

## Effect of Lead on the Room-Temperature Colorability of KCl\*

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The introduction of  $F$  centers in Pb-doped KCl by ionizing radiation has been measured as a function of lead content for different radiation intensities. For the lowest intensity (gamma irradiation), as little as 0.5-ppm impurity caused a marked decrease in the late-stage coloration and less than 100 ppm completely suppressed the late stage. Lead impurities are less effective in decreasing late-stage colorability when higher irradiation intensities (electron irradiation) are used. These results suggest that previously observed variations in the late-stage coloration characteristics could have been due to trace amounts of impurities of the order of 1 ppm. Furthermore, it is suggested that these trace impurities are not depleted during irradiation, but affect the late-stage colorability by acting as electron or hole traps, or as recombination centers.

### INTRODUCTION

THE complicated nature of room-temperature coloration of alkali halide crystals has been well documented.<sup>1-4</sup> In general, however, the coloration can be divided into two stages, early and late.<sup>5</sup> The early or rapid stage of coloration is characterized by the relatively easy production of  $F$  centers, the easy destruction of these centers by optical bleaching,<sup>6</sup> and by saturation. The saturation level depends upon divalent impurity content, plastic strain, and radiation intensity. In late-stage coloration the  $F$  centers are more difficult to produce and to bleach<sup>6</sup> while the rate of coloration still depends upon radiation intensity and sample history.<sup>4,7</sup> Much of the past experimental work was done using radiation doses for which the early and late stage contributions to the coloration were comparable. The experimental results were, therefore, difficult to interpret in terms of any particular coloration model. We have recently made observations of colorability well into the late stage using an intense gamma-ray source and an electron accelerator.<sup>7,8</sup> It became clear from these experiments that large variations exist in the late stage coloration of different samples. These variations could not be correlated with such measurable properties as the dislocation density and major impurities. Therefore, it was suggested that trace impurities present in amount of 1 ppm or less which would not be detectable might affect the colorability of a sample containing many more  $F$  centers than impurities.

A number of years ago Schulman, in discussing this very problem,<sup>9</sup> suggested that impurities might act as electron or hole traps. Provided the steady-state electron or hole concentration influenced the production

of stable defects, trapping and recombination processes would make it possible for trace amounts of certain specific impurities to affect late stage coloration. In addition, the recent observation of a radiation equilibrium between different color centers<sup>7</sup> lends credence to models taking account of the steady-state concentration of electrons and holes present during irradiation.<sup>10</sup>

The present experiment was initiated in order to obtain data which might clarify our understanding of such trapping and recombination processes. Lead was chosen as the doping agent because of indications that some of the samples previously investigated<sup>4</sup> contained lead. Also, lead-doped alkali halide crystals had been used in a number of earlier studies.<sup>11-13</sup> These studies indicated that the absorption band characteristic of the lead gave a convenient way of measuring the lead concentration accurately for each sample utilized.

### EXPERIMENTAL

Single crystals of KCl and KCl:Pb, about 4 cm in diameter and 8 cm long, were grown by the Kyropoulos method. The starting material was prepared by recrystallizing Johnson, Matthey, and Company, Ltd. "Specpure" powder in a quartz container using triply distilled water. The major metallic impurities in this starting material were Rb (2.1  $\mu\text{g/g}$ ) and Cu and Fe (0.5  $\mu\text{g/g}$ ). Ca and Sr were not detected (<2  $\mu\text{g/g}$ ) and the only other major impurity was Br (2.5  $\mu\text{g/g}$ ). All other impurities seemed to be well below the 0.5- $\mu\text{g/g}$  level. Reagent-grade  $\text{PbCl}_2$  was mixed with the KCl starting material as the doping agent. The powder, in a Pt crucible, was slowly heated in vacuum to about 650°C and left overnight. The crystals were then grown under a  $\text{N}_2$  atmosphere. Figure 1 illustrates the relation of lead concentration in the melt to the total lead concentration in the crystal grown from the melt. The result is similar to those obtained previously for KCl:Pb<sup>12</sup> and for NaCl:Pb.<sup>11</sup> From the figure it is

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<sup>1</sup> R. V. Hesketh, *Phil. Mag.* **4**, 114 (1959).

<sup>2</sup> P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **121**, 484 (1961).

<sup>3</sup> P. G. Harrison, *J. Chem. Phys.* **37**, 388 (1962).

<sup>4</sup> W. A. Sibley and E. Sonder, *Phys. Rev.* **128**, 540 (1962).

