

## Thermal Equilibrium of Color Centers in Doped KCl Crystals

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In additively colored crystals of KCl:Sr a thermal reaction between  $F$  and  $Z_2$  centers is observed. The reaction is reversible and approaches equilibrium in a few hours in the range of temperatures between 70°C and 170°C. The equilibrium value of the ratio between the concentrations of  $F$  and  $Z_2$  centers,  $(x_F/x_{Z_2})$ , does not depend upon the total amount of coloration nor upon the past history of the crystal, and for a given impurity content is a function only of temperature. For crystals containing  $2.5 \times 10^{-4}$  molar fraction of Sr, the experimental points fit the equation:

$$x_F/x_{Z_2} = 0.8 \times 10^{-4} \exp(-0.28/kT), \quad kT \text{ in ev.}$$

A comparison of the latter empirical equation with those that can be derived through the application of the mass-action law to some specific models of the  $F \rightleftharpoons Z_2$  conversion is discussed.

IN recent years considerable investigation has been concerned with the properties of color centers which are associated with divalent cations in alkali halide crystals. Studies of the optical properties,<sup>1</sup> luminescence,<sup>2</sup> photoconductivity,<sup>3</sup> and paramagnetic resonance<sup>4</sup> of the  $Z$  centers have provided useful information on the electronic structure of the centers, as well as on the nature of the point defects associated with them. However, an unambiguous choice between the different models proposed for the  $Z$  centers<sup>5,6</sup> has not yet been possible. In this respect, the observation of the thermal reactions and equilibria in which  $Z$  centers are involved might prove to be particularly interesting.

It has been shown previously that mutual conversion between  $F$  and  $Z_2$  centers can be thermally stimulated in colored KCl containing  $\text{Sr}^{++}$ .<sup>7,8</sup> The reaction is reversible, and approaches equilibrium in a few hours at temperatures of the order of 100°C. The aim of the present work is to investigate some quantitative aspects of the  $F \rightleftharpoons Z_2$  equilibrium, and to compare the results with those to be expected assuming a particular model of the  $Z_2$  center.

### EXPERIMENTAL METHODS

The crystals of KCl:Sr were grown in our laboratory by the Kyropoulos technique from reagent grade materials. The Sr content of the crystals actually used in the measurements was determined by means of flame spectrophotometry, and was of the order of  $2 \times 10^{-4}$  molar fraction, varying slightly among spec-

imens from the same batch.<sup>9</sup> The crystals were additively colored at 550°C in potassium vapor; the density of color centers was normally of the order of  $1 \div 5 \times 10^{16}/\text{cm}^3$ .

The absorption measurements were taken at liquid nitrogen temperature, using a Beckman DU spectrophotometer, and a metal vacuum cryostat. The crystal holder contained a small heater, which allowed the sample to be annealed in vacuum up to about 200°C.

In order to study the thermal equilibrium between  $F$  and  $Z_2$  centers the following procedure was used: the colored crystal was annealed in the dark at a certain temperature (in the range between 70°C and 170°C), quenched to liquid nitrogen temperature, and measured for optical absorption; then it was reannealed at the same temperature, quenched, remeasured, and so on until no further change in the absorption spectrum was found. The same procedure was repeated at several temperatures, and the ratio between the heights of the  $F$  and  $Z_2$  bands in mutual equilibrium was determined as a function of the temperature of annealing.

### RESULTS

The curves of Fig. 1 show an example of the different equilibria between the  $F$  band and the  $Z_2$  band, attained at various temperatures in a crystal of KCl containing  $2.5 \times 10^{-4}$  molar fraction of Sr. It can be seen that the equilibrium ratio between the concentrations of  $F$  and  $Z_2$  centers increases with temperature. Measurements made on several specimens showed that this ratio does not depend upon the amount of coloration, nor upon the previous history of the crystal, but for a given concentration of impurities is a function only of the temperature of annealing.

In Fig. 2 the ratio between the heights of the resolved  $F$  and  $Z_2$  bands at equilibrium is plotted on a semi-logarithmic scale, as a function of  $1/T$ , for three different crystals containing approximately the same

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

<sup>2</sup> E. J. West and W. D. Compton, *Phys. Rev.* **108**, 576 (1957).

<sup>3</sup> G. R. Cole and R. J. Friauf, *Phys. Rev.* **107**, 387 (1957).

<sup>4</sup> H. Kawamura and K. Ishiwatari, *J. Phys. Soc. Japan* **13**, 574 (1958).

<sup>5</sup> H. Pick, *Ann. phys.* **35**, 73 (1938).

<sup>6</sup> F. Seitz, *Phys. Rev.* **83**, 134 (1951).

<sup>7</sup> P. Camagni, *Suppl. Nuovo cimento* **9**, 372 (1958).

<sup>8</sup> G. Chiarotti, F. Fumi, and L. Giulotto *Defects in Crystalline Solids* (The Physical Society, London, 1955), p. 317.

<sup>9</sup> It was also found by arc analysis that small traces of Ca were present. A rough estimate gave a concentration of the order of  $10^{-5}$  molar fraction.

amount of Sr but different concentrations of color centers.

