

## Fluorescence of Cubic ZnS:Cl Crystals

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A series of fluorescence spectra (between 10°K and 300°K) and thermoluminescence measurements have been performed on self-activated cubic ZnS crystals prepared by two different methods. The vacuum-grown crystals (type I) show two series of edge emission lines (*A* and *B*) and a broad-band blue emission (self-activated). Thermoluminescence results indicate the presence of three traps. Crystals grown in H<sub>2</sub>S-HCl atmosphere (type II) show only the long-wavelength series of edge emission lines (*B*), the same blue emission and, at low temperature, a weaker broad-band emission at an intermediate wavelength. The thermoluminescence results indicate the presence of only one trap.

Using only the defects known to be present (Cl substituted at S sites, S vacancies, and Zn vacancies) and the decay of excitons, a model is proposed to account for the observed luminescent processes.

### 1. INTRODUCTION

THE fluorescent properties of pure ZnS and ZnS:Cl have been studied extensively over the last decade. A recent summary of the experimental work and interpretation has been published by Van Gool.<sup>1</sup> All the past work has been carried out on powders prepared under a variety of conditions. In this paper we shall report measurements made on two types of single crystals whose structure, in one case, is reversed cubic and, in the other, pure cubic.

It is well known that pure and Cl-coactivated crystals have a characteristic broad-band emission in the blue region of the spectrum which has often been referred to as "self-activated" (SA) emission. At low temperatures under excitation in the region of 3000 Å most crystals show a complex emission between 3200 Å and 3600 Å also. This was first discovered by Kroger<sup>2</sup> on ZnS powders and is usually referred to as "edge emission" (EE). So far, it has not been reported in single-crystal specimens of zinc sulfide.

A similar emission occurs in CdS crystals and has recently received extensive examination.<sup>3-6</sup> The similarities and differences between the two cases will be discussed. However, it is to be remembered that CdS occurs only in hexagonal form. The different symmetry and band structure introduce essential differences, such as the polarization of emission which is absent in cubic ZnS. We have attempted to correlate the optical energies of edge emission lines with estimates of the band gap and depths of traps obtained from thermoluminescence experiments.

<sup>1</sup> W. Van Gool, thesis, University of Amsterdam, January, 1961 (unpublished).

<sup>2</sup> F. A. Kroger, *Physica* **7**, 1 (1940).

<sup>3</sup> L. S. Pedrotti and D. C. Reynolds, *Phys. Rev.* **119**, 1897 (1960); **120**, 1664 (1960).

<sup>4</sup> C. C. Klick, *J. Phys. Chem.* **57**, 776 (1953).

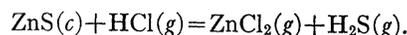
<sup>5</sup> D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **116**, 573 (1960).

<sup>6</sup> J. L. Birman, H. Samelson, and A. Lempicki, *Gen. Telephone & Electronics Res. Devel. J.* **1**, 2 (1961).

### 2. EXPERIMENTAL

#### 2.1 Materials

The ZnS crystals used in these experiments were grown by two different methods. Those of type I were the result of a controlled sublimation of zinc sulfide in an evacuated quartz tube, as described in a previous paper.<sup>7</sup> Those of type II were grown by a chemical transport process utilizing the reaction



This will be described in detail at a later time.

These two types of crystals can be compared with regard to their crystal structure and chemistry. Structurally, crystals of type I are designated as reversed cubic. That is to say, that the normal stacking sequence *ABCABC*... is interrupted at random intervals by a reversal to a sequence *ABCBACBA*... and this continues to the next reversal. Crystals of type II have a normal uninterrupted three-layer sequence. These two types are easily distinguished by a back reflection Laue x-ray photograph, those of type I displaying a spot pattern with sixfold symmetry and those of type II showing only a threefold symmetry.

Chemically, one can compare these on the basis of the type of defect to be expected from the growth conditions and from the impurities found by chemical and spectrographic analysis. In both types of crystals, the cation impurities exceed a few parts per million only in the case of silicon, and this seems to be accidental, as is discussed in reference 7. Of the customary activators and killers, copper appears in the greatest concentration and this never exceeds three parts per million. Of the cations, only chlorine was looked for. In the type I crystals, its concentration varies from 500 to 600 parts per million, and in the type II crystals from 200 to 1000 parts per million. The chlorine values are given in Table I; they were obtained from samples of crystals from the same run as the crystals listed in the table.

<sup>7</sup> H. Samelson, *J. Appl. Phys.* **32**, 309 (1961).

TABLE I. Summary of the properties of the crystals studied.

	Edge emission	Fluorescence	Traps (ev)	Chemical analysis % Cl
Type I				
1	A, B	SA	0.17, 0.21, 0.30	0.015
2	A, B	SA	0.17, 0.21, 0.30	0.018
3	A, B	SA	0.18, 0.22, 0.30	0.015
Type II				
5	B	SA, SAL	0.22	0.032
6	B	SA, SAL	0.23	0.030
7	B	SA, SAL	0.21	0.088
8	B (weak)	SA, SAL	0.21	0.009
9	None	SA, SAL	0.22	0.009
10	B	SA, SAL	0.22	0.026
11	B	SA, SAL	0.22	0.020

The type I crystals were grown in a vacuum and the principal defects to be expected are zinc and sulfur vacancies. From the analytical results on chlorine, we would also expect to find chlorine present at sulfur sites or interstitially.

The type II crystals are grown in the presence of approximately 1.3 atm. of HCl and 0.2 atm. of H<sub>2</sub>S. These conditions would be expected to produce zinc vacancies and chlorine at sulfur sites as Kroger<sup>8</sup> has reported.