<sup>5</sup> R. B. Gordon and A. S. Nowick, *Phys. Rev.* **101**, 977 (1956).

<sup>6</sup> W. E. Bron, *Phys. Rev.* **119**, 1578 (1963).

<sup>7</sup> E. Sonder and W. A. Sibley, *Phys. Rev.* **129**, 1578 (1963).

<sup>8</sup> C. T. Butler, W. A. Sibley, and E. Sonder, *J. Chem. Phys.* **39**, 242 (1963).

<sup>9</sup> J. H. Schulman, *J. Phys. Chem.* **57**, 749 (1953).

<sup>10</sup> J. H. Crawford, Jr., *Phys. Rev. Letters* **12**, 28 (1964).

<sup>11</sup> J. H. Schulman, R. J. Ginther, and C. C. Klick, *J. Opt. Soc. Am.* **40**, 854 (1950).

<sup>12</sup> W. Koch, *Z. Physik* **57**, 638 (1929).

<sup>13</sup> E. Burstein, J. J. Oberly, B. W. Henvis, and J. W. Davisson, *Phys. Rev.* **81**, 459 (1951).

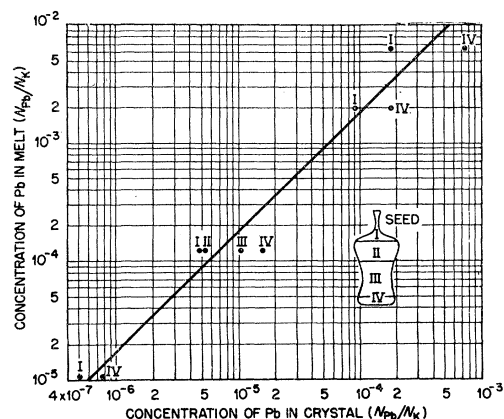


FIG. 1. Lead concentration in KCl single crystals pulled from the melt plotted against the lead concentration of the melt. The Roman numerals indicate the section of the ingot, as shown in the inset, from which the analyzed specimens were cleaved.

seen that there is a variation of lead concentration within a particular crystal boule. The lead analysis was done by atomic absorption spectroscopy after extraction of the lead from the KCl. Flame photometric analysis of the crystals showed that no detectable amounts of Ca or Sr were introduced by the growth procedures.

The method used to obtain the coloration curves was the same as has been described previously<sup>4,7</sup>; however, the samples were all cleaved to 0.06 cm or less and the  $\text{Co}^{60}$  gamma source had decayed to a strength of  $3.5 \times 10^6$  R/h. For the specimens irradiated with electrons, an energy of 1.5 MeV and current density of  $0.18 \mu\text{A}/\text{cm}^2$  were used. The specimens attained a temperature of from  $30\text{--}32^\circ\text{C}$  during the electron irradiations.

It became apparent during some preliminary gamma-irradiation experiments that different coloration rates were obtained in winter than in summer. This suggested that the late stage colorability is influenced by ambient temperature to a greater extent than had previously been supposed. The data shown in Fig. 2 confirm this observation and, therefore, a temperature

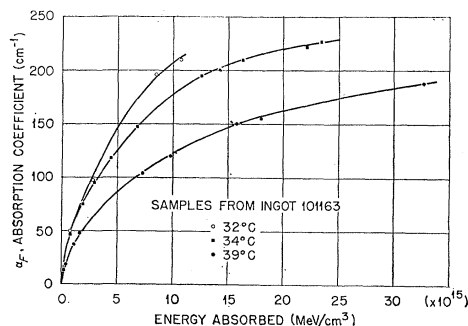


FIG. 2.  $F$ -center coloration curves obtained for irradiation at different temperatures. For each curve the absorption coefficient at the peak of the  $F$  band is plotted versus the energy absorbed by the crystal from the gamma-ray field.

controller was attached to the gamma irradiation facility which maintained the irradiation temperature of the samples at  $34 \pm 1^\circ\text{C}$ .

