

## Excitation Spectra and Temperature Dependence of the Luminescence of ZnS Single Crystals

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The luminescence of ZnS:Cl and ZnS:Cu:Cl crystals was measured for the temperature region 80–500°K and for different wavelengths of exciting light. The behavior of the luminescence *versus* temperature curves differed from similar curves for powders reported in literature.

Excitation spectra were also obtained for the green and blue luminescence bands. These were found to consist of a complexity of fine bands. Each of the bands was found not to shift when varying the temperature of the crystal. The relative intensity of the bands near the absorption edge of the crystal, however, changed with temperature in such a way as to cause an apparent shift in the maximum of the excitation spectrum in this region.

### INTRODUCTION

THE term "excitation spectrum" is commonly used to describe, as a function of wavelength of exciting light, the relative luminescence intensity per unit of exciting energy *incident* on the surface of the phosphor. It differs from the "luminescence efficiency" which is defined as the luminescence intensity per unit of exciting energy *absorbed* in the crystal.

The dependence of the luminescence of ZnS on exciting light and on temperature has been the subject of many investigations. Garlick and Gibson<sup>1</sup> have found that the excitation spectrum of self-activated ZnS has a maximum at about the wavelength of the absorption edge of the crystal and shifts with increasing temperature towards longer wavelengths, with a temperature coefficient equal to that of the shift in the absorption edge. They have shown that such a shift should result in a decrease in luminescence with increasing temperature on excitation within the region of the lattice absorption, while a rise in luminescence on warming the crystal from low temperatures is to be expected when excited with light of longer wavelengths. This was found to fit well the experimental results obtained by Garlick and Gibson,<sup>1</sup> and also by Peyrou.<sup>2</sup>

Adirowitsch<sup>3</sup> did not accept this explanation. Instead, he based his calculations on simple assumptions as to the kinetics of the electron transitions involving the luminescence centers. On these grounds he has been able to show that on varying the temperature the luminescence should behave just as described above.

Adirowitsch has gone so far as to take this behavior as a criterion for the absorption edge which is often difficult to fix directly by optical absorption measurements.

The aforementioned experimental work<sup>1,2</sup> was carried out on powder samples. Single crystals were used in other investigations. Kröger<sup>4</sup> has recently measured the temperature dependence of the luminescence of

ZnS:Cl single crystals, and paid attention to the temperature quenching of the luminescence which is usually attributed to the release of the holes from the activator levels.<sup>5,6</sup>

Excitation spectra were also reported recently<sup>7,8</sup> for single crystals of ZnS. The maximum of the excitation spectrum was found in these works at about 3700 Å instead of below 3400 Å as reported by Garlick and Gibson.<sup>1</sup> Broser and Broser-Warminsky<sup>8</sup> attributed this maximum to an absorption band which they had observed at the same wavelength. This absorption band was found not to shift at all with temperature.

It was the aim of the present work to investigate in detail the dependence on temperature of the luminescence and the excitation spectra of ZnS. Single crystals were used throughout this work, as surface effects are less pronounced in single crystals compared to powder samples. In addition, powders would show the average of the many grains, and thus might mask important details revealed by single crystals.

### EXPERIMENTAL

The crystals used in the present work were grown by Hamilton, who used the Reynolds-Czyzak method with some modifications.<sup>9</sup> The crystals contained chlorine in concentration of about 100 parts per million and some of them contained copper in concentrations of up to 20 parts per million.<sup>10</sup> The latter showed some green luminescence in addition to the blue band. The green component was in most of the crystals very weak at liquid air temperature, but became more pronounced on raising the temperature of the crystal.

A mercury compact-source lamp in a quartz envelope (Mazda ME/D, 250w) in conjunction with a quartz

<sup>1</sup> G. F. J. Garlick and A. F. Gibson, *Nature* **161**, 359 (1948).

<sup>2</sup> Ch. Peyrou, *Ann. phys.* **3**, 459 (1948).

<sup>3</sup> E. I. Adirowitsch, *Einige Fragen Zur Theorie der Lumineszenz der Kristalle* (Akademie-Verlag, Berlin, 1953), Chap. 5.

<sup>4</sup> F. A. Kröger, *Physica* **22**, 637 (1956).