## 2.2 Apparatus

The fluorescence measurements were carried out from room temperature down to 10°K using an all-metal liquid helium Dewar. The samples were attached to a holder by means of silver paint and the assembly cooled by conduction. The temperature of the holder was measured by a Cu-Au:Co or Cu-constantan thermocouple placed near the crystal. Quartz windows were

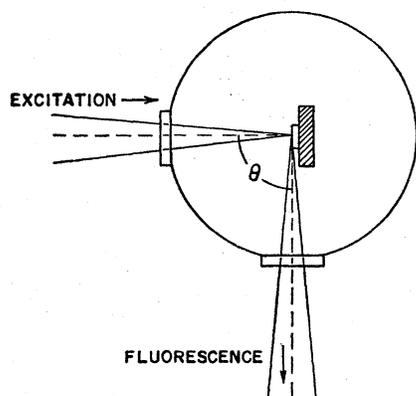


FIG. 1. Geometry of the experimental setup for fluorescence measurements.  $\theta$  is the angle between the crystal face and the excitation beam.

<sup>8</sup> F. A. Kroger, *Physica* 22, 637 (1956).

used to permit the entry of the exciting radiation and for the observation of the fluorescence. Figure 1 shows the arrangement schematically. The sample holder could be rotated inside the Dewar about a vertical axis, but for most measurements the  $\theta=90^\circ$  orientation was used. The exciting radiation was obtained from a high-pressure (HB0500) Osram Hg arc and passed through a single quartz prism Leiss monochromator. When looking at rather low-intensity fluorescence, the low purity of the output of the Leiss monochromator represents a problem. This is especially serious in the region of the edge emission where intense mercury lines are present. The  $\theta=90^\circ$  orientation minimizes the interference of these lines because the radiation is specularly reflected towards the monochromator. On the other hand, care must be taken to position the exciting beam close to the edge of the specimen since otherwise most of the short-wavelength emission may be self-absorbed. The fluorescent radiation was focused on the slit of a Bausch & Lomb 0.5-m grating spectrometer equipped with an automatic drive. Unless otherwise stated, the 3130-A line of mercury was used for excitation and the spectral band width of the analyzing instrument was 8 Å. A 1P28 photomultiplier was used as a detector.

The lowest temperature that could be reached with the Dewar was about 10°K. The rate of warming up after evaporating the liquid helium was slow enough to obtain a whole spectrogram with a temperature variation of 1 or 2°K. Stable temperature measurements could be made at liquid nitrogen temperature and about 10° below by pumping on the liquid nitrogen.

Thermoluminescence measurements were used to determine the depth of electron traps in these crystals.

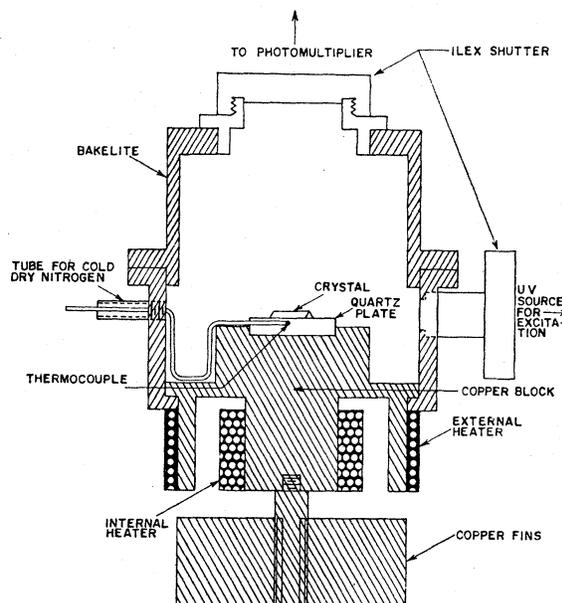


FIG. 2. Apparatus used for the measurement of thermoluminescence.

In this type of experiment, the crystal is excited by 3650-Å radiation while it is at a low temperature. After the excitation is removed, the crystal is warmed at a uniform rate. This provides sufficient thermal energy to release the electrons from the traps, and the number of subsequent radiative recombinations is measured as a function of the temperature.

The apparatus used for these experiments is shown in Fig. 2. The crystal is attached to a  $\frac{1}{16}$ -in. thick quartz plate by silver paint and the plate is set in a shallow recess in the copper block. The temperature is measured by copper-constantan thermocouple set into a hole drilled in the quartz plate so that the junction is located directly beneath the crystal. The copper fins indicated in the figure are used only to facilitate cooling and are removed before the warming. The light output is measured by a 6217 photomultiplier and the light and the temperature are simultaneously recorded by a dual recorder. In these experiments the heaters are adjusted to provide a linear warming rate of  $1^\circ\text{C}/\text{sec}$  from 90 to  $350^\circ\text{K}$ .

### 3. RESULTS

#### 3.1 Thermoluminescence

Typical thermoluminescence curves of type I (crystal No. 1) and type II (crystal No. 7) crystals are shown in Fig. 3. The curve of the type II crystals is considerably simpler, in that it shows only one peak at about  $165^\circ\text{K}$ . That of the type I crystal shows several peaks with the principal one usually at  $125^\circ\text{K}$ , and the others at  $160^\circ$  and  $230^\circ\text{K}$ . The peak intensity of the type II crystals is at least an order of magnitude greater than that of the type I crystals for an equivalent weight of sample.

#### 3.2 Self-Activated Emission

A typical spectral distribution for type I crystals is illustrated in Fig. 4. It will be noticed that at room

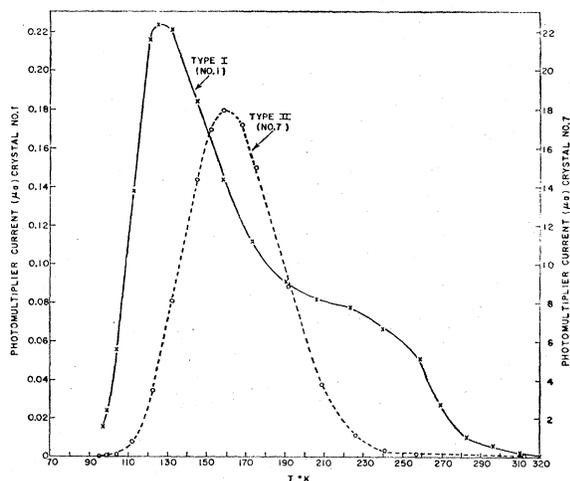


FIG. 3. Typical thermoluminescence curves for the two types of crystals.