## RESULTS

### A. Optical Absorption of Lead in KCl

Addition of  $\text{PbCl}_2$  to KCl produced the expected ultraviolet  $A$ -,  $B$ -, and  $C$ -absorption bands.<sup>14</sup> The  $B$  and  $C$  bands were not well resolved at room temperature and appeared at about 210 and 195  $m\mu$ , respectively. The  $A$  band at 272  $m\mu$  (4.56 eV) was well resolved and had an asymmetric, approximately Gaussian shape with semi-half-widths of 0.072 and

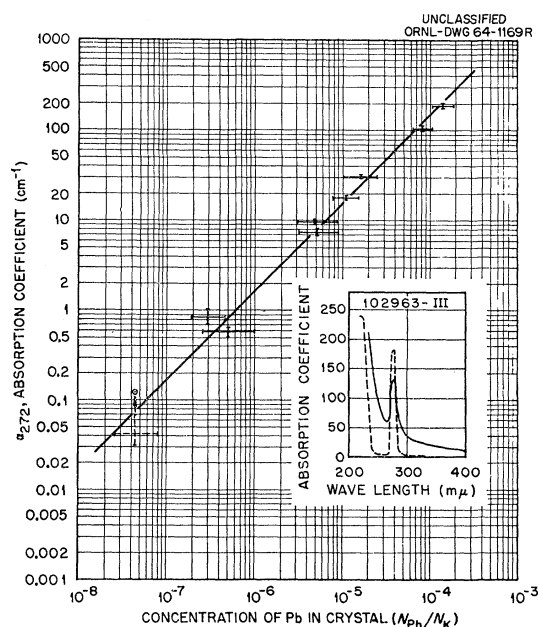


FIG. 3. Relation between the  $A$  band (272  $m\mu$ ) and the lead content of various KCl crystals. The point shown dashed at the lower left was obtained for a commercial KCl sample; the vertical arrow shows that for this sample, heating and quenching caused the  $A$  band to increase in height. The inset shows shape and irradiation behavior of the  $A$  band.

0.088 eV on the high- and low-energy sides, respectively.<sup>15</sup> Schulman *et al.*<sup>11</sup> have shown that the lead concentration in NaCl crystals is proportional to the height of the lead absorption band over a wide range of concentrations. We found a similar proportionality for lead in KCl. This is shown in Fig. 3 where the results of the measurements of the height of the absorption band at 272  $m\mu$  are plotted versus the total lead concentrations in the samples. Estimated uncertainties are shown by the horizontal and vertical lines through each point. For a few of the points, several sets of analyses

<sup>14</sup> R. A. Eppler, Chem. Rev. 61, 523 (1961).

<sup>15</sup> The asymmetry is opposite from what one would expect for the  $F$  band. [C. C. Klick, D. A. Patterson, and R. S. Knox, Phys. Rev. 133, A1717 (1964).]

were performed and the results in all cases were well within the indicated uncertainty. With this information it can be seen that the *A* band is a convenient measure of the amount of lead in the crystal for concentrations up to about 150 ppm.

When the half-width *W* and the proportionality constant  $d\alpha/dN$  between the peak absorption coefficient and the lead content is known, the oscillator strength of the *A* band can be easily computed. Using Dexter's modification<sup>16</sup> of the Smakula equation,<sup>17</sup> which should be applicable to an approximately Gaussian absorption line, the oscillator strength

$$f = 8.7 \times 10^{16} [n/(n^2 + 2)^2] W d\alpha/dN$$

turns out to be 0.11 when 1.58 is used for the index of refraction *n* at the peak of the band.

The configuration of the center giving rise to the lead absorption bands is not known. In fact there is some indication that lead can be present in KCl in several different states. For example, radiation causes the *A* band to diminish rapidly although it does not cause it to disappear completely. The absorption on both sides of the *A* band increases upon irradiation. This is shown in the inset of Fig. 3 where the *A* band for an unirradiated crystal (dashed line) and for the same crystal after a short irradiation (solid line) is plotted versus wavelength. Also, previous workers<sup>18</sup> have shown that heat treatment with rapid cooling of lead-doped samples causes changes in the low temperature growth rate of centers such as the  $V_K$  center. We also found that heat treating lead-doped samples to 450°C for 10 min caused both the *F*- and  $V_K$ -coloration behavior at liquid-nitrogen temperature to change. However, no change was found in the late-stage room-temperature colorability for similarly treated samples. Nor did we observe any effect of quenching from as high as 650°C on the 272-m $\mu$  band in any of the samples grown at this laboratory.

There was an effect of heat treatment on the *A* band in a number of Optovac KCl crystals. (These samples contained less lead than any of our doped crystals. They also had other impurities such as  $Ca^{++}$  and  $OH^-$  in amounts comparable to, or greater than, the lead.) In Fig. 3 the absorption coefficient of the *A* band and the total lead concentration of such a sample before heat treatment are shown by the dotted cross (lower left-hand point). The solid arrow indicates the change of the absorption coefficient resulting from heating to 450°C and cooling rapidly. The point of the arrow is close to an extrapolation of the best line drawn through the data points obtained for crystals grown at this laboratory and containing less than  $3 \times 10^{18}$  Pb atoms/cm<sup>3</sup>.

