

less decay, while 13(b) gives rise to luminescence. The occurrence of the 13(a) or 13(b) condition depends upon the relaxation of the lattice around the exciton ion. The relaxation of the lattice could be greatly modified by the presence of a defect such as a dislocation. In particular, the change of density near a dislocation or the Coulombic action of debris of charges at jogs could decrease the relaxation of the lattice and thus favor the occurrence of the condition 13(b).

It is often assumed that the configurational curves of Fig. 13 for the fundamental and excited state are parabolas, with the one representing the fundamental state more concave.<sup>23</sup> Under this assumption Dexter,

<sup>23</sup> A. von Hippel, *Z. Physik* **101**, 680 (1936).

Klick and Russell<sup>24</sup> derived an upper limit for the wavelength  $\lambda_{lum}$  of the emitted light:

$$\lambda_{lum} \leq 2\lambda_{abs}, \tag{5}$$

where  $\lambda_{abs}$  is the wavelength of the exciting light. The data of Fig. 8 show that the condition (5) is not satisfied for the luminescence of strained KI crystals. This means probably that the parabolic assumption which leads to (5) is not correct in regions of strained lattice.

ACKNOWLEDGMENTS

The author wishes to thank Professors F. Seitz and R. J. Maurer for many stimulating discussions and advice.

<sup>24</sup> Dexter, Klick, and Russell, *Phys. Rev.* **100**, 603 (1955).

Photoconductivity of Z Bands in KCl and an Associated New Band\*

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Photoconductivity measurements have been made on colored KCl crystals, both pure and strontium doped. Assuming the room-temperature quantum efficiency for photoconductivity of the *F* center to be unity, the room-temperature quantum efficiencies of the *Z*<sub>1</sub> and *Z*<sub>2</sub> bands are found to be 0.3±0.03 and 1.0±0.2, respectively. The comparison of these results to the previously reported observations on optical bleaching is discussed. Estimates of quantum efficiencies for other bands in pure crystals are *R*<sub>1</sub>, 0.9; *R*<sub>2</sub>, 0.5; *M*, 0.15; *N*, 0.6, with an accuracy of about 25%. Low-temperature absorption measurements (100°K) accompanying this work show a small band at 860 millimicrons in the doped crystals. Its proximity to the *M* band prevents complete resolution, but its behavior is similar to that of the *Z*<sub>1</sub> band. The possibility of contamination by an unknown impurity exists, but it seems likely that the new band is genuinely due to the strontium additive. It has been named the *Z*<sub>4</sub> band, and probable models for the *Z*<sub>4</sub> center are considered.

I. INTRODUCTION

IN 1939 Pick<sup>1</sup> reported the experimental facts and a tentative set of models for an interesting series of optical absorption bands (the *Z* bands) which were observed in colored KCl crystals with alkaline-earth additive. More recently Seitz<sup>2</sup> has summarized the available information on these bands and has proposed a new set of models for the color centers associated with them. The work of Camagni and Chiarotti<sup>3</sup> on the conversion of the *F* band into the *Z*<sub>1</sub> band provides support for Seitz's models, which are shown in Fig. 1.

The *Z*<sub>2</sub> band has been observed to bleach somewhat under light which it absorbs, while the *Z*<sub>1</sub> band has not, and it has therefore been suggested that the *Z*<sub>2</sub> center should be photoconductive and the *Z*<sub>1</sub> center

should not be. We have studied the photoconductivity *versus* wavelength of incident light for colored KCl crystals, both pure and strontium-doped, at room temperature. In the course of the investigation a new absorption band was seen which appears to be associated with the presence of the strontium additive. A tentative model is proposed on the basis of the available information.

II. EXPERIMENTAL METHODS

The KCl crystals were grown from J. T. Baker Chemical Company reagent-grade chemicals by with-

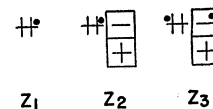


FIG. 1. The *Z*-center models of Seitz. Only the changes in the otherwise undisturbed lattice are shown. The *Z*<sub>1</sub> center consists of an electron bound to a divalent ion. The *Z*<sub>2</sub> center is obtained by combining a *Z*<sub>1</sub> center and a pair consisting of a positive- and a negative-ion vacancy. The *Z*<sub>3</sub> center is obtained when a *Z*<sub>2</sub> center captures a second electron.

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<sup>1</sup> H. Pick, *Ann. Physik* **35**, 73 (1939).

<sup>2</sup> F. Seitz, *Phys. Rev.* **83**, 134 (1951).