<sup>5</sup> H. A. Klasens, *Nature* **158**, 306 (1946).

<sup>6</sup> M. Schön, *Tech. Wiss. Abhandl. Osram-Ges.* **6**, 49 (1953).

<sup>7</sup> A. Lempicki, *J. Opt. Soc. Am.* **48**, 67 (1958).

<sup>8</sup> I. Broser and R. Broser-Warminsky, *Z. Elektrochem.* **61**, 209 (1957).

<sup>9</sup> D. R. Hamilton, *J. phys. radium* **17**, 797 (1956); *Brit. J. Appl. Phys.* **9**, 103 (1958).

<sup>10</sup> D. R. Hamilton (private communication). We are indebted to Dr. Hamilton for providing the crystals and for valuable information regarding the preparation of the crystals.

monochromator provided the monochromatic exciting radiation. An ultraviolet-transmitting filter (Corning 7-54) was inserted in the light path in order to reduce the stray-light in the monochromator. Effective spectral slit widths were kept in most of the measurements below 20 Å throughout the whole spectral range.

A neutral-wedge filter, calibrated with the light source and monochromator, ensured constant intensity of the exciting radiation throughout the whole spectral range.

The crystals were mounted in a cryostat near the exit slit of the monochromator. The construction of the cryostat was as described elsewhere.<sup>11</sup> A heating element in the cryostat enabled temperature variation between liquid-air temperature and 600°K.

An RCA-1P21 photomultiplier was used as a detector for the emitted radiation. Care was taken to measure separately the blue and green components of the emitted luminescence. A combination of 5 mm of nitrobenzene (in a cell) with a Wratten 34 gelatine filter was used to isolate the blue band and to cut out the exciting light, while Wratten 9+Wratten 61 filters were used for the green band.

The output of the photomultiplier, after suitable amplification, was led to a recorder on which the curves of luminescence *versus* temperature were directly recorded. Care has been taken in these measurements to eliminate effects of trapping or emptying of traps. For

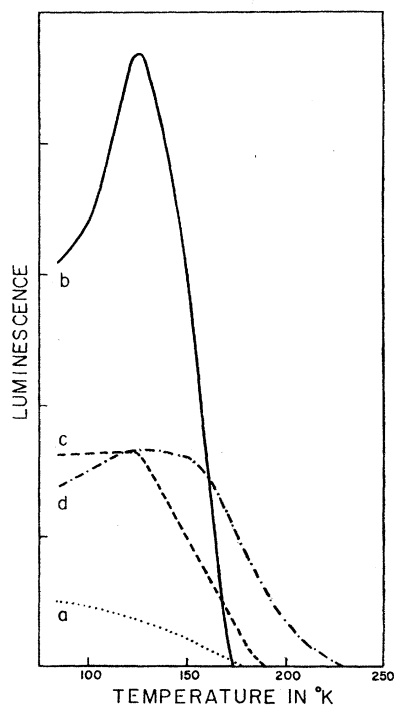


FIG. 1. Luminescence *versus* temperature curves for a ZnS:Cl crystal (blue luminescent). Wavelength of exciting light: *a*—3150 Å, *b*—3310 Å, *c*—3600 Å, *d*—3690 Å.

<sup>11</sup> A. A. Braner and A. Halperin, *Phys. Rev.* **108**, 932 (1957).

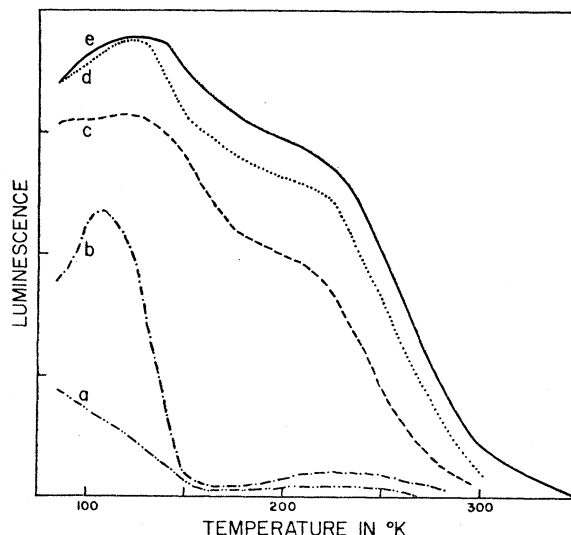


FIG. 2. Luminescence *versus* temperature curves for the blue luminescence band of a ZnS:Cu:Cl crystal. Wavelength of exciting light: *a*—3250 Å, *b*—3300 Å, *c*—3400 Å, *d*—3600 Å, and *e*—3700 Å.

this purpose the curves were recorded both on cooling down the crystal and on warming it up. In addition, the rates of warming or cooling were kept low (less than 5°/min), which reduced the effects of stored energy.