<sup>16</sup> D. L. Dexter, Phys. Rev. **101**, 48 (1956).

<sup>17</sup> A. Smakula, Z. Physik **59**, 603 (1930).

<sup>18</sup> T. J. Neubert and J. A. Refiner, J. Chem. Phys. **36**, 2780 (1962); also, C. J. Delbecq and P. H. Yuster (private communication).

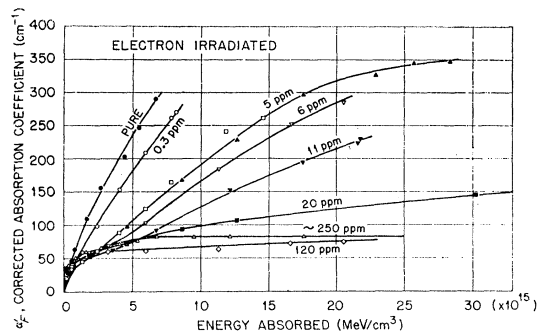


FIG. 4. Coloring curves for electron irradiated samples. The lead content for each sample in ppm is shown on the curves.

### B. Growth of the *F* Band

Growth curves for the *F* band produced by electron and gamma irradiation are shown in Figs. 4 and 5, respectively. In these figures the corrected<sup>19</sup> absorption coefficient for the *F* band,  $\alpha'_F$ , is plotted against the energy (in MeV per cm<sup>3</sup>) absorbed by the sample so that a comparison can be made between the electron and gamma irradiations. The rates at which energy was absorbed by the samples differed by a factor of about 50 between the electron irradiation and the gamma irradiation, and were 46 and  $1.0 \times 10^{14}$  MeV/cm<sup>3</sup> sec, respectively.

Figure 4 shows clearly that for electron irradiation, the late-stage colorability decreases when more than about 1 Pb<sup>++</sup> ion in  $10^7$  K<sup>+</sup> ions is present in the sample. In fact, as the lead content increases through 0.3, 5.0,

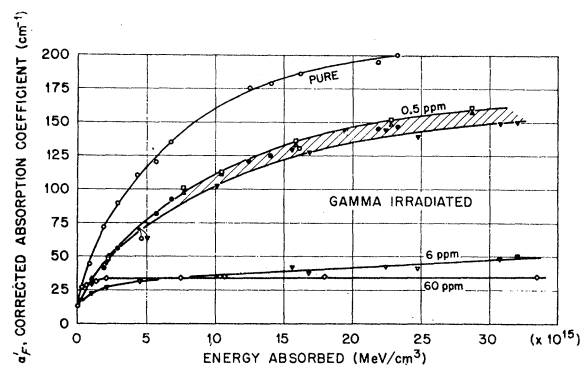


FIG. 5. Coloring curves for gamma irradiated samples. The labels indicate the lead content. A number of samples containing about 0.5 ppm lead fell within the cross-hatched area. The point symbols, sample designation, and actual lead content of each of these is given in Table I.

<sup>19</sup> Analysis of the dichroic absorption in the *F*-band region [F. Okamoto, Phys. Rev. **124**, 1090 (1961)] has shown that one-half to one times the intensity of the *M*-band absorption also appears as additional *M*-center absorption under the *F* band. In past work we have subtracted 0.8 times the height of the *M* band from the measured height of the *F* band. Since the exact amount of *M* and other cluster center absorption at the peak of the *F* band is somewhat uncertain, we have now adopted the simpler procedure of subtracting the full *M*-band absorption height from the measured *F* band.

and 20.0 ppm, the rate of  $F$ -center production becomes increasingly smaller until, in the heavily doped materials (250 ppm), a horizontal line is obtained on the graph. This would indicate that virtually no late-stage  $F$  centers are produced in these heavily doped samples. Also, we found that all visible coloration bleached out rapidly and completely under white or  $F$ -light illumination. This supports the conclusion that late-stage  $F$  centers are not produced in heavily doped material since it has been shown<sup>6</sup> that late-stage  $F$  centers are not readily destroyed by  $F$  light.

