

## Z<sub>2</sub> and Z<sub>3</sub> Color Centers in KCl and KBr†

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The optical and electron-spin-resonance properties of potassium-chloride and -bromide crystals which contain divalent strontium ions have been examined. The conversion of the Z<sub>2</sub> optical absorption band into the Z<sub>3</sub> band has been studied and two new absorption bands have been discovered. One of these bands, the S band, appears to be due to optical transitions to excited states of the Z<sub>2</sub> center which lie above the excited state responsible for the Z<sub>2</sub> band. The second band, the ξ<sub>3</sub> band, is interpreted as an exciton absorption band associated with the Z<sub>3</sub> center. It is proposed that the Z<sub>3</sub> center is the product of photoionization of the Z<sub>2</sub> center; that the Z<sub>2</sub> center is an electrically neutral center which consists of a divalent strontium ion and an F' center on nearest-neighbor sites; that the Z<sub>3</sub> center consists of a divalent strontium ion and an F center on nearest-neighbor sites.

### INTRODUCTION

ALKALI-HALIDE crystals which contain small amounts of divalent alkaline earth ions exhibit the F optical absorption band after additive coloration and rapid cooling to room temperature. The F band of these impure crystals can be converted by optical and thermal bleaching into the Z bands of which four have been identified. The early studies of the color centers which are responsible for the Z bands have been reviewed by Seitz.<sup>1</sup>

Pick, the discoverer of the Z bands, and Seitz have proposed models of the Z<sub>2</sub> and Z<sub>3</sub> centers, the subject of the present investigation.<sup>2</sup> Their models are illustrated in Fig. 1. Pick suggests that the Z<sub>2</sub> center is formed by the capture of an electron by a divalent alkaline earth ion and that the capture of a second electron by the Z<sub>2</sub> center results in a Z<sub>3</sub> center, an alkaline earth atom. Seitz has proposed that a Z<sub>2</sub>

center is a monovalent alkaline earth ion which is associated with an adjacent vacancy pair and that the trapping of an electron by this center converts it into a Z<sub>3</sub> center. The relationship between Z<sub>2</sub> and Z<sub>3</sub> centers is the same as that between F and F' centers according to these authors. But the Z<sub>3</sub> band is not similar to the F' band. The Z<sub>3</sub> band lies on the short-wavelength side of the Z<sub>2</sub> band and has a half-width that is almost the same as that of the F band. The F' band is very broad and has its maximum on the long-wavelength side of the F band. It is the purpose of this paper to show that the Z<sub>3</sub> center is formed by the loss of an electron by a Z<sub>2</sub> center. New models of the Z<sub>2</sub> and Z<sub>3</sub> centers are proposed.

### EXPERIMENTAL

Single crystals of potassium chloride and bromide were grown from the melt in an atmosphere of nitrogen by the Kyropoulos technique. A platinum crucible contained the melt which was prepared from reagent grade salts or crystals obtained from the Harshaw Chemical Company or Optovac, Inc. Strontium chloride or bromide was added to the melt to provide the desired strontium concentration in the crystals.

The crystals were additively colored in potassium vapor at high temperature and were quickly cooled to room temperature where they exhibited the typical F absorption band. Z<sub>2</sub> centers were formed in potassium chloride by absorbing light in the F band at temperatures between 80 and 150°C.<sup>3</sup> The corresponding temperature range for this process in potassium bromide was from 30 to 50°C. At the temperature of liquid nitrogen, the maximum of the Z<sub>2</sub> absorption band is at 635 mμ in potassium chloride and at 710 mμ in potassium bromide.

The Z<sub>3</sub> and F' bands were formed by absorbing light in the Z<sub>2</sub> or the F band at low temperature. This photochemical process is most efficient at -100°C in potassium chloride and at -150°C in potassium bro-

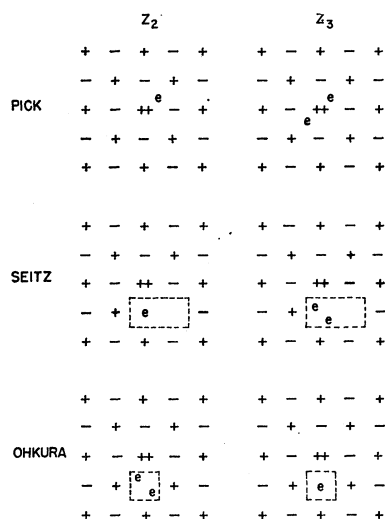


FIG. 1. Models of the Z<sub>2</sub> and Z<sub>3</sub> centers according to Pick, Seitz, and Ohkura.