<sup>3</sup> P. Camagni and G. Chiarotti, *Nuovo cimento* **11**, 1 (1954).

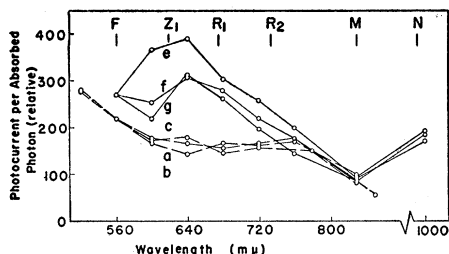


FIG. 2. Photocurrent per absorbed photon at room temperature for additively colored crystals following *F*-light illumination; the  $Z_1$  band is present in the doped crystals. *a, b, c*: Strontium-doped KCl. *e, f, g*: Pure KCl.

drawal from the melt at a rate of about 1 cm per hour. The impurity-doped crystals were grown from a melt containing about  $5 \times 10^{-4}$  mole fraction of strontium; an estimate based on the growth rate used gave  $10^{-4}$  as the mole fraction of strontium in the doped crystals.<sup>4</sup> The crystals were colored either additively with sodium metal at approximately 600°C or by x-raying at 200 kilovolts and 25 milliamperes for times up to one hour with an exposure rate of 4500 roentgens per minute.

A crystal specimen to be studied was mounted in a metal vacuum Dewar with quartz windows in such a way that either photocurrent measurements or liquid-nitrogen temperature absorption measurements could be made. Optical absorption measurements were made with a Beckman Model DK Recording Spectrophotometer, which also served as a variable-wavelength light source (slit width constant at 1.0 mm) for the photocurrent measurements. A Dershem electrometer was used to measure the photocurrents, which were of the order of  $10^{-12}$  ampere with a 22.5-volt applied potential.

Space-charge buildup at the negative electrode causes an exponential decay of photocurrent; this behavior is perturbed after a short time by the onset of field emission.<sup>5,6</sup> It was determined experimentally that the approximation that charge flow is proportional to elapsed time was appropriate for the small currents and short light pulses (ranging from one-half to two seconds long) used here. To avoid buildup of polarization effects the applied potential was reversed for alternate readings, and the crystal was shorted out for approximately five minutes between readings. The light shutter was actuated and timed by use of an Atomic Scaler connected to count the sixty-cycle ac line.

The chief effect inhibiting clear interpretation of the results was the overlapping of the *Z* bands by the *F*,  $R_1$ , and  $R_2$  bands. Comparison of results from a doped crystal before and after the *Z* bands had been produced proved difficult from a practical standpoint because the process of cleaning and mounting an additively colored

doped crystal invariably produced some  $Z_1$  band. Control crystals were employed to circumvent this difficulty. The pure (control) and doped crystals were subjected to identical treatments and measurements of photocurrent *versus* wavelength. The final curves of photocurrent per absorbed quantum were normalized and averaged so that comparisons between doped crystals, containing  $Z_1$  or  $Z_2$  centers, and the appropriate controls could be made. Conclusions regarding the quantum efficiencies of the  $Z_1$  and  $Z_2$  centers relative to that of the *F* center are drawn from these results. An implicit assumption is that the behaviors of the *R* and *M* bands are essentially the same in the doped crystals as in the pure ones. Qualitative observations confirm this for the *M* band.

The most useful presentation of the results is in the form of relative photocurrent per absorbed photon *versus* wavelength. An optical pyrometer was used to obtain the energy distribution *versus* wavelength of the Beckman tungsten lamp, and this result was corrected for spectrophotometer dispersion and absorption of the lamp glass. The fraction of incident light absorbed *versus* wavelength was determined by optical absorption measurements. The results for the different crystals were normalized to coincide at 560 millimicrons. Graphs of photocurrent per absorbed photon for three doped and three pure crystals are shown in Fig. 2 ( $Z_1$  band present for the doped crystals) and Fig. 3 ( $Z_2$  band present for the doped crystals).

### III. PHOTOCONDUCTIVITY RESULTS

A standard development presents photoconductivity results in terms of the product of quantum efficiency (the probability that an electron is freed whenever a light quantum is absorbed), electron mobility, and mean life of a conduction electron in the crystal.<sup>7,8</sup> Since, for a given crystal at a constant temperature, electron mobility and mean life of the freed electrons should be independent of the wavelength of the absorbed light, the variation of photocurrent per absorbed photon with wavelength represents the variation of quantum efficiency with wavelength.