Excitation spectra were taken point by point. For each wavelength the neutral wedge was set for constant exciting intensity, and the crystal was excited to saturation, after which the reading of luminescence intensity for the given wavelength was made.

## RESULTS

### (a) Temperature Dependence of the Luminescence

Luminescence *versus* temperature curves were recorded for different wavelengths of exciting light. Many ZnS crystals were used in these measurements in order to find out whether the shape of the curves at lower temperatures fits that given theoretically by Adirovitsch.<sup>3</sup> In particular, a check was made of the criterion given by Adirovitsch for the position of the absorption edge of the crystal (see the foregoing).

Adirovitsch's criterion was found to hold for a few crystals; it failed, however, for some others. Examples are shown in Figs. 1, 2, and 3. The accepted value for the absorption edge of ZnS at liquid-air temperature is between 3340<sup>12</sup> and 3350 Å.<sup>3</sup> Curve *b* (Fig. 1), however, shows an initial rise in luminescence with temperature, and according to Adirovitsch's criterion the absorption edge is therefore below 3310 Å. On the other hand, curve *c* does not show any rise, which would imply that 3600 Å is still within the lattice absorption.

<sup>12</sup> G. F. J. Garlick, *Luminescent Materials* (Clarendon Press, Oxford, 1949), Chap. 4.

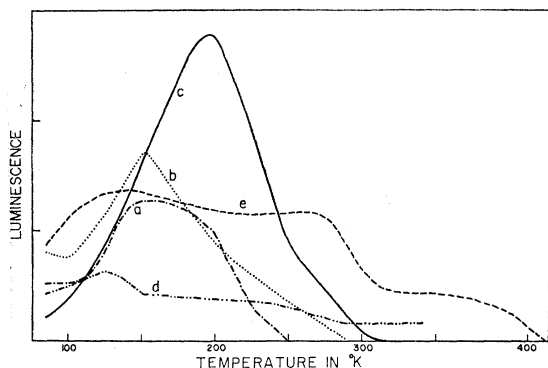


FIG. 3. As Fig. 2 but for the green luminescence band of the same crystal. Wavelength of exciting light: *a*—3000 Å, *b*—3150 Å, *c*—3350 Å, *d*—3600 Å, and *e*—3700 Å.

Another example is shown in Figs. 2 and 3. This crystal emitted blue and green luminescence, and curves corresponding to the blue and green bands are shown in Figs. 2 and 3, respectively. The deviations from Adirowitsch's rule are for the blue luminescence similar to those described in Fig. 1, while for the green band the curves show maxima even on excitation at 3000 Å, so that Adirowitsch's rule does not hold at all.

The behavior of the luminescence at higher temperatures is also of interest. In some of the curves the luminescence is not completely quenched after the first maximum is reached, and maxima (or shoulders) appear at higher temperatures. The behavior at higher temperatures is shown to depend on the wavelength of the exciting light. The temperature at which the temperature-quenching takes place seems to shift towards higher values with an increase in the wavelength of the exciting light. In Fig. 2, for example, the luminescence disappears almost completely below 150°K on excitation with light of 3300 Å (curve *b*), while temperature quenching occurs at about 250°K on exciting at 3400 Å (curve *c*), and at still higher temperatures on exciting with light of longer wavelengths (curves *d* and *e*).