Coloration curves for samples irradiated with gamma rays at a lower rate of energy absorption are presented in Fig. 5. What is most pertinent is the fact that for gamma irradiation only about 0.5 ppm of lead will cause a decrease in late stage colorability—roughly comparable to the decrease caused by 5–10 ppm lead for the higher intensity electron irradiation. Also, Fig. 5 shows that as little as 6 ppm lead virtually removes late-stage colorability; whereas, between 20 to 120 ppm are necessary for a similar effect for electrons as shown in Fig. 4. This indicates that the effectiveness of an impurity like lead for decreasing the late-stage colorability is greater at a lower irradiation rate.

Even though the trend of decreasing colorability with increasing lead content is clear, a few apparent discrepancies were observed. Table I gives the lead concentration (obtained from the 272- $m\mu$  absorption band and Fig. 3), and point symbols used for the samples in Figs. 4 and 5. One of the discrepancies is seen in Fig. 4 where the open squares for sample 2b indicate that this specimen had somewhat less suppression of the

colorability than sample 2a (filled triangles), even though it contained more lead. A similar case is evident for samples 1b through 1e in Fig. 5. These inconsistencies could be caused by small variations in the temperature or intensity of irradiation, other types of trace impurities, or by different amounts of strain introduced into the samples during cleaving.

### C. Other Observations

Lead impurity in KCl crystals, in addition to suppressing the late stage, markedly enhances early-stage coloration, as can be observed in Figs. 4 and 5. However, the number of the early-stage  $F$  centers per atom of added impurity is smaller for lead than for calcium. Perhaps a careful study of early-stage height as a function of impurity concentration and of impurity type would help clarify the problem of the easy production of  $F$  centers.

In heavily lead-doped samples, as mentioned earlier,  $F$  centers,  $M$  centers, and  $R$  centers are rather easily removed by optical bleaching. A band at 935  $m\mu$  grows in very rapidly during bleaching but can be bleached out completely. However, the crystal still has a slight brown tinge due to the tails of ultraviolet bands that the optical bleaching does not remove. All of the radiation induced optical absorption bands between 190 and 1500  $m\mu$  can be removed by heating to 450°C for about 10 min. When these bands disappear, the lead  $A$ ,  $B$ , and  $C$  bands return to their preirradiation heights.

Comparison of the  $M$ - and  $F$ -center concentrations shows that the ratio  $\alpha_M/(\alpha'_F)^2$  increases with lead content above the value found for an undoped sample for the same radiation intensity. This is just the opposite from the shift observed previously<sup>4</sup> for gamma-irradiated Ca-doped KCl where the relative  $M$ -center concentration decreases.

### DISCUSSION

The decrease in colorability caused by as little as one-half ppm lead (as shown in Figs. 4 and 5) is comparable to the variations in colorability observed previously in undoped KCl. There are indications that small amounts of calcium similarly suppress the late stage.<sup>4,20</sup> Thus, it is not unreasonable to expect that other impurities could also affect late-stage coloration. This would explain why the variations observed in the earlier work could not be correlated with any measure of a specific impurity (e.g., ultraviolet lead absorption bands, flame photometric analysis of Ca, etc.).

It is probable that impurities remain effective for as long as the radiation is continued. For the case of lead, irradiations much longer than those shown in Figs. 4 and 5 were performed; the data showed no sign of the positive curvature that one would expect if the lead were being used up. These observations are con-

TABLE I. List of samples irradiated with electrons and gamma rays. (The samples in the upper part of the table were irradiated with electrons; those below were gamma irradiated. The lead content and the point symbols used for Figs. 4 and 5 are also given.)

Sample	Ingot growth date and section <sup>a</sup>	Concentration of lead Pb atoms	Symbol used
		10 <sup>6</sup> K atoms	
0a	101163 II	<0.01	●
1a	12363 I	0.33	○
2a	102463 I	4.7	▲
2b	102463 I	5.2	□
2c	102463 II	6.3	▽
2d	102463 III	11	▼
2e	102463 IV	20	■
3a	102963 III	120	◇
4a	103163 IV	~250	△
0b	101163 II	<0.01	○
1b	120363 I	0.41	△
1c	120363 I	N.M.	●
1d	120363 IV	0.61	□
1e	120363 IV	0.64	▼
2f	102463 I	6.1	▽
3b	102963 I	62	◇

<sup>a</sup> The six-digit number designates month, day, and year in order, the Roman numeral indicates the section of the ingot according to the inset in Fig. 1.