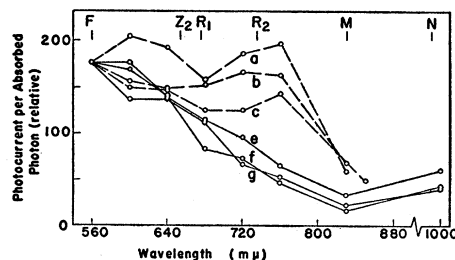


FIG. 3. Photocurrent per absorbed photon at room temperature for additively colored crystals following *F*-light illumination and subsequent heating to 125°C; the  $Z_2$  band is present in the doped crystals. *a, b, c*: Strontium-doped KCl. *e, f, g*: Pure KCl.

<sup>4</sup> H. Kelting and H. Witt, *Z. Physik* **126**, 697 (1949).

<sup>5</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 118.

<sup>6</sup> von Hippel, Gross, Jelatis, and Geller, *Phys. Rev.* **91**, 568 (1953).

<sup>7</sup> H. Rögner, *Göttingen Nachr.* **3**, 219 (1941).

<sup>8</sup> F. Seitz, *Revs. Modern Phys.* **18**, 384 (1946).

One expects unit quantum efficiency of the  $F$  band<sup>9</sup> to be evidenced by a maximum of photocurrent per absorbed photon through the wavelength region dominated by the  $F$  band. The curves for pure KCl crystals after heating exhibit this behavior (see Fig. 3), but those for pure KCl before heating show a rise from 560 to 640  $m\mu$  (see Fig. 2). Such behavior might be due to absorption in the  $F$  region by centers other than  $F$  centers. The subject of hitherto unresolved structure in the  $F$  band received considerable attention at the recent (October 31–November 2, 1956) color center symposium held at Argonne National Laboratory.

Assuming the quantum efficiency of the  $F$  center to be unity, one can compute the quantum efficiency of the  $Z_1$  center on the basis of the relative change in photocurrent per absorbed photon from the  $F$  region to the  $Z_1$  region in a doped crystal compared with analogous results for the pure, or control, crystals. The room-temperature parameters (peak locations and half-widths at half-height) quoted by Camagni and Chiarotti<sup>3</sup> for the  $F$  and  $Z_1$  bands were used to compute the relative absorptions at 560, 600, and 640  $m\mu$ ; calculations of quantum efficiency were based on measurements made at these three wavelengths, where  $F$  and  $Z_1$  predominate. Since there were no individual correspondences between the doped and pure crystals, the calculations were made by comparing each doped crystal with the average of the three pure crystals. Considering the relative changes in photocurrent per absorbed photon, one can write

$$\frac{p(600)/p(560)}{p_0(600)/p_0(560)} = \frac{\eta(F)f(600) + \eta(Z_1)z(600)}{\eta(F)f(560) + \eta(Z_1)z(560)},$$

where  $p(600)$  = photocurrent per absorbed quantum for a doped crystal when illuminated by 600- $m\mu$  light,  $p_0(600)$  = the same quantity for a control crystal,  $\eta$  = quantum efficiency of the indicated center,  $f(600)$  = the fraction of light absorbed by  $F$  centers at 600  $m\mu$ , and  $z(600)$  = the same quantity for the  $Z_1$  centers.

One would expect the denominator of the left-hand side of the above equation to be unity; as already remarked, however, the observations did not bear this out. Under the assumption that  $\eta(F)$  is unity, the values for  $\eta(Z_1)$  were calculated by using data from three additively colored doped crystals compared with averages from three additively colored pure crystals, and from one x-ray colored doped crystal compared with one x-ray colored pure crystal. The results are shown in Table I. Average results from the four specimens were assigned weights in the customary fashion<sup>10</sup> in order to find the mean and standard deviation,

$$\eta(Z_1) = 0.30 \pm 0.03.$$

<sup>9</sup> H. Pick, Ann. Physik 31, 365 (1938).

<sup>10</sup> H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand Company, Inc., New York, 1948), p. 498.

TABLE I. Results for  $\eta(Z_1)$  from four specimens. The different values for each crystal are obtained by using observations at different pairs of the wavelengths 560, 600, and 640  $m\mu$ .