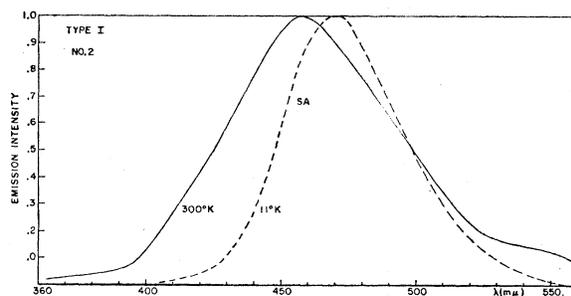


FIG. 4. Self-activated emission of type I crystal at  $300^\circ\text{K}$  and  $11^\circ\text{K}$ . Normalized intensity. Excitation wavelength 3130 Å.

temperature, the band shows evidence of a subsidiary emission at the long-wavelength end.<sup>9</sup> This characteristic is not universal. Other type I crystals do not show evidence of a separate emission in the green region. From the analytical results, it is doubtful that this band may be due to Cu impurities since the green ZnS:Cu emission occurs at much higher Cu concentrations<sup>10</sup> than are likely here. We can offer no explanation of its origin. By examining the emission over a temperature range from  $300^\circ$  to  $10^\circ\text{K}$  there is no evidence whatever of the existence of any other structure or subsidiary bands.

The emissions of type II specimens are shown in Fig. 5. It is difficult to make quantitative comparisons of intensity of luminescence on different crystals (effect of shape, size, surface, etc.). Nevertheless, the type II specimens are easily an order of magnitude brighter than the type I specimens. Here, it is seen that at low temperatures a separate band can be distinguished on the short-wavelength side. Other workers have also reported the existence of an emission band in this

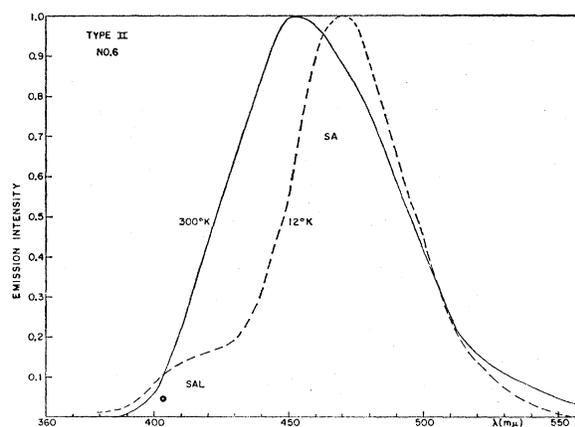


FIG. 5. Self-activated emission of type II crystal at  $300^\circ\text{K}$  and  $12^\circ\text{K}$ . Normalized intensity. Excitation wavelength 3130 Å.

<sup>9</sup> If the sensitivity of the photomultiplier was taken into account, this would become even more pronounced since the tube is about twice as sensitive at 4500 Å as at 5500 Å.

<sup>10</sup> R. Bowers and N. T. Melamed, *Phys. Rev.* **99**, 1781 (1955).

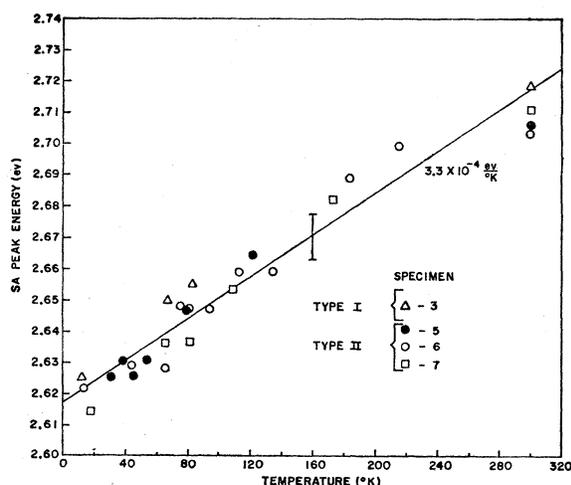


FIG. 6. Temperature dependence of SA peak.

region.<sup>1,11</sup> In accordance with their notation this is designated as the SAL band. It is by no means certain that these SAL emissions are the same. The SAL emission in our crystals is not excited by 3650 Å radiation.

It is of great interest to compare the single emission of the type I crystals with the SA emission of the type II crystals. Their over-all characteristics are very similar, as evidenced by the data presented in Figs. 6 and 7. Figure 6 gives a plot of the peak SA position as function temperature. It is seen that points for both type crystals fall on approximately the same line. Figure 7 shows the width of the emission bands (normalized to unity at

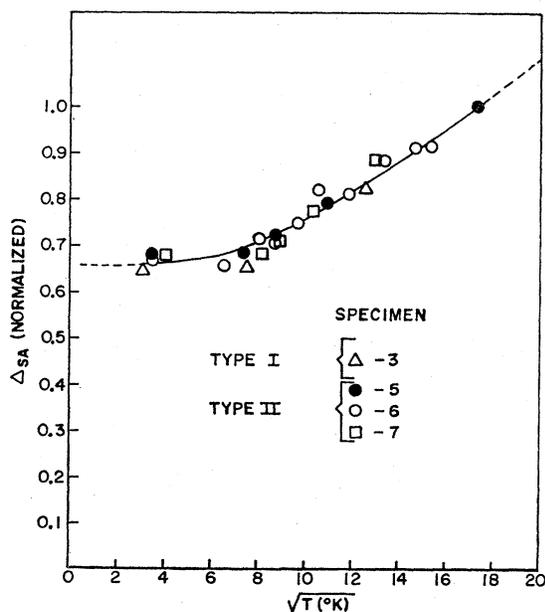


FIG. 7. Half-width of SA band as a function of temperature.