<sup>20</sup> W. A. Sibley and J. R. Russell (unpublished results).

sistent with the idea that trace impurities act as electron or hole traps, or recombination centers in the crystal,<sup>11</sup> and that by so doing they shift the steady-state concentration of holes or electrons present during irradiation.

The possibility that lead acts through the electronic system makes the understanding of the radiation chemistry of the Pb impurity crucial. Presumably the lead is initially either a substitutional divalent ion or is covalently bonded to some of the Cl atoms.<sup>13,21</sup> However, since during the first few minutes of irradiation the lead band decreases, it is possible that a different state of lead is involved in the late-stage *F*-center production chemistry at room temperature. There are other pieces of evidence that also suggest that late-stage room-temperature colorability may be influenced

<sup>21</sup> W. J. Fredericks and A. B. Scott, *J. Chem. Phys.* **28**, 249 (1958).

by a state modified from that in the grown crystal. We find, for instance, that quenching of a heavily doped sample changes the liquid-nitrogen colorability. Similarly, Schulman<sup>11</sup> found changes in luminescence of NaCl resulting from quenching and room-temperature storage. But in spite of all these effects, no change in room-temperature late-stage colorability or, for that matter, the height of the *A* band was found in our experiments.

#### ACKNOWLEDGMENTS

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## Nature of the Self-Activated Blue Luminescence Center in Cubic ZnS:Cl Single Crystals

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Over-all optical properties of cubic ZnS:Cl single crystals were studied in order to clarify the nature of the self-activated luminescence center. The characteristic polarizations found both in fluorescence and in thermoluminescence provide the first information about the optical symmetry inherent in the luminescence center in sulfide crystals. From details of the observed azimuthal dependences of the polarization, it is concluded that the luminescence is due to the  $\sigma$  electric-dipole oriented along the tetrahedral bond direction in the cubic lattice of ZnS, and direct evidence is given for the identification of the luminescence center with the *A* center responsible for the electron-spin resonance absorption. There were found two excited states in the polarization spectra, the lower one being located at about 3.42 eV (363  $m\mu$ ) and the other at about 3.76 eV (330  $m\mu$ ) above the ground state. According to the observed polarization rules for the optical transitions between these states, the ground state is assigned to an *A*<sub>1</sub> state, while the emitting state and the second excited state, respectively, are assigned to *E* and *A*<sub>1</sub> states belonging to the *C*<sub>3v</sub> symmetry center, the luminescence being due to the *E*→*A*<sub>1</sub> transition. Physical pictures of these energy levels are given by simple molecular-orbital treatment on the basis of the model of a Zn<sup>2+</sup> ion vacancy associated with a substitutional Cl<sup>-</sup> ion, as proposed by Prener and Williams, for the luminescence center. The effects of the stacking faults and of possible Jahn-Teller distortion expected in the excited center are also discussed.

### I. INTRODUCTION

**D**URING the past decade, a great deal of effort has been spent in investigating the nature of centers responsible for the various kinds of luminescences in crystals of zinc sulfide and related compounds. In the course of these studies, it has been gradually revealed that some native lattice defects seem to play important roles in the luminescences characteristic of these crystals. Among such luminescences, the origin of the "self-activated" blue luminescence in ZnS has been discussed in a number of papers in the literature. As the atomic models for this center presented up to now one

finds an isolated zinc-ion vacancy,<sup>1-5</sup> a zinc-ion vacancy associated with substitutional coactivator ion,<sup>6</sup> or a sulfur-ion vacancy coupled with an oxygen ion.<sup>7</sup> These models, however, were all based either on the results of chemical or heat treatment of the phosphors or on

<sup>1</sup> R. H. Bube, *J. Phys. Chem.* **47**, 785 (1953).

<sup>2</sup> F. A. Kröger and H. J. Vink, *J. Chem. Phys.* **22**, 250 (1954).

<sup>3</sup> R. Bowers and N. T. Melamed, *Phys. Rev.* **99**, 1781 (1955).

<sup>4</sup> A. Addamiano, *J. Chem. Phys.* **23**, 1541 (1955).

<sup>5</sup> H. Samelson and A. Lempicki, *Phys. Rev.* **125**, 901 (1962).

<sup>6</sup> J. S. Prener and F. E. Williams, *J. Chem. Phys.* **25**, 361 (1956).

<sup>7</sup> N. Riehl and H. Ortmann, *J. Gen. Chem. USSR* **25**, 1057, 1289, 1639 (1955); *J. Phys. Radium* **17**, 620 (1956).