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<sup>1</sup> F. Seitz, Phys. Rev. 83, 134 (1951); Rev. Mod. Phys. 26, 7 (1954).

<sup>2</sup> H. Pick, Ann. Physik 35, 73 (1939); Z. Physik 114, 127 (1939).

<sup>3</sup> G. Chiarotti, F. G. Fumi, and L. Giulotto, Report of the Conference on Defects in Crystalline Solids (The Physical Society, London, 1954), p. 317.

mide. The formation of the Z<sub>3</sub> and F' bands is accompanied by a decrease in the Z<sub>2</sub> and F bands.

The optical absorption of the Z<sub>2</sub> center overlaps that of the F center. It is because of this overlap that irradiation with light in the wavelength region of F-center absorption converts Z<sub>2</sub> centers into Z<sub>3</sub> centers. Careful experiments with strontium-doped crystals established that in the absence of Z<sub>2</sub> centers low-temperature optical bleaching of the F band resulted only in the formation of F' centers.

The optical absorption measurements were made with Cary Model 14R and 15 spectrophotometers. An X-band microwave apparatus was used for the electron-spin-resonance studies.<sup>4</sup> The static magnetic field was 3300 Oe and the microwave power was modulated at 455 kc/sec.

### RESULTS

The optical absorption of an additively colored KCl-SrCl<sub>2</sub> crystal at 78°K is shown in Fig. 2 by the dashed curve. The strontium concentration of the melt from which this crystal was grown was  $1 \times 10^{-4}$  mole fraction and the strontium concentration of the crystal was estimated to be  $3 \pm 1 \times 10^{-5}$  mole fraction.<sup>5</sup> Curve a of Fig. 2 is the result of absorbing light in the F band at 150°C. The optical bleaching of the F band was continued to saturation, that is, until it ceased to decrease. The Z<sub>2</sub> band has appeared on the long-wavelength side of the F band and a broad absorption

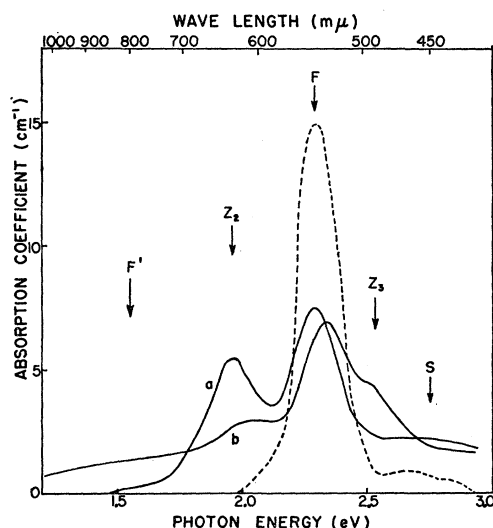


FIG. 2. The optical absorption of a KCl-SrCl<sub>2</sub> crystal at 78°K. Dashed curve is F absorption band after additive coloration. Initial F-center concentration was  $3.9 \times 10^{16}$  cm<sup>-3</sup>. Curve a: Absorption after optical bleaching of the F band and formation of Z<sub>2</sub> and S bands. Curve b: Absorption after optical bleaching of the Z<sub>2</sub> band and formation of Z<sub>3</sub> and F' bands.

<sup>4</sup>H. Ohkura and K. Murase, J. Phys. Soc. Japan 18, Suppl. II, 255 (1963).

<sup>5</sup>J. S. Cook and J. S. Dryden, Australian J. Phys. 13, 260 (1959); H. Kelting and H. Witt, Z. Physik 126, 697 (1949).