#### EXCITATION SPECTRA

In the beginning excitation spectra were taken with spectral slit widths of 50–100 Å, when curves similar to those reported by Broser and Broser-Warminsky<sup>8</sup> and by Lempicki<sup>7</sup> were obtained. Irregularities observed occasionally in these curves, however, indicated the presence of finer structure in the excitation spectra. Attempts were then made to ensure the exciting light intensity and the amplification needed to measure with adequate accuracy the luminescence intensity with spectral slit widths of less than 20 Å. Measurements were then taken at intervals of 20 Å, or even every 10 Å.

Figure 4<sup>13</sup> shows a set of excitation spectra as ob-

<sup>13</sup> Figure 4 was drawn with the experimental points on each curve. These were, however, omitted in the other figures in order to make the curves clearer.

tained after the higher spectral resolution was secured. This crystal emitted only blue luminescence and the different curves correspond to measurements at different temperatures. The excitation spectra appear now resolved into a few bands, and the shoulders of the bands indicate that each is still composed of more than one component.

Curves *a*, *b*, *c*, and *d* were obtained at 85, 130, 160, and 205°K, respectively. An interesting result is that the maxima at wavelengths above 3400 Å do not show any temperature shift at all, while the peaks at about the wavelength of the absorption edge of the crystal (above 3300 Å), seem to shift with temperature. The maximum in this region appears at 3285 Å at 85°K, above 3300 Å at 130°K, at 3320 Å at 160°K, and at 3350 Å at 205°K. This shift (of about 0.5 Å/deg) fits well the shift in the absorption edge as was observed by Garlick and Gibson.<sup>1</sup> It will, however, be shown soon

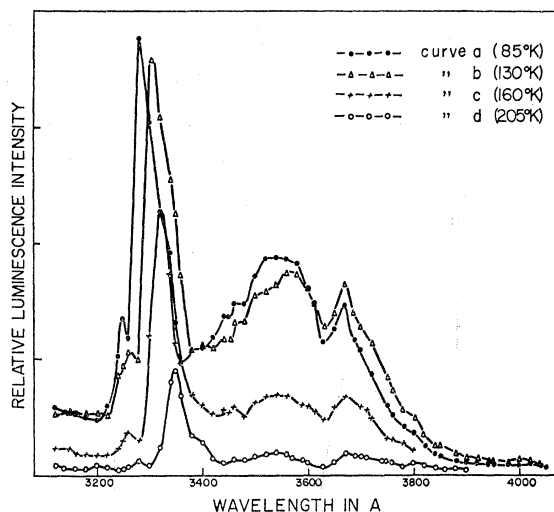


FIG. 4. Excitation spectra of a ZnS:Cl crystal (blue luminescent), at various temperatures.

that the shift is not a real one, as it is rather a result of a change with temperature of the relative efficiencies of the different components of the band in this region of the excitation spectrum.

The excitation spectra shown in Fig. 4 were taken with the crystal still with its natural outer faces. The part of the excitation spectrum below 3400 Å was, however, found to be sensitive to the surface conditions of the crystal. This is shown in Fig. 5, in which excitation spectra are given again for the same crystal but after grinding away its outer natural growth faces. The relative intensities are now completely different from those obtained for the same crystal before grinding (Fig. 4). The main effect of grinding seems to be a comparative reduction in the shorter wavelength side of the excitation spectrum, and the peak at 3285 Å, which was the strongest before grinding, seems to have almost completely disappeared now. The lower inten-

sity obtained now resulted also in better resolution of the bands, and it can be seen clearly that there is no real shift with temperature in the individual peaks of the excitation spectra. Thus the peak at 3350 Å remains practically at the same wavelength in curves *a*, *b*, and *c* (Fig. 5), which correspond to 85, 125, and 170°K respectively. The same can be said about the peak at 3310 Å, which still appears as a shoulder in curve *c*. The small apparent shift between curves *a* and *b* at this wavelength might be explained by assuming that the peak at 3310 Å is still composed of more than one component. The existence of such a fine structure was indicated in our measurements, but we were not able to get the band resolved into its fine components. In any case, if there is any shift, it is certainly small compared to the shift with temperature of the absorption edge.