<sup>11</sup> R. W. A. Gill and S. Rothschild, Enlarged Abstracts, Electrochem. Soc. Meeting, Chicago, 1960 and Indianapolis, 1961 (unpublished).

300°K) as a function of the square root of the temperature. This type of plot can be used to determine the vibrational frequency of the excited state of the center if a configuration coordinate model is adopted (see Sec. 4.3).<sup>4</sup> Again, it is apparent that there are no differences between the behavior of the main blue emission bands in the two types of crystals.

An important point which we want to stress is that the shift of SA peak with temperature is not due to the growth of SAL band. In fact, the SAL band disappears completely at about 120°K—well before the SA band has broadened sufficiently to obscure the picture.

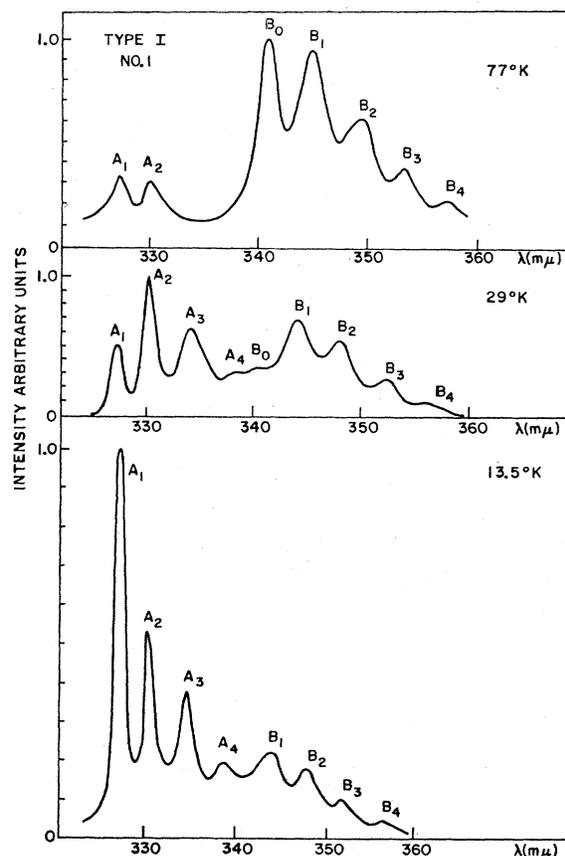


FIG. 8. Edge emission of type I crystal at three temperatures. Intensity scales not comparable. Excitation wavelength 3130 Å.

Moreover, the same shift of SA occurs in type-I crystals which do not exhibit SAL emission.

### 3.3 Edge Emission

Using fundamental excitation at low temperatures, we observe the edge emission (EE) first reported by Kroger<sup>2</sup> on powder samples. EE occurs in both type I and type II crystals, but the differences in the spectra are rather striking. Figures 8 and 9 represent typical results for both types. We shall first describe type II which gives rise to a simpler pattern.

At about liquid nitrogen temperature the emission consists of 4 or 5 lines which are not well resolved (Fig. 9). The highest energy line  $B_0$  is invariably of lower intensity than the next line  $B_1$ . As the temperature is increased, the pattern begins to wash out and eventually disappears at about 120°K. When the temperature is decreased below liquid nitrogen, the  $B_0$  line degenerates into a shoulder and disappears at about 40°K. The other lines become narrower and increase in intensity.

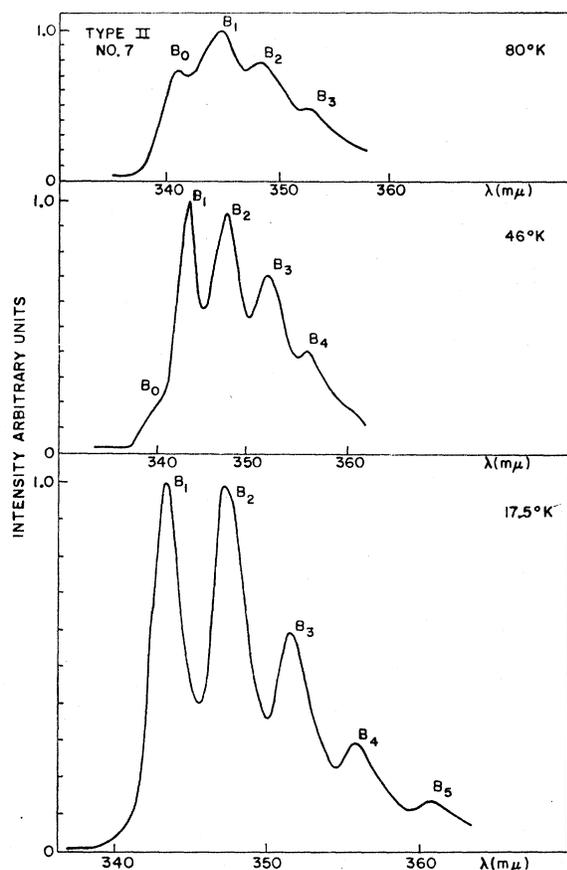


FIG. 9. Edge emission of type II crystal at three temperatures. Intensity scales not comparable. Excitation wavelength 3130 Å.