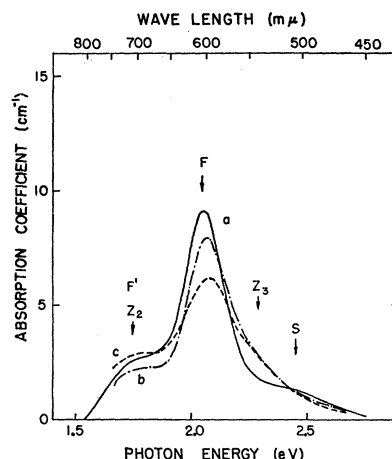


FIG. 3. The optical absorption of a KBr-SrBr<sub>2</sub> crystal at 78°K. The initial concentration of F centers was  $4.8 \times 10^{16}$  cm<sup>-3</sup>. Curve a: Absorption after optical bleaching of the F band and formation of the Z<sub>2</sub> and S bands. Curve b: Absorption after optical bleaching of the Z<sub>2</sub> band and formation of the Z<sub>3</sub> and F' bands at -150°C. Curve c: Absorption after optical bleaching of the F band at -150°C.

band, which has not been previously described, has appeared on the short-wavelength side of the F band. This band, which will be referred to as the S band, has a maximum at 450 mμ.

Curve a of Fig. 3 shows the optical absorption of a KBr-SrBr<sub>2</sub> crystal after optical bleaching to saturation of the F band at 50°C. The Z<sub>2</sub> band has appeared on the long-wavelength side of the F band and, as in the case of the KCl-SrCl<sub>2</sub> crystal, there is a broad S band with a maximum at 510 mμ. The KBr-SrBr<sub>2</sub> crystal was grown from a melt with a strontium bromide concentration of  $1 \times 10^{-5}$  mole fraction.

The effect of optical bleaching of the potassium chloride crystal at -100°C with light absorbed by the Z<sub>2</sub> band is shown by curve b of Fig. 2. The Z<sub>2</sub>, F, and S bands have decreased and the Z<sub>3</sub> and F' bands have appeared. The absorption of light by the Z<sub>2</sub> band of potassium bromide at -150°C results in a decrease in the magnitude of the Z<sub>2</sub>, F, and S bands and the appearance of the Z<sub>3</sub> band as shown by curve b of Fig. 3. Although it is not shown in Fig. 3, separate experiments have established that the F' band is also formed during this process.

The S band appears to be intimately associated with the Z<sub>2</sub> band and probably represents higher energy transitions of the Z<sub>2</sub> center. When potassium chloride crystals containing Z<sub>2</sub> and F centers, as illustrated by curve a of Fig. 2, were irradiated at -100°C by light of 400-mμ wavelength which was absorbed by the high-energy side of the S band, the result was the same as that obtained with light absorbed by the Z<sub>2</sub> band; i.e., the Z<sub>3</sub> and F' bands grew while the Z<sub>2</sub>, F, and S bands decreased. Similar results were obtained when this experiment was performed with potassium bromide at -150°C with light of 460-mμ wavelength. The pres-

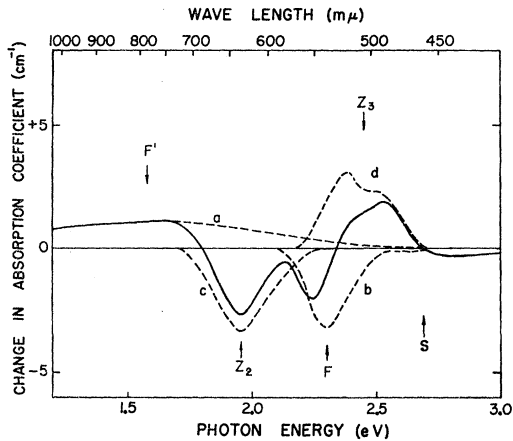


FIG. 4. Difference spectrum after optical bleaching of the  $Z_2$  band in KCl-SrCl<sub>2</sub>. The solid curve is the difference between curves b and a of Fig. 2. Curve a: the  $F'$  band formed. Curve b: the  $F$  band bleached. Curve c: the  $Z_2$  band bleached. Curve d: the  $Z_3$  band formed.

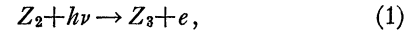
ence of a 450-m $\mu$  peak in the excitation spectrum of the luminescence of additively colored KCl-SrCl<sub>2</sub> which contained  $F$  and  $Z_2$  centers has been reported.<sup>6</sup> Optical excitation of the  $F$  band also resulted in  $Z_2$  center luminescence at 1.14  $\mu$ . These results are consistent with the present interpretation of the  $S$  band since there is considerable overlap of it with the  $F$  band.