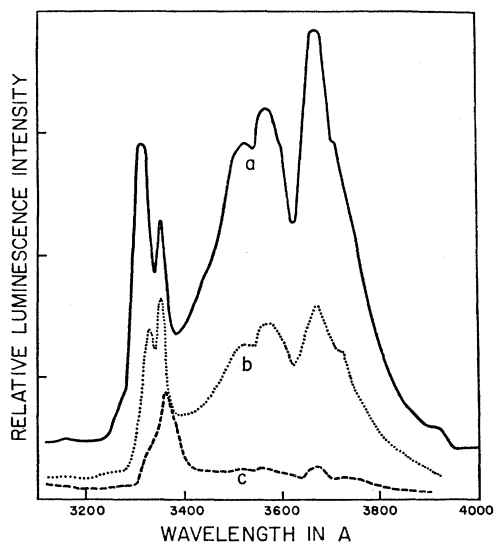


Fig. 5. As Fig. 4 but after grinding away the crystal surfaces; *a*—at 85°K, *b*—at 125°K, and *c*—at 170°K.

Similar structure was obtained for the green luminescence band. Figure 6 shows a set of green excitation spectra—curve *a* was taken at liquid air temperature, curve *b* at 160°K, and curve *c* at 300°K.

The structure in the region of the absorption edge is similar to that of the blue band and includes the apparent shift with temperature of the maxima in this region. Again it is clear that the individual bands do not shift, and it is only the change in the relative efficiencies which caused the apparent shift in the maximum of the excitation spectrum.

Grinding away of the outer natural faces of the crystal affects the green excitation spectrum in a way similar to that already described for the blue band, i.e., the relative intensity is reduced at the shorter wavelength side of the excitation spectrum.

The blue and green excitation spectra for a crystal which emitted both the bands, are given for comparison

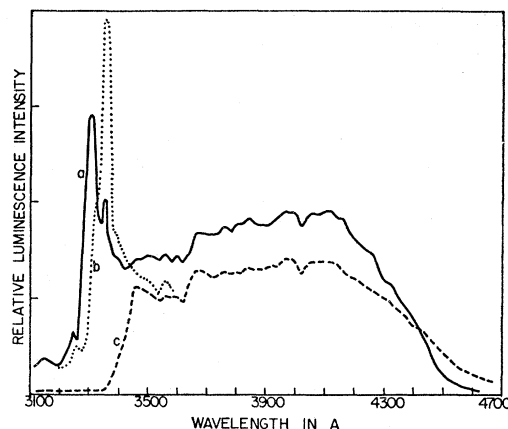


Fig. 6. Excitation spectra for the green luminescence band of a ZnS:Cu:Cl crystal. *a*—at 80°K, *b*—160°K, and *c*—at 300°K.

in Fig. 7. The main differences are the extension towards longer wavelengths of the green excitation spectrum compared to the blue one, and the comparatively low intensity in the blue excitation spectrum in the region near the absorption edge. In some way the two curves seem to be complementary, as the region where the blue excitation spectrum reaches its maximum (3350–3700 Å) appears as a depression in the curve corresponding to the green band. For some crystals this depression was much more pronounced as can be seen in Fig. 3, where excitation with 3600 Å (curve *d*) gives a very weak luminescence compared to that obtained with light of longer or shorter wavelengths.

## DISCUSSION

It was shown in the present work that the excitation spectra for the blue and green luminescence of ZnS consist of a complexity of fine bands. It seems that the failure of other investigators in observing this fine structure should be attributed to low spectral resolution or to too large intervals between subsequent wavelengths chosen in the measurements.

The yield for blue and green luminescence is certainly not the same for light absorbed in different spectral

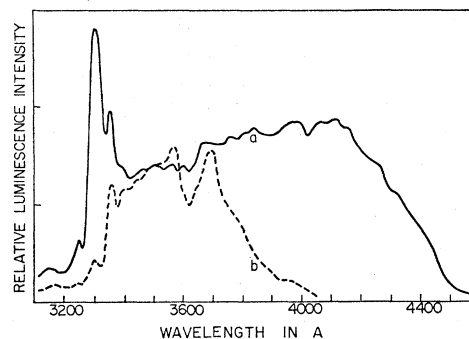


Fig. 7. Green (curve *a*) and blue (curve *b*) excitation spectra of the same ZnS:Cu:Cl crystal at 80°K.

regions. This is easily seen in the excitation spectra, where the strongly-absorbing region within the absorption edge yields very weak luminescence compared to that around 3650 Å. There must, however, be an absorption band for every excitation band. Absorption measurements carried out in the present work, however, did not show any fine structure corresponding to that observed in the excitation spectra. It seems that the low concentrations of the activators in the crystals used were not enough to produce measurable absorption bands, although they are detected easily by the much more sensitive luminescence measurements.