The EE for a type I crystal is shown in Fig. 8. Two separate sets of lines become distinguishable at about 80°K. The long-wavelength or  $B$  set is much less intense than in type II crystals, but otherwise shows some similar characteristics. One of the differences concerns the line  $B_0$  which occurs at about the same energy as in type II crystals, but is here the most intense line of the set. At shorter wavelength, a second set of lines ( $A$ ) just begins to appear at about 80°K. As the temperature is decreased, the  $B_0$  line rapidly decreases in intensity, but still can be detected at 25°K. Its behavior, therefore, is slightly different from the

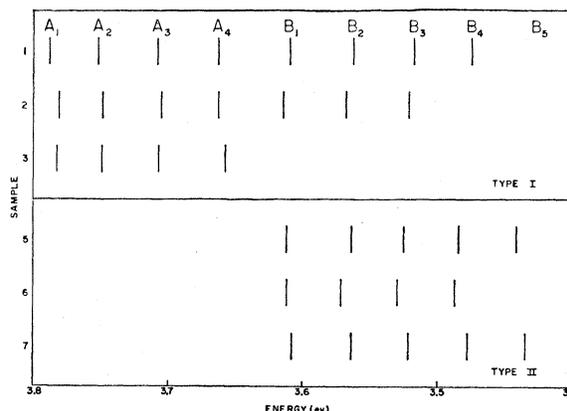


FIG. 10. Positions of the edge emission lines at 10°K.

analogous line in type II crystals. The remaining  $B$  lines behave like those of type II crystals.

The temperature dependence of the  $A$  set is more complicated. At the lowest temperatures which could be reached in our cryostat ( $\sim 10^\circ\text{K}$ ), a well-defined series of sharp lines were observed (Fig. 8). When the temperature is increased, the dominant  $A_1$  line shows the most rapid decrease in intensity. In fact, it becomes less intense than the  $A_2$  line. At about 70°K the balance is again restored with  $A_1$  being equal or slightly larger than  $A_2$ . By this time, however, the intensity is very low. Figure 10 gives a comparison of the line positions for six specimens. The shifts in the positions of the  $A_1$  and  $B_1$  lines have been determined and are given in Figs. 11 and 12. It is seen that the energy of the  $A_1$  line (Fig. 11) is essentially constant except for a slight tendency to decrease near the higher temperature end of the range. The  $B_1$  line (Fig. 12) energy has a steady negative temperature coefficient of  $1.7 \times 10^{-4} \text{ ev}/^\circ\text{K}$ . The spacing between all the  $A$  and  $B$  lines, except the  $A_1-A_2$  pair, is  $(44 \pm 2) \times 10^{-3} \text{ ev}$ . For the  $A_1-A_2$  spacing the energy is  $(34 \pm 3) \times 10^{-3} \text{ ev}$ . A similar

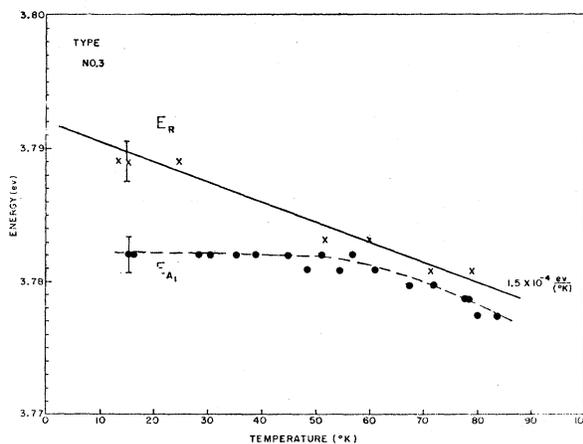


FIG. 11. Position of  $A_1$  edge emission line (●) and reflection peak (X) as a function of temperature for type-I crystal.

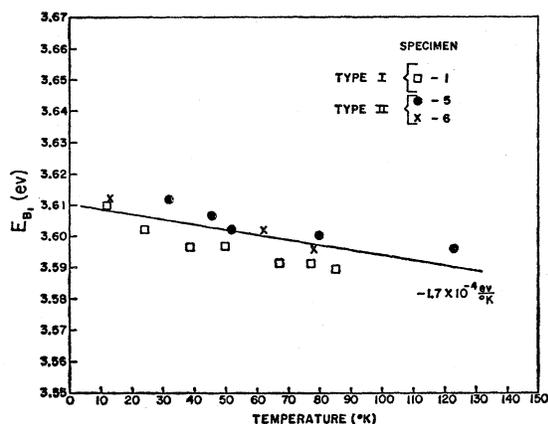


FIG. 12. Temperature dependence of the energy of the  $B_1$  edge emission line.

decrease in spacing between the first two peaks, as compared to the others, in the blue edge emission of CdS can be found by examining the data of Reynolds and Pedrotti.<sup>3</sup>

The energy of the  $A_1$  line appears to fall very close to the low-energy peak observed in reflection measurements.<sup>6</sup> This peak is due to an exciton originating in the uppermost valence band. In order to check this more precisely, reflection measurements were performed on specimen 3, and the positions of the reflection peak ( $E_R$ ) are given in Fig. 11. We see that at high temperatures there is an excellent agreement between the two energies. At low temperatures, a difference of about  $8 \times 10^{-3}$  eV is observed.

#### 4. DISCUSSION

##### 4.1 Thermoluminescence

The interpretation of thermoluminescence curves has been discussed in the literature<sup>12-16</sup> and it is still a matter of some uncertainty. The most extensive work is that of Hoogenstraaten,<sup>16</sup> and the following discussion is based mostly on his work. The glow peak found in type II crystals has been associated with the trap caused by the substitution of chlorine at a sulfur site and it is the determination of this energy level that will be made. As Hoogenstraaten points out, and as has been found in the present case when trying to determine the trap depth by the method of using the initial rise of the glow curve, the trap is distributed in depth and one can determine only the average value of this depth from the temperature of the maximum of the glow curve. This is more reliable in the case of a single peak, as is found in the type II crystals, than in the case of the multiple peaks of the type I crystals.