The solid curve of Fig. 4 is the difference between curves b and a of Fig. 2. An attempt has been made to resolve this difference spectrum into its components. The  $F'$  band has been drawn as curve a of Fig. 4 by using the known shape of the  $F'$  band in pure potassium chloride. The  $F$  band has been drawn as curve b by using the known shape of the  $F$  band and the magnitude of the  $F'$  band. It was assumed that one  $F$  center was destroyed for each  $F'$  center created during the bleaching of the  $Z_2$  band. After subtraction of these two components from the solid curve, there remains curve c, the  $Z_2$  band which has been bleached, and curve d, the  $Z_3$  band which has been formed. The  $Z_3$  band is not of simple shape; it appears to have two major components.

The decrease in the maximum of the  $Z_2$  band during optical bleaching of it is proportional to the increase in the maximum height of the  $F'$  band. This result is shown in Fig. 5 for KCl-SrCl<sub>2</sub> where the concentration of  $F'$  centers formed has been plotted as a function of the concentration of  $Z_2$  centers which were destroyed. These concentrations were calculated from Smakula's equation and the assumption that the oscillator strengths of the bands are unity.<sup>7</sup> It should be noted that one  $F'$  center is created for each  $Z_2$  center which is destroyed. It was also found that the magnitude of the increase in the  $Z_3$  band was proportional to the

decrease in the magnitude of the  $Z_2$  band. The height of the  $Z_3$  band at 488 m $\mu$  was used as a measure of its magnitude.

The observations that have been described are neatly explained by the assumption that the absorption of a photon by a  $Z_2$  center converts it into a  $Z_3$  center and a free electron and that the free electron is captured by an  $F$  center to form an  $F'$  center. These processes are summarized by the equations



This description of the photochemical conversion of  $Z_2$  centers into  $Z_3$  centers is, however, inconsistent with the relationship of the centers proposed by Pick and Seitz. According to these authors, a photon may free an electron from a  $Z_2$  center. The electron is subsequently captured by either a  $Z_2$  center with the formation of a  $Z_3$  center, or by an  $F$  center with the formation of an  $F'$  center. The  $Z_2$  and  $F$  centers are competitive traps for free electrons. The processes summarized in Eqs. (1) and (2) present the  $Z_3$  center as the direct product of the photoionization of the  $Z_2$  center. The role of the  $F$  centers is to trap the free electrons and prevent their return to the  $Z_3$  centers where their capture would reform  $Z_2$  centers. In the absence of  $F$  centers, the photoproduction of  $Z_3$  centers from  $Z_2$  centers should be impossible.

Figure 6 shows the results of a series of experiments in which the fractional decrease in the concentration of  $Z_2$  centers after optical bleaching of the  $Z_2$  band to saturation was measured as a function of the ratio of the initial concentrations of  $F$  and  $Z_2$  centers. The experiments were performed with potassium chloride at  $-100^\circ\text{C}$  after forming the  $Z_2$  centers at  $140^\circ\text{C}$  by optical bleaching of the  $F$  band. As the concentration

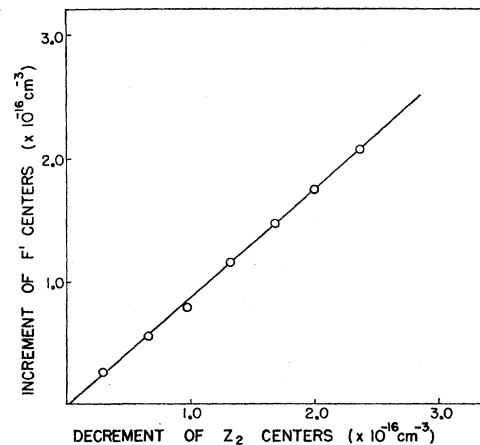


FIG. 5. The increase in the concentration of  $F'$  centers as a function of the concentration of optically bleached  $Z_2$  centers in KCl-SrCl<sub>2</sub> at  $-100^\circ\text{C}$ . The initial concentration of  $F$  centers was  $2.0 \times 10^{17} \text{ cm}^{-3}$ . The optical absorption measurements were made at  $78^\circ\text{K}$ .

<sup>6</sup> E. J. West and W. Dale Compton, Phys. Rev. **108**, 576 (1957).