	$\eta(Z_1)$			Average
	Additively colored doped KCl			
<i>a</i>	0.31	0.35	0.30	0.32
<i>b</i>	0.13 <sub>s</sub>	0.24 <sub>s</sub>	0.20 <sub>s</sub>	0.19 <sub>s</sub>
<i>c</i>	0.18	0.51	0.36	0.35
	X-ray colored doped KCl			
<i>d</i>	0.14	0.46	0.33	0.31

The analogous computation for the  $Z_2$  band is less precise. Accurate values of the room-temperature parameters of the  $Z_2$  band are not available, so the relative contributions of the  $F$  and  $Z_2$  bands to the absorption have to be estimated. The curves of photocurrent per absorbed photon (Fig. 3) indicate directly that the  $Z_2$ -band quantum efficiency is essentially the same as that of the  $F$  band. The calculated result is approximately  $1.0 \pm 0.2$ .

The observation of  $Z_2$ -band bleaching led Seitz<sup>2</sup> to suggest that the  $Z_2$  band should be photoconductive. Failure to observe  $Z_1$  bleaching seems to imply the converse. The existence of some  $Z_1$ -center photoconductivity can be reconciled with the lack of observed bleaching by the room-temperature overlapping of the  $Z_1$  and  $F$  bands and the wavelength range usually covered by the bleaching light. Moderate loss of  $Z_1$  centers during illumination with  $Z_1$ -band light might well be compensated for by the reaction  $F$  to  $Z_1$  caused by light absorbed by  $F$  centers. Photons absorbed by  $F$  centers would be over three times as effective as those absorbed by  $Z_1$  centers in bleaching the absorbing center if the quantum efficiencies stated above are correct.

The contributions of the various other bands to the absorption at any given wavelength could not be determined precisely, but rough estimates of the quantum efficiencies of the  $R$ ,  $M$ , and  $N$  bands can be made. The results are

$$R_1, 0.9; R_2, 0.5; M, 0.15; N, 0.6;$$

with an accuracy of approximately 25% in all cases. Results of Oberly<sup>11</sup> for x-ray colored KBr indicate the same general behavior, and Barth<sup>12</sup> has found a result of 0.10 for the  $M$  center in KCl.

#### IV. NEW BAND

Absorption measurements at 100°K show the presence of a new band at 860  $m\mu$  in the strontium-doped crystals<sup>13</sup> (see Figs. 4 and 5). The band is of the same

<sup>11</sup> J. J. Oberly, Phys. Rev. 84, 1257 (1951).

<sup>12</sup> C. Barth, Z. Physik (to be published). Reference given by F. Seitz, Revs. Modern Phys. 26, 7 (1954).

<sup>13</sup> This band was first reported at the Fifth Annual Midwest Solid State Conference, University of Chicago, October 6, 1956 (unpublished). Since this paper has been in preparation, the

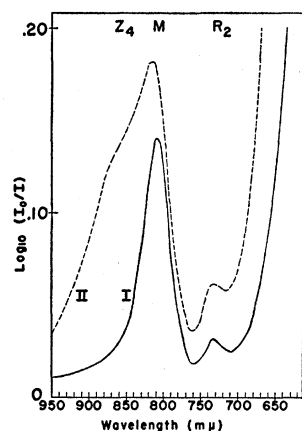


FIG. 4. Absorption curves (100°K) for an x-ray colored strontium-doped KCl crystal. I: Initially. II: After prolonged *F*-light illumination.

order of size as the *M* band and overlaps it considerably. In a colored doped crystal the band appears during the *F*-light illumination applied to produce the *Z*<sub>1</sub> band (see Fig. 4). Heating to cause the *Z*<sub>1</sub> to *Z*<sub>2</sub> reaction in an additively colored crystal causes the new band to disappear (see Fig. 5). For an x-ray colored crystal the effect of room-temperature thermal bleaching is much more pronounced on the *Z*<sub>1</sub> band and the new band than it is on the *F* band; subsequent *F*-light illumination can re-establish them at the expense of the *F* band, however.

The possibility that the new band is due to some impurity other than strontium is nearly ruled out by the following considerations. (1) The same procedures and equipment were used for growing both pure and doped crystals, and the new band was observed in all of the doped crystals tested but in none of the pure ones; the doped crystals were grown after the pure ones, however. (2) Any impurity present in the SrCl<sub>2</sub> additive should be negligible in the doped crystals; the largest impurity specified was magnesium to less than 0.05%. (3) Reports in the literature<sup>14-18</sup> concerning the effect of various additives on colored KCl do not mention a band anywhere near the wavelength region occupied by the new band.