Randall and Wilkins<sup>12</sup> established a relationship between the depth of the trap and the temperature of the glow maximum that is given by Eq. (1).

$$E(\text{ev}) = T_m(^{\circ}\text{K})/C, \quad (1)$$

where  $E$  is the depth of the trap in electron volts,  $T_m$  is the temperature of the glow maximum, and  $C$  is a constant to which they assign a value of 500. The region of validity of this formula for traps between 0.2 and 1.0 eV and heating rates of 0.1 to 3 degs/sec is based on an escape frequency from the traps of  $10^8$  to  $10^9$  sec<sup>-1</sup>. Hoogenstraaten, studying the same trap in ZnS:Cu:Cl powders, concluded that the constant  $C$  in Eq. (1) should be 740. This is based on experiments done with various heating rates and with mixed crystals of CdS and ZnS. Kroger,<sup>8</sup> from thermoconductivity data, concludes that the larger value for the constant is more consistent with his experiments. Using this value of the constant in Eq. (1), the trap depths listed in Table I were obtained. The value of 0.22 eV found for the trap associated with chlorine substituted at a sulfur site in the type II crystals is in reasonable agreement with the values found by Kroger<sup>8</sup> on crystals and by Hoogenstraaten<sup>16</sup> and Bube<sup>17</sup> on powders having a cubic structure.

The shallower trap depth values found in the type I crystals probably represent a trap quite different from the 0.22-eV trap found in the type II crystals, despite the fact that nearly the same amount of chlorine is found in both types of crystals. The complex structure of the type-I crystal glow curve can be partially broken down by using the method of decayed glow curves. From this sort of experiment, it is found that in the type I crystals there is a trap at about 0.21 eV in addition to the 0.17- and 0.30-eV traps. It is likely that the 0.17-eV trap, which will have to be considered later, is due to a sulfur vacancy. From the conditions of preparation of these crystals, such a defect would be expected as has been pointed out earlier. The 0.21-eV trap is assigned to chlorine substituted at a sulfur site; the chlorine is known to be present from chemical analysis. The 0.30-eV trap has no assignment at this time.

The concentration of traps as measured by the intensity of the glow peak is lower in the type I than in the type II crystals. This is particularly true of the 0.22-eV trap. In view of the results of chemical analysis that show the chlorine concentration to be no more than three times greater in type II crystals than in type I crystals, it is surprising to find a trap concentration in type II crystals of the order of 100 times greater than in type I crystals. It must be pointed out that a low concentration of luminescent recombination centers can independently limit the intensity of the glow peak. The type I crystals were grown under conditions that would introduce a much lower concen-

<sup>12</sup> J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) **A184**, 366 (1945).

<sup>13</sup> R. H. Bube, Phys. Rev. **80**, 655 (1950).

<sup>14</sup> A. Halperin and A. A. Brauer, Phys. Rev. **117**, 408 (1960).

<sup>15</sup> H. Arbell and A. Halperin, Phys. Rev. **117**, 45 (1960).

<sup>16</sup> W. Hoogenstraaten, Philips Research Repts. **13**, 515 (1958).

<sup>17</sup> R. A. Bube, J. Chem. Phys. **20**, 708 (1952).

tration of zinc vacancies which we believe to be the luminescent recombination center. Hence, in the type I crystals, the apparently low concentration of chlorine traps may reflect a low concentration of recombination centers.

Summarizing, the thermoluminescence experiments indicate the existence of three traps in the type I crystals at 0.17, 0.21, and 0.30 eV, and one in the type II crystals at 0.22 eV. The intermediate trap is assigned to chlorine at a sulfur site and the shallowest one to a sulfur vacancy; no assignment to a specific defect is made for the third trap. These experiments also indicate that in type I crystals the concentration of Cl donors greatly exceeds the concentration of zinc vacancies.

#### 4.2 Edge Emission

The evidence presented in Sec. 3 shows that conditions of preparation have a very marked effect on the edge emission, especially the short-wavelength set of lines. As for the long-wavelength set present in all crystals, they seem to be analogous to the green edge emission lines of CdS. Their positions relative to the absorption edge, and general shape are very similar. Since no polarization phenomena are observed in cubic ZnS crystals, we cannot perform the experiments that led us to believe that the green emission of CdS is caused by a recombination of trapped electrons and free holes.<sup>6</sup> It should also be noted that none of the wavelengths associated with the *A* or *B* edge emissions is found during a thermoluminescence experiment. This is consistent with an assignment of these emissions to a recombination with a free hole since these are present only during excitation. If we assume this to be true in ZnS, then the electron trap level must be below the conduction band by more than the energy separation  $A_1 - B_1$  (approximately 0.17 eV). One of the reasons for choosing the  $B_1$  rather than the  $B_0$  lines as the leading member of the *B* set is connected with the different temperature dependence of the  $B_0$  lines from the rest of the set. It is generally assumed that the individual lines located on the soft energy side of the first line are due to a phonon emission process. Indeed, their separation is consistent with the value of  $43.2 \times 10^{-3}$  or  $45.5 \times 10^{-3}$  eV reported<sup>18</sup> for a longitudinal optical phonon.

At present, we have only a partial explanation for the behavior and origin of the  $B_0$  lines in both types I and type II crystals. It can be safely concluded that they are not due to phonon absorption processes, because the probability of such an event should be vastly smaller than for emission, and yet the intensities of  $B_0$  are comparable to  $B_2, B_3 \dots$  at least at 80°K.

A distinct possibility exists that the *B* edge emission originates from two trap levels. In fact, the glow curve results indicate that the dominant traps in type I crystals are at 0.17 eV and 0.22 eV, and only 0.22 in

type II. The difference of 0.05 eV is close enough to the separation  $B_0 - B_1$  to be experimentally indistinguishable, and suggests that the  $B_0$  line is due to a transition from the 0.17-eV trap to the valence band. The concentration of the shallower trap (0.17 eV), relative to the deeper ones, is greater in type I crystals which show prominent  $B_0$  lines. According to this interpretation the 0.22-eV trap will always correspond to the  $B_1$  lines in all crystals. The question remains, then, why do the  $B_0$  lines decrease so fast below liquid nitrogen temperature. This may reflect a change in the relative population of the 0.17- and 0.22-eV traps or in the relative capture cross sections of these traps as the temperature decreases, but a more precise answer cannot be given from these experiments.