<sup>7</sup> A. Smakula, Nachr. Akad. Wiss. Göttingen Math. Physik Kl. **1**, 55 (1934).

of *F* centers became small in comparison with the concentration of *Z*<sub>2</sub> centers, the fraction of the *Z*<sub>2</sub> centers which could be bleached approached zero. This result is inconsistent with the proposals of Pick and Seitz, but is in agreement with the photochemical reaction described by Eqs. (1) and (2).

Additional information concerning the nature of the *Z*<sub>3</sub> center was obtained by observing the changes in the ultraviolet absorption of potassium bromide at  $-150^{\circ}\text{C}$  that accompanied the optical bleaching of the *Z*<sub>2</sub> band. Curve *a* of Fig. 7 is the ultraviolet absorption spectrum of the crystal whose visible absorption spectrum is shown as curve *a* of Fig. 3. Since the crystal contains a large number of *F* centers, the long-wavelength absorption tail of the beta band is observed.<sup>8</sup> The beta band, whose peak position is shown by the arrow of Fig. 7, is due to exciton transitions occurring at *F* centers.<sup>9</sup> After the optical bleaching to saturation of the *Z*<sub>2</sub> band that transformed curve *a* into curve *b* of Fig. 3, the ultraviolet absorption was that of curve *b* of Fig. 7. The difference between curves *b* and *a* of Fig. 7 is an absorption band whose maximum is at  $198\text{ m}\mu$  and whose half-width is  $0.25\text{ eV}$ . This band will be called the  $\zeta_3$  band. Although it is similar to the alpha band, which is due to exciton transitions occurring at anion vacancies, it is definitely a different band.<sup>9</sup> The alpha band in potassium bromide has a half-width of  $0.23\text{ eV}$ , but its maximum is located at  $201.5\text{ m}\mu$ . The alpha band would not, of course, be expected to appear during the optical bleaching of the *Z*<sub>2</sub> band if Eqs. (1) and (2) are correct, since anion

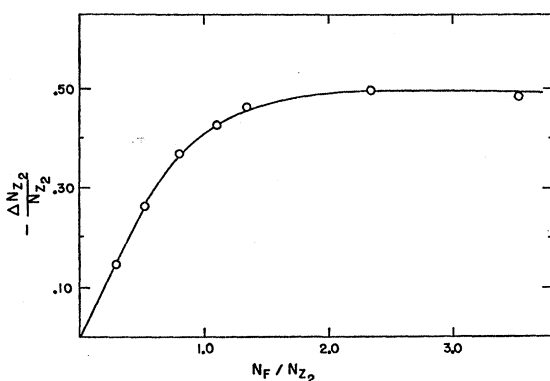


FIG. 6. The maximum attainable fractional decrease in the *Z*<sub>2</sub> center concentration as a result of optical bleaching of the *Z*<sub>2</sub> band as a function of the ratio of the concentration of *F* centers to *Z*<sub>2</sub> centers. The KCl-SrCl<sub>2</sub> crystal had an initial concentration of *F* centers of  $2.0 \times 10^{17}\text{ cm}^{-3}$  and the bleaching of the *Z*<sub>2</sub> centers was carried out at  $-100^{\circ}\text{C}$ .

<sup>8</sup> An absorption band on the short-wavelength side of the beta band at  $189.5\text{ m}\mu$  with a half-width of  $0.18\text{ eV}$  has been found. The height of this band is proportional to the height of the *Z*<sub>2</sub> band. This band may be the  $\zeta_2$  band, the exciton absorption band associated with the *Z*<sub>2</sub> center. Experiments are in progress to test this hypothesis.

<sup>9</sup> C. J. Delbecq, P. Pringsheim, and P. Yuster, *J. Chem. Phys.* **19**, 574 (1951); W. Martienssen, *Z. Physik* **131**, 488 (1952).