Broser and Broser-Warminsky,<sup>8</sup> using ZnS crystals activated by higher concentrations of copper (about  $10^{-3}$  gram atom per mole), were able to observe an absorption band at 3650 Å, which did not show any shift with temperature. It seems, however, that they did not secure the spectral resolution needed for resolving the fine bands.

Furlong and Ravilious,<sup>14</sup> who measured the edge-emission of CdS crystals at low temperatures, observed a few sharp absorption bands, with half-widths of about 1 Å, near the absorption edge of their crystals. A set of narrow absorption bands was recently observed also by Broude *et al.*<sup>15</sup> in CdS crystals. These authors could show that some of their fine absorption bands should be attributed to surface effects, which is in accord with our results for ZnS.

As shown in the present work, the individual bands in the excitation spectrum do not shift when the temperature of the crystal is changed. The relative intensities of the individual bands near the absorption edge, however, do change in such a way that the relative maximum moves from one band to another in parallel with the temperature shift of the absorption edge.

To explain this effect we introduce the "effective depth" ( $d_e$ ) of the luminescent layer in the crystal, which is taken as the depth at which practically all the exciting light is absorbed. The contribution of deeper layers to the luminescence would then be negligible and should not be considered.

The effective depth is confined to a thin surface layer, of the order of  $10^{-5}$  cm, for wavelengths within the region of the lattice absorption, and grows suddenly when the absorption edge is passed. It continues to grow for longer wavelengths until a wavelength  $\lambda_c$  is reached at which the effective depth is equal to the thickness of the crystal.  $\lambda_c$  varies slightly with the thickness of the sample, in addition to variations due to differences in the absorption coefficient from sample to sample.

Variation of the temperature of the crystal causes its absorption edge to shift, and thus affects the effective depth at a given wavelength. This should be par-

ticularly pronounced at wavelengths near the absorption edge, where  $d_e$  may change from practically the whole thickness of the crystal to a very small value, or vice versa, by a comparatively small temperature variation.

The number of luminescence centers which are able to take part in the luminescence process is proportional to the volume of the luminescent layer, and for a given illuminated surface area it is therefore proportional to  $d_e$ . The drastic reduction in  $d_e$ , which occurs at wavelengths just outside the absorption edge on raising the temperature of the crystal, should, therefore, suppress the luminescence in this region. This is just what was obtained in our measurements (Figs. 4-7), where more and more of the short-wavelength part of the excitation spectra was found to be suppressed on warming the crystals. It is evident that this effect should advance in parallel with the shift in the absorption edge.

It follows also from the foregoing considerations that for wavelengths within the lattice absorption the luminescence is independent on the thickness of the specimen (for thicknesses larger than  $10^{-5}$  cm). It would rise, however, with the thickness of the specimen on excitation at longer wavelengths. This part of the excitation spectrum would therefore become less and less pronounced on reducing the thickness of the specimen, e.g., on using a layer of powder a few microns thick instead of a single crystal about 1-mm thick. This explains the difference between excitation spectra of powders where the main maximum occurs below 3400 Å,<sup>1</sup> and those obtained in the present work as well as by other investigators who worked on single crystals,<sup>7,8</sup> where a prominent maximum was obtained at longer wavelengths.

It should be added that the surface effects are much more pronounced in powders, which as shown above, acts again in favor of the short-wavelength part of the excitation spectrum, and seems to contribute the main part to the luminescence excited by light within the lattice absorption.

These surface effects seem to be bound to layers near the outer crystal faces, and are gradually diminished on grinding the faces away. Similar surface effects in electroluminescent ZnS phosphors have been described as due to copper-rich layers by Zalm *et al.*<sup>16</sup> Furlong and Ravilious,<sup>14</sup> on the other hand, have ascribed the surface effects in the luminescence of CdS to adsorption of gases from the air.