We now want to discuss the short-wavelength set (*A*) of edge emission lines. We have remarked before that, depending on the temperature, the  $A_1$  line falls between zero and  $8 \times 10^{-3}$  eV from the reflection maximum attributed to an exciton. Let us therefore assume that the *A* set is due to exciton annihilation with or without phonon emission. We have to explain (a) the  $8 \times 10^{-3}$  eV difference in energy at low temperature, (b) the temperature dependence of the  $A_1$  line, and (c) the smaller spacing of  $A_1 - A_2$  compared to the spacing of other lines.

Nothing is known concerning the detailed nature of the absorption process occurring along the tail of the absorption spectrum in ZnS. If we assume that the processes are similar to those occurring in CdS,<sup>19</sup> then at the threshold of absorption direct excitons are formed with phonon cooperation. The minimum energy necessary for such a process would be  $E_{A_1} - E_p$  where  $E_{A_1}$  corresponds to the lowest energy exciton, and by our assumption the first line  $A_1$ , and  $E_p$  is the phonon energy.  $E_{A_1} - E_p$  should then correspond exactly to  $E_{A_2}$ . At the lowest temperatures there are no phonons and the absorption edge should therefore start at  $E_{A_1}$ . From the data of Thomas, Hopfield, and Powers<sup>19</sup> on CdS, it appears that the absorption constant can change very rapidly on approaching the exciton energy. Hence, a pronounced self-absorption of the fluorescence can be expected over the energy range covered by the  $A_1$  line. This absorption edge can distort the line and effectively shift the peak towards lower energy. If this is the case, then the reduced spacing  $E_{A_1} - E_{A_2}$  ( $34 \times 10^{-3}$  eV instead of  $44 \times 10^{-3}$  eV) can be attributed to such a distortion. This  $10 \times 10^{-3}$  eV difference in the spacings is very close to the measured difference between the position of the  $A_1$  line and the reflection peak (Fig. 11).

As the temperature is raised new phonon-assisted absorption processes start to occur at lower energies. We attribute the large relative decrease in the intensity of  $A_1$  to a rapid rise of the absorption constant over the energy range  $E_{A_1} - E_{A_2}$ . According to data of Thomas, Hopfield, and Powers,<sup>19</sup> the absorption con-

<sup>18</sup> F. A. Kroger and H. J. G. Meyer, *Physica* **20**, 1149 (1954).

<sup>19</sup> D. G. Thomas, J. J. Hopfield, and M. Powers, *Phys. Rev.* **119**, 570 (1960).

stant at the midway point between  $A_1$  and  $A_2$  can rise by an order of magnitude between 20°K and 55°K. The temperature quench of the entire series of  $A$  lines is thus a composite effect of absorption edge shift and occurrence of nonradiative exciton annihilation at higher temperatures.<sup>20</sup> It should be mentioned that an alternative explanation involving transverse optical phonons is perhaps possible. The observed spacing  $E_{A_1} - E_{A_2}$  agrees well with values of  $33.9 \times 10^{-3}$  and  $35.4 \times 10^{-3}$  eV reported for this phonon. However, as pointed out by Kroger and Meyer,<sup>17</sup> interaction with longitudinal vibrations is more likely where polar forces are sufficiently large. Also, the uniqueness of this particular spacing, the temperature dependence of the  $A_1$  line, and the low-temperature discrepancy with reflection peak would not be easy to account for.

The absence of the  $A$  emission in the type II crystals may be due to a much higher probability of non-radiative annihilation of the exciton as a consequence of the much greater defect concentration in these crystals.

### 4.3 Self-Activated Emission

Van Gool<sup>1</sup> has recently summarized the experimental facts and interpretations concerning the SA emission in ZnS. The conclusions are rather incomplete, since they cover the work of many investigators who performed experiments under varying conditions of preparation, excitation, temperature, etc. The main questions one would like to answer are (1) how many distinct bands of SA are there, and what is their temperature dependence; (2) to what extent is the emission dependent on the coactivator; and (3) are the results comparable with center models proposed in the literature (Zn vacancy, associated Zn vacancy and coactivator, coactivator alone). The last is discussed in more detail in Sec. 5.

Our work indicates clearly that both types of crystals show the same SA band. Depending upon the growth condition, another band (SAL) may also be observed. The identity of the SA band in the various specimens is indicated by Figs. 6 and 7. If we assume that the luminescent center can be represented by a configuration coordinate, then, according to the work of Williams and Hebb,<sup>21</sup> and Klick,<sup>4</sup> the emission half-width should approach a constant at low temperatures. This, indeed, is the case as shown in Fig. 7. From the curves, one can estimate (see reference 4) the vibrational energy in the excited state of the center which turns out to be  $6 \times 10^{12}$  sec<sup>-1</sup> or  $24 \times 10^{-3}$  eV. When we examine the shapes of the blue emission spectra, it appears that they are not quite symmetrical but have an extended long-wavelength tail. This is very similar

to the spectra of Mn in various lattices. The asymmetry of the Mn emission bands has been extensively studied by Klick and Schulman,<sup>22</sup> who concluded that it is consistent with a configuration coordinate model. Since there is nothing that distinguishes the SA bands (except intensity) in type I and type II crystals, we conclude that the same center is responsible.

The SAL band has not been reported in single crystals, but Rothschild and Gill<sup>11</sup> have observed analogous emissions in Zn: CdS powders. They claim that it occurs whenever conditions prevail that would lower the concentration of halogen, and attribute it to uncoactivated centers presumably Zn vacancies. Our analytical results (Table I) show that the actual Cl concentrations are not significantly different in type I and type II crystals. However, as pointed out before, type II crystals probably contain a far larger concentration of Zn vacancies. The ratio Cl/ $V_{Zn}$  is therefore smaller for type II than for type I, and the hypothesis of Rothschild and Gill is not in disagreement with our results.

### 5. MODEL

We would like now to discuss a model which we propose for the emissions described in this paper. The approximate placement of various energy levels will be made by using plausibility arguments. Having done this, we shall try to fit the optical and thermoluminescence data to the energy scheme. The conditions of preparation of the type I and type II crystals are such that only levels due to Zn and S vacancies and Cl will be considered.