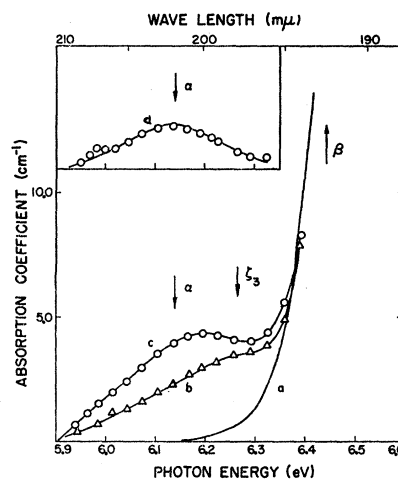


FIG. 7. The ultraviolet absorption of a KBr-SrBr<sub>2</sub> crystal. Curve *a*: After optical bleaching of the *F* band with formation of the *Z*<sub>2</sub> and *S* bands. Curve *b*: After optical bleaching of the *Z*<sub>2</sub> band and formation of the *Z*<sub>3</sub> and *F*' bands. Curve *c*: After optical bleaching of the *F* band at low temperatures. Insert: The alpha band, the difference between curves *c* and *b*.

vacancies are not created by these reactions; the decrease in the concentration of *F* centers is due to the formation of *F*' centers.

The formation of an alpha band in KBr-SrBr<sub>2</sub> crystals was observed in the following experiment: The crystal in the state shown by curves *b* of Figs. 3 and 7 was warmed from  $-190^{\circ}\text{C}$  to room temperature. The optical absorption was again that shown by curves *a* of Figs. 3 and 7 after this annealing. The crystal was then irradiated at  $-150^{\circ}\text{C}$  with light absorbed by the *F* band until the *F* band ceased to bleach. The optical absorption after this irradiation is shown by curves *c* of Figs. 3 and 7. A comparison of curve *c* with curves *a* and *b* of Fig. 3 shows that the *F* and *S* bands have been partially bleached and the *Z*<sub>3</sub> band has been formed. Also, a larger *F*' band has been formed than in the similar experiment in which the *Z*<sub>2</sub> band was bleached by light absorbed by it (curve *b*). That the absorption of light by the *F* band has resulted in the formation of anion vacancies is shown by the subtraction of curve *b* from curve *c* of Fig. 7. The difference of these two curves is shown as curve *d* of the insert of Fig. 7. This curve is clearly the alpha band. It has its maximum at  $202\text{ m}\mu$  and the proper half-width. Furthermore, the ratio of the maximum height of this alpha band to that of the simultaneously formed *F*' band is 0.51, the same ratio that has been observed after optical bleaching of *F* centers in pure potassium bromide crystals.

The existence of the  $\zeta_3$  band, its association with the *Z*<sub>3</sub> band, and its similarity to the alpha band strongly suggest that the *Z*<sub>3</sub> center is similar to the alpha center or anion vacancy in possessing a positive charge. The *Z*<sub>2</sub> center is a neutral center like the *F* center if Eq. (1) is correct.

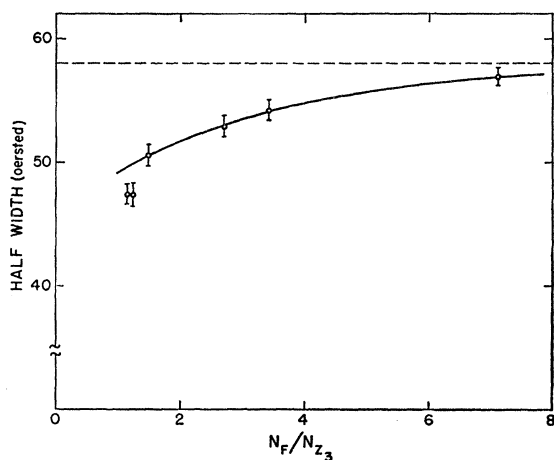


FIG. 8. The change in half-width of the electron-spin-resonance signal of KCl-SrCl<sub>2</sub> containing *F*, *Z*<sub>2</sub>, *Z*<sub>3</sub>, and *F'* centers as function of the ratio of the concentrations of *F* and *Z*<sub>3</sub> centers. The dashed line is the half-width of the *F*-center resonance signal. The initial concentration of *F* centers was  $3.0 \times 10^{17}$  cm<sup>-3</sup>. The measurements were made at  $-150^\circ\text{C}$ .