Assuming that the new band is the result of the strontium impurity, we shall call it the *Z*<sub>4</sub> band and go on to consider its possible nature. An outstanding characteristic of the *Z*<sub>4</sub> band is its appearance and disappearance in company with the *Z*<sub>1</sub> band. This suggests that the two bands are somehow related. Unfortunately the absorption measurements were not sensitive over a wide enough range to show whether the ratio of the *Z*<sub>1</sub>- to *Z*<sub>4</sub>-band peaks was constant. In any case it is

appearance of a band at 850 mμ under similar circumstances has been mentioned by E. J. West and W. D. Compton, *Bull. Am. Phys. Soc. Ser. II*, 2, 155 (1957).

<sup>14</sup> M. Blau, *Gött. Nachr., Math.-Phys. Kl.* p. 401 (1933).

<sup>15</sup> A. D. von Lupke, *Ann. Physik* 21, 1 (1934).

<sup>16</sup> K. Korth, *Gött. Nachr., Math.-Phys. Kl. (N.F.)* 1, 221 (1935).

<sup>17</sup> O. Stasiw, *Gött. Nachr., Math.-Phys. Kl. (N.F.)* 2, 1 (1936).

<sup>18</sup> R. W. Pohl, *Physik. Z.* 39, 36 (1938).

unlikely that the *Z*<sub>4</sub> band is due to absorption by the same center as the *Z*<sub>1</sub> band because this would require that the low-energy transition have a much lower transition probability than the high-energy transition.

The models of Seitz<sup>2</sup> for the *Z*<sub>1</sub> and *Z*<sub>2</sub> centers will be assumed; this eliminates as a *Z*<sub>4</sub> possibility the unit composed of a *Z*<sub>1</sub> center and a neutral vacancy pair. The analogous locations of the *F* and *M* bands to the *Z*<sub>1</sub> and *Z*<sub>4</sub> bands suggest such a model, but it has already been identified with the *Z*<sub>2</sub> center. The two most likely *Z*<sub>4</sub> models are discussed below.

A strong possibility for the *Z*<sub>4</sub> center is that of an electron trapped at an impurity complex (a divalent ion with an associated positive-ion vacancy) [see Fig. 6(A)] since many such complexes are present in the crystal. In fact, since the work of Camagni and Chiarotti<sup>3</sup> has shown that only about one-thirtieth of the strontium-ion complexes are dissociated at room temperature, the concentration of impurity complexes is approximately equal to the total concentration of strontium. When electrons are freed by *F*-light illumination, there are

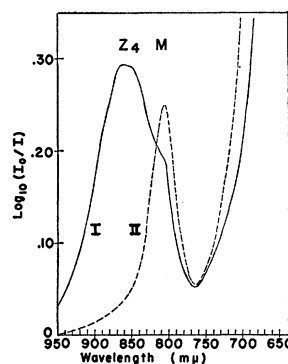


FIG. 5. Absorption curves (100°K) for an additively colored strontium-doped KCl crystal. I: After *F*-light illumination. II: After subsequent heating to 125°C.

several possibilities: (1) The impurity complexes do not trap electrons. (2) The impurity complexes do trap electrons to some extent. Assuming that such trapping does occur, there are two sub-possibilities: (2a) The trapped electrons are retained, thus forming the suggested *Z*<sub>4</sub> centers. (2b) The unit resulting from the trapping dissociates into a *Z*<sub>1</sub> center and a positive-ion vacancy. (3) The *Z*<sub>4</sub> centers do exist as suggested, and there is an equilibrium between *Z*<sub>4</sub> centers on the one hand and *Z*<sub>1</sub> centers and positive-ion vacancies on the other. Such an equilibrium would allow these *Z*<sub>4</sub> centers to exist under the assumptions of (1) or (2b) above as well as (2a).

A rough estimate can be made of the extent of association to be expected in the *Z*<sub>1</sub> to *Z*<sub>4</sub> equilibrium by comparison to the association of impurity complexes. Let  $x_v$ ,  $x_{++}$ ,  $x_e$ ,  $x_{++'}$ , and  $x_e'$  represent the concentrations of positive-ion vacancies, divalent ions, impurity complexes (divalent ions with an associated positive-ion vacancy), divalent ions with an electron (*Z*<sub>1</sub> centers), and impurity complexes with an electron (proposed *Z*<sub>4</sub>

centers). Then the two equilibria are governed by

$$\begin{aligned}x_o/(x_{++}x_v) &= 12 \exp(W_o/kT), \\x'_o/(x_{++}'x_v) &= 12 \exp(W'_o/kT),\end{aligned}$$