The deviations of the luminescence *versus* temperature curves from Adiwitsch's criterion may be partly explained by the foregoing considerations, according to which the number of luminescence centers in the illuminated crystal volume at a given wavelength is not a constant as assumed by Adiwitsch, but is rather a function of temperature, especially at wavelengths just

<sup>14</sup> L. R. Furlong and C. F. Ravilious, *Phys. Rev.* **98**, 954 (1955).

<sup>15</sup> Broude, Eremenko, and Rashba, *Doklady Akad. Nauk S.S.S.R.* **114**, 520 (1957) [translation: *Soviet Phys. Doklady* **2**, 239 (1957)].

<sup>16</sup> Zalm, Diemer, and Klasens, *Philips Research Repts.* **9**, 81 (1954).

outside the absorption edge. In addition, the complexity of the bands of which the excitation spectrum consists does not fit the simple model of a single activator level on which Adirwitsch based his calculations. The behavior of the blue luminescence band, though not good enough to serve as a criterion for fixing the wavelength of the absorption edge, fitted in some cases Adirwitsch's theory; the green band, however, did not fit it at all.

The dependence of the high-temperature part of the curves on exciting light shows that the quenching is not always due to the release of holes. Here, again, the shift in the absorption edge plays a part. On raising the temperature, the effective depth of the luminescent layer is reduced, which causes an early "temperature quenching" of the luminescence when excited by light of wavelengths not far away from the absorption edge. It appears from the experimental results (Figs. 1 and 2) that some quenching due to this effect occurs even on excitation with wavelengths a few hundred angstroms from the edge.

Peaks in the excitation spectrum appear even at wavelengths within the region of the lattice absorption. These include, besides the band at about 3300 Å, peaks at 3150 and 3250 Å. It is of interest that absorption peaks were also observed in the same region. Shalimova<sup>17</sup> has obtained for a number of pure ZnS films, absorption peaks at 2840 and 3130 Å, while an additional peak at 3340 Å was observed for activated films. The peak at 3130 Å might be related to the one at about 3150 Å in our excitation spectra, while the one observed in the activated films at 3340 Å might correspond to the band at this region in our experiments.

<sup>17</sup> K. V. Shalimova, *Doklady Akad. Nauk S.S.S.R.* **80**, 587 (1951).

Coogan<sup>18</sup> has observed an absorption peak at 3300 Å, and attributed it to an exciton absorption band.

Further experimental results are needed before one tries to offer a model for the luminescence centers, and a level diagram to account for the fine structure in the excitation spectra which was observed in the present work.

Prener and Williams<sup>19</sup> have put forward a substitutional model for ZnS, in which, for example, a copper ion is substituted for zinc and a chlorine ion for sulfur. It seems that on such a model the bands in the excitation spectra resulting from transitions involving the perturbed levels should shift with a temperature coefficient similar in order of magnitude to that of the absorption edge. This, however, does not fit our results, which seem therefore to be in favor of other models including vacancies in the luminescence centers.<sup>20</sup>

Broser and Broser-Warminsky<sup>8</sup> have offered a hydrogen-like model for the energy levels of the impurity-activated ZnS phosphor. Their model was based on maxima at 3700 and 3350 Å in their excitation spectra. Choosing these two wavelengths seems somewhat arbitrary in light of the many maxima revealed now in the excitation spectra. Our attempts to fit our results into a hydrogen-like model were hitherto unsuccessful.

Experiments are continuing in our laboratory in order to obtain more information on the properties of ZnS and CdS crystals. These include the spectra of the luminescence and thermoluminescence and their dependence on the exciting light, as well as similar investigations on the photoconductivity and infrared quenching and stimulation of the crystals.

<sup>18</sup> C. K. Coogan, *Proc. Phys. Soc. (London)* **B70**, 845 (1957).

<sup>19</sup> J. S. Prener and F. E. Williams, *Phys. Rev.* **99**, 1781 (1955); J. S. Prener, *J. Chem. Phys.* **25**, 1924 (1956); F. E. Williams, *J. Opt. Soc. Am.* **47**, 869 (1957).

<sup>20</sup> F. A. Kröger, *Brit. J. Appl. Phys. Suppl. No. 4*, 58 (1955); N. Riehl and H. Ortmann, *Angew. Chem.* **68**, 513 (1956).