It has been shown that during the optical bleaching of *F* centers and the formation of *Z*<sub>2</sub> centers in KCl-SrCl<sub>2</sub> crystals, the decrease in magnitude of the observed electron-spin-resonance signal is approximately proportional to the decrease in the peak height of the optical absorption band with no change in half-width or *g* value.<sup>4</sup> It was concluded that the observed signal was due entirely to the *F* centers with no contribution from the *Z*<sub>2</sub> centers which are, therefore, diamagnetic and probably "two-electron" centers. This result has been confirmed by Takeuchi and co-workers.<sup>10</sup> Bushnell has not found spin-resonance absorption due to *Z*<sub>2</sub> centers in his electron nuclear double resonance studies.<sup>11</sup> Conklin and Friauf have reported, however, a spin-resonance absorption which they ascribed to *Z*<sub>2</sub> centers.<sup>12</sup>

The optical conversion of *Z*<sub>2</sub> centers into *Z*<sub>3</sub> centers in crystals containing *F* centers, as illustrated by curves a and b of Fig. 2, does result in a very small decrease in the magnitude of the electron-spin-resonance signal and a reduction in its half-width with no change in *g* value. The half-width of the spin-resonance signal at  $-150^\circ\text{C}$  is shown as a function of the ratio of the concentrations of *F* and *Z*<sub>3</sub> centers in Fig. 8. If the *Z*<sub>2</sub> center is diamagnetic, the observed changes are due to the paramagnetism of the *Z*<sub>3</sub> center since the *F'* center is diamagnetic. The half-width of the *Z*<sub>3</sub> spin-resonance signal was calculated to be  $39 \pm 2$  Oe from the data and Weger's formula.<sup>13</sup> This formula takes account of the fast passage effect which was present

because of the use of the 455-kc/sec modulation frequency.

It was assumed that the spin-lattice relaxation time *T*<sub>1</sub> of the *Z*<sub>3</sub> center was 50% larger than that of the *F* center. This assumption was necessary to explain the very small decrease in the observed resultant electron-spin-resonance signal during the conversion of *Z*<sub>2</sub> into *Z*<sub>3</sub> centers, since the half-width of the *Z*<sub>3</sub> center signal is less than that of the *F*-center signal. These observations suggest that the *Z*<sub>3</sub> center is a paramagnetic, "one-electron" center like the *F* center.

#### DISCUSSION

The optical and spin-resonance studies that have been described are consistent with the assumption that the *Z*<sub>3</sub> center is a "one-electron" paramagnetic center which can be formed by the photoionization of a "two-electron" diamagnetic *Z*<sub>2</sub> center. The resemblance of the ζ<sub>3</sub> band to the alpha band suggests that the *Z*<sub>3</sub> center is similar to the anion vacancy, at least in the possession of a positive charge.

These observations lead rather directly to the model of the *Z*<sub>3</sub> center that is illustrated in Fig. 1. This model may be described as a divalent strontium ion and an *F* center on adjacent lattice sites, or alternatively, as a monovalent strontium ion and an anion vacancy occupying adjacent lattice sites. A model of the *Z*<sub>2</sub> center is obtained by adding an electron to the *Z*<sub>3</sub> center; it may be described as a divalent strontium ion and an *F'* center on adjacent lattice sites. An equivalent description is a strontium atom and an anion vacancy on adjacent lattice sites. This model of the *Z*<sub>2</sub> center is also shown in Fig. 1.

The model of the *Z*<sub>3</sub> center is similar to that of the *F*<sub>A</sub> center which in potassium chloride or potassium bromide consists of an *F* center and a sodium ion on adjacent lattice sites.<sup>14</sup> The resemblance of the models of the *F*<sub>A</sub> and *Z*<sub>3</sub> centers extends to their absorption spectra. There are two absorption bands, the *A*<sub>1</sub> and the *A*<sub>2</sub> bands, associated with the *F*<sub>A</sub> center and the *Z*<sub>3</sub> band has two components as illustrated in Fig. 4, curve d. The dichroic properties of the components of the *Z*<sub>3</sub> band, which have not been investigated, should be examined to determine if they are similar to those of the *F*<sub>A</sub> center.

The *Z*<sub>2</sub> and *F* bands in KCl-SrCl<sub>2</sub> and NaCl-SrCl<sub>2</sub> at room temperature have been reported to show dichroism when examined with [100] oriented polarized light.<sup>15</sup> The dichroism of the *F* band, which was of opposite sign to that of the *Z*<sub>2</sub> band, may have been apparent and due to the overlapping *S* band. The luminescence of the *Z*<sub>2</sub> center that was excited by polarized radiation was found, however, to be unpolarized.<sup>7</sup>

<sup>10</sup> T. Takeuchi, Y. Mizuno, H. Sasakura, and M. Ishiguro, J. Phys. Soc. Japan 18, 743 (1963).