Cl: The replacement of a sulfur ion by chlorine has been discussed many times.<sup>1,8,16</sup> We accept the model of Cl as being essentially a donor-like center, i.e., having one excess, rather loosely bound electron. The level will be located 0.22 eV below the conduction band.

$V_S$ : The removal of a neutral sulfur atom leaves a defect with two bound electrons. The ionization of the first electron should require about the same order of energy as the Cl donor. Hoogenstraaten places the  $V_S$  trap at about 0.25 eV below the conduction band; however, 0.17 eV is more consistent with our data.

$V_{Zn}$ : The removal of a neutral Zn atom leaves the center with a deficiency of two electrons. By supplying either one or two electrons to this center, we obtain two recombination levels designated as  $V_{Zn}'$  and  $V_{Zn}''$ . This is illustrated in Fig. 13. From center  $V_{Zn}''$ , one electron can be excited into the conduction band. The excitation of a second electron requires more energy and corresponds to  $V_{Zn}'$ .

The occurrence of the various defects and their concentrations will depend upon the preparation of the crystals.

If the Cl concentration exceeds the Zn-vacancy concentration by a factor of two or more, all the

<sup>20</sup> The nonradiative processes must also play a role since self-absorption would not be expected to occur at energies as low as  $E_{A_3}$  and  $E_{A_4}$ .

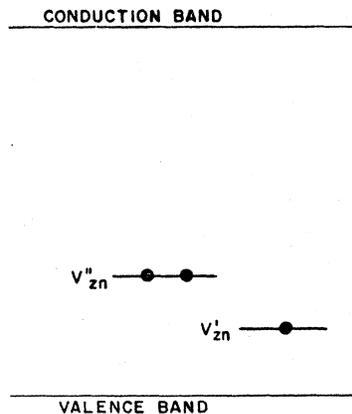
<sup>21</sup> F. E. Williams and M. H. Hebb, Phys. Rev. **84**, 1181 (1951).

<sup>22</sup> C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. **42**, 910 (1952).

vacancies will be in the  $V_{Zn}''$  state. Phosphor powders prepared under conditions approximately the same as those of the growth of type II crystals have been found by Bowers and Melamed<sup>10</sup> to be diamagnetic, but paramagnetism has been observed under excitation.<sup>23</sup> This is consistent with only  $V_{Zn}''$  centers and empty Cl traps present in the absence of excitation. At Zn vacancy concentration below one half the Cl concentration, one would expect  $V_{Zn}''$  centers to be present together with un-ionized Cl traps. The thermoluminescence data indicate that this may be the situation in type I crystals. Also, the probability of association of chlorine trap-zinc vacancy centers should be reduced.

Upon excitation at 3650 Å, both types of crystals show the same SA emission. This has been ascribed by Kroger and Vink<sup>24</sup> to an excitation of an electron from the  $V_{Zn}''$  center to the conduction band and subsequent recombination. Excitation in the fundamental region leads to the same recombination path via the production of free holes and electrons. The SAL emission is somewhat more difficult to interpret. The pertinent facts are (a) it is observed only in type II crystals which have a relatively high concentration of Zn vacancies; (b) a greater excitation energy is required than for the SA emission; and (c) the emission occurs only at low temperature and decays with increasing temperature in the same manner as the  $B$  edge emission. A model which is consistent with these observations is one which involves a transition between an associated Cl donor and Zn vacancy. One would not expect this process to occur in type I crystals where association is improbable. The high excitation energy requirement indicates that an electron must be ionized from the  $V_{Zn}'$  center to

FIG. 13. Luminescent recombination centers arising from Zn vacancies: dots denote electrons.



<sup>23</sup> P. H. Karai and Y. Otomo, Phys. Rev. Letters 7, 17 (1961).  
<sup>24</sup> F. A. Kroger and H. J. Vink, J. Phys. Chem. 22, 250 (1954).

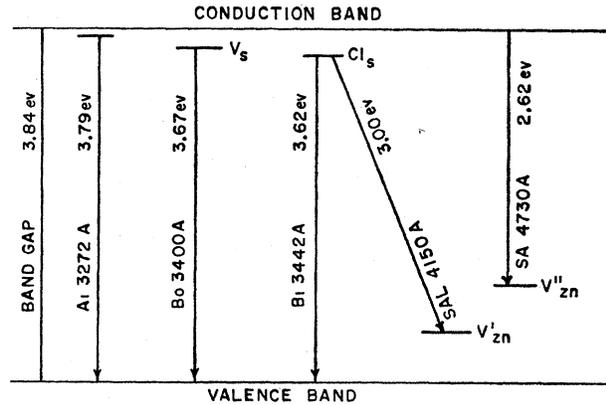


FIG. 14. Proposed energy level scheme for fluorescence of self-activated crystals of ZnS (cubic) at 10°K.

provide a recombination center for this emission. Finally, the similarity of the temperature dependence between SAL and  $B$  edge emission suggests that they have one level in common, namely, the Cl trap level.

The model for both  $A$  and  $B$  edge emission has already been given. Summarizing then, we attribute the  $B$  edge emission to a recombination between an electron in a trap due to a chlorine substituted at a sulfur site located 0.22 eV below the conduction band and a free hole in the valence band. Associated with this there is the  $B_0$  line that is due to a similar transition originating at a trap due to a sulfur vacancy located 0.17 eV below the conduction band. The  $A$  edge emission is attributed to phonon-assisted exciton annihilation. The SA emission is attributed to the recombination of a free electron and a hole trapped in a singly charged Zn vacancy and the SAL emission to the recombination of an electron trapped at a chlorine-substituted sulfur site and a hole trapped at an associated neutral Zn vacancy site.

This model accounts for the fluorescent emissions observed in these crystals using energy levels arising only from those crystal defects known to be present either from chemical analysis or from the conditions existing during the growth of these crystals. The energy-level diagram derived from these considerations is given in Fig. 14.

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