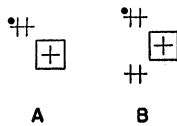
where the factor of 12 occurs because each of the impurity complexes can have 12 different spatial orientations. From these equations the following ratio can be obtained:

$$\frac{x_o/x_{++}}{x'_o/x_{++}'} = \exp[(W_o - W'_o)/kT].$$

For the association of impurity complexes Camagni and Chiarotti report values of  $W_o = 0.3$  ev and  $x_o/x_{++} \cong 30$  at room temperature.<sup>8</sup> The observed ratio of the  $Z_4$  to  $Z_1$  peak heights is approximately 1/20; this value will be obtained for  $x'_o/x_{++}'$  in the above equation if  $W'_o = 0.13$  ev. Since a very rough estimate of the association energy of the proposed  $Z_4$  centers by purely electrostatic considerations indicates that  $W'_o$  should be one-third to one-half as large as  $W_o$ , the observed equilibrium ratios are entirely consistent with the expected values.

For the production of  $Z_1$  centers by  $F$ -light illumination, the results of Camagni and Chiarotti show first a

FIG. 6. Suggested models for the  $Z_4$  center. Model A: An electron trapped at an impurity complex (a divalent ion with an associated positive-ion vacancy). Model B: An electron trapped at a complex consisting of two divalent ions and one positive-ion vacancy.



rapid increase in the number of  $Z_1$  centers, presumably caused by the trapping of electrons at unassociated divalent ions, and then a leveling off as the number of unassociated divalent ions is exhausted.<sup>8</sup> There is an indication in their graphs, however, of a much slower continued increase in the number of  $Z_1$  centers, and it is possible that this increase may be due to the capture of electrons by impurity complexes, followed in most cases by dissociation into  $Z_1$  centers as proposed above. If this mechanism is tentatively assumed, it is possible to calculate the ratio of the trapping cross section of impurity complexes for electrons to the trapping cross section of unassociated divalent ions for electrons. The calculated ratio of 0.0003 is quite in accord with Harten's work<sup>19</sup> on x-ray produced photocurrents in KCl doped with calcium or strontium, which fact indi-

cates that the complexes are ineffective electron traps at room temperature.

Since the discussions above merely serve to indicate that the proposed model is not in conflict with other observations, it seems worthwhile to consider another possible model for the  $Z_4$  center. The analogy to the  $M$  center suggests a  $Z_4$  center containing two divalent positive ions, just as the  $M$  center is thought to contain two negative-ion vacancies. Such a unit is shown in Fig. 6(B). This center could be formed if double complexes consisting of two divalent positive ions and two positive-ion vacancies were present in the lattice. Capture of a conduction-band electron would probably result in expulsion of a positive-ion vacancy. Such expulsion processes are thought to occur in other cases.<sup>8,20</sup> A small concentration of the double complexes necessary for this formation mechanism could result from clustering of the complexes at room temperature if they are sufficiently mobile or could be "frozen in" from some higher temperature experienced when the crystal was grown or colored.

Let us designate the model just proposed as Model B. The single impurity complex with a trapped electron will be called Model A; the equilibrium process between it and the  $Z_1$  center will be assumed. Now let us consider the relative merits of the two models. The suggested formation processes appear equally reasonable, but the existence of the trapping centers necessary for formation is much better established for Model A than for Model B. The long-wavelength location of the absorption band is appropriate to either model because the electron binding in either case should be less tight than that of the  $F$  or  $Z_1$  center. The new absorption band is not so sharp as the  $M$  band (see Figs. 4 and 5), which is thought to be a neutral center (like Model B), but it is not so broad as the  $F'$  or  $Z_3$  bands,<sup>1</sup> which are thought to be centers of net negative charge (like Model A); the band-shape evidence is thus inconclusive. The similarity of behavior of the  $Z_1$  and  $Z_4$  bands is nicely accounted for by the equilibrium postulated as a part of Model A. Mechanisms agreeing with the observed behavior can be devised for Model B, but simplicity is lacking.

In view of the evidence available at present the writers feel that Model A is the more likely. Further studies which would help to select the correct  $Z_4$  model include careful determinations of the  $Z_1$ - to  $Z_4$ -band ratios under various conditions and the measurement of  $Z_4$ -band size as a function of strontium impurity concentration.

<sup>19</sup> H. U. Harten, Gött. Nachr., Math.-Phys. Kl. IIa, No. 3, 15 (1950).

<sup>20</sup> F. Seitz, Revs. Modern Phys. 26, 7 (1954).