society for Metals, Cleveland, 1955); *Vacancies and Other Point Defects in Metals and Alloys* (The Institute of Metals, London, 1958).

² R. Feder and A. S. Nowick, *Phys. Rev.* **109**, 1959 (1958).

³ F. Seitz, in *Phase Transformation in Solids* (John Wiley & Sons, Inc., New York, 1951), p. 77.