<sup>11</sup> J. Bushnell (private communication).

<sup>12</sup> G. E. Conklin and R. J. Friauf, Phys. Rev. 132, 189 (1963).

<sup>13</sup> M. Weger, Bell System Tech. J. 39, 1013 (1960).

<sup>14</sup> M. Ishiguro and E. Sugioka, Phys. Rev. 110, 1070 (1958); K. Kojima, N. Nishimaki, and T. Kojima, J. Phys. Soc. Japan 16, 2033 (1961); F. Lüty, Z. Physik 165, 17 (1961).

<sup>15</sup> M. Ishiguro, E. Sugioka, and N. Takeuchi, J. Phys. Soc. Japan 15, 1302 (1960).

The half-width of the electron-spin absorption band of the Z<sub>3</sub> center, 39 Oe, is less than that of the F center in KCl which is 58 Oe.<sup>16</sup> This difference can be understood qualitatively in terms of our Z<sub>3</sub>-center model since there is no hyperfine interaction between the electron and the strontium nucleus which has zero magnetic moment.

ENDOR studies should provide an important test

<sup>16</sup> A. F. Kip, C. Kittel, R. A. Levy, and A. M. Portis, *Phys. Rev.* **91**, 1066 (1953).

of the Z<sub>3</sub>-center model that is proposed in this paper. Such measurements and photoconductive studies have been planned.

#### ACKNOWLEDGMENTS

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## Theory of the Absorption and Emission of the F Center in Alkali-Halide Crystals\*†

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The absorption and emission processes of the F center and their relationship to each other are treated using a model which contains many of the features of an exact treatment. The calculations are based on a formulation in which the total energy of the crystal in the ground and excited states is expressed as a function of the variational parameters in the F-center wave functions and of the displacements of the neighboring ions. The F electron is treated quantum-mechanically, but classical ionic crystal theory is used for all other terms in the total energy. A modified method of steepest descents is used to minimize the total energy. The electronic structure of the outer shells of the first nearest neighbor ions is taken into account in detail in the expression for the energy of the F-center electron. Simple, one-parameter, vacancy-centered wave functions are used to describe the F electron. A large Stokes shift is obtained in all crystals. The distortions are small in the ground state but, in the relaxed excited state, they are of the order of 10% of the nearest-neighbor distance and have a pronounced asymmetry.

### I. INTRODUCTION

THE F-center lattice defect in alkali-halide crystals consists of an electron trapped at a vacant negative ion site. This defect is one of the simplest which can occur in ionic crystals, and in the physics and chemistry of lattice defects in these crystals it occupies a position of importance roughly comparable to that of the hydrogen atom in ordinary chemistry. It is not surprising, then, that many calculations of the electronic structure of the F center have appeared. The most detailed of these have been made by Kojima,<sup>1</sup> Gourary and Adrian,<sup>2</sup> Pekar,<sup>3</sup> and Wood and Korrington.<sup>4</sup> Gourary and Adrian<sup>5</sup> have given a review of many of the theoretic

calculations carried out up until about 1960. Most of the calculations have been limited to an investigation of the ground and first excited states of the center in a rigid, undistorted lattice. The lattice has usually been treated either as a continuum or as made up of simple point ions, although in Refs. 1, 4, and 5 an effort has been made to take into account the structure of the lithium ions which are first-nearest-neighbors (1nn) to the vacancy in LiF<sup>1,5</sup> and LiCl.<sup>4</sup> The effect of lattice distortions on the energy levels has not yet been treated in a consistent manner, although a first step has been made in Ref. 4. The importance of lattice distortions can be inferred from the emission spectra of the F center.

The principal emission band of the F center in alkali-halide crystals exhibits a large Stokes shift. In these crystals, the peak of the emission band corresponds to a transition energy  $\Delta\epsilon_e$  which is usually about half as large as the F-band absorption energy  $\Delta\epsilon_a$ ; that is,  $\Delta\epsilon_e \approx 0.5\Delta\epsilon_a$ . To understand how this large Stokes shift can come about, we must consider that the electronic wave function of the ground state of the F-center elec-

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