No other bands (in particular no  $Z_1$  band) were found present to an appreciable extent during the  $F \rightleftharpoons Z_2$  conversion. This fact allows us to determine the oscillator strength of the  $Z_2$  band, assuming that the total number of color centers is conserved. In this way we find  $f_{Z_2} = 0.45 \pm 0.05$ . With this value of the oscillator strength, the experimental points of Fig. 2 fit the equation:

$$x_F/x_{Z_2} = A \exp(H/kT), \quad A = 0.8 \times 10^4, \\ H = -0.28 \text{ eV}, \quad (1)$$

where  $x_F$  and  $x_{Z_2}$  are the molar fraction of centers in mutual equilibrium.

Similar measurements were performed on crystals containing other impurities, though with less clear results. In KCl:Ba the variations of the  $Z_2$  band with temperature are comparatively small; furthermore, a strong  $M$  band appears at the various stages of the transformation, participating in the  $F \rightleftharpoons Z_2$  equilibrium. On the other hand, in crystals of KCl:Ca the amount of  $Z_2$  band which can be obtained thermally is always very small. In both cases it was difficult to follow the equilibrium.

#### DISCUSSION

It seems interesting to compare the empirical Eq. (1) with those which can be obtained through the application of the mass-action law to some specific models of the process  $F \rightleftharpoons Z_2$ . Two different models of the  $Z_2$  center, proposed by Pick and Seitz, are shown in Fig. 3.<sup>5,6</sup>

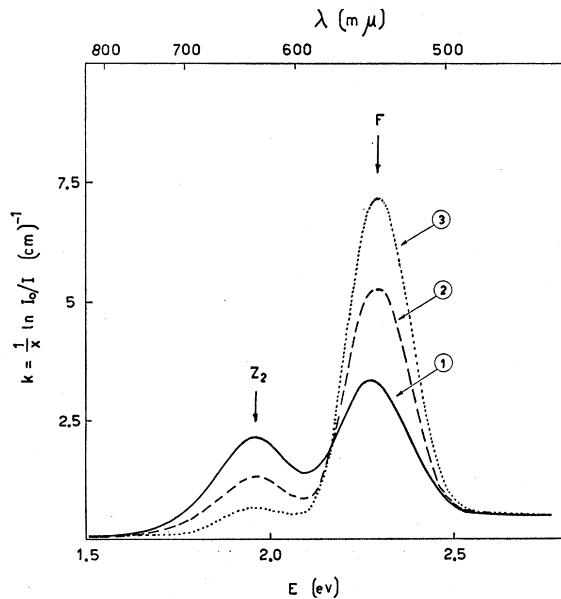


FIG. 1. Equilibrium between  $F$  and  $Z_2$  bands at various temperatures: 80°C (curve 1); 120°C (curve 2); 160°C (curve 3). The absorption measurements were taken at liquid nitrogen temperature.

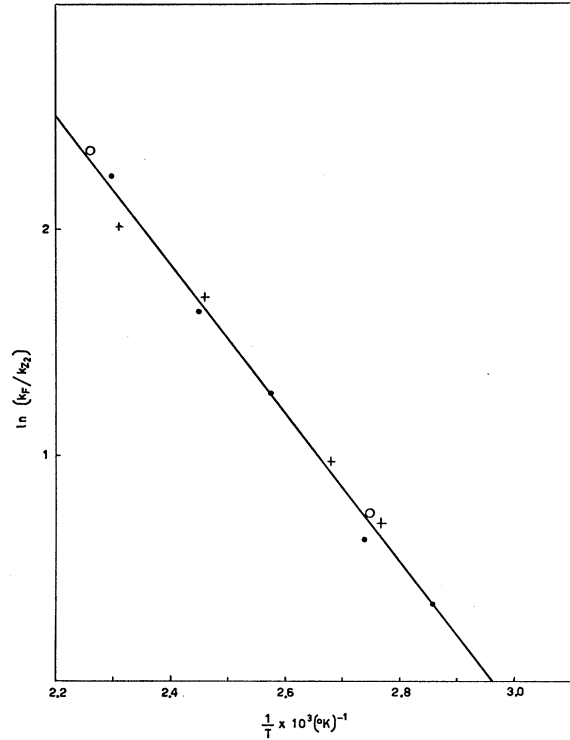


FIG. 2. A logarithmic plot of the equilibrium ratio between the heights of the  $F$  and  $Z_2$  bands, as a function of reciprocal temperature. The experimental points refer to three crystals containing the same amount of Sr ( $2.5 \times 10^{-4}$  mol. fract.), but different concentrations of color centers: (●)  $2.7 \times 10^{16}$  centers/cm<sup>3</sup>; (+)  $4.7 \times 10^{16}$  centers/cm<sup>3</sup>; (○)  $6.6 \times 10^{16}$  centers/cm<sup>3</sup>.

According to Seitz's model, the thermal reaction between  $F$  and  $Z_2$  centers could be a diffusion-controlled association such as



where the symbols stand for  $\text{Sr}^{++}$ -positive ion vacancy complex,  $F$  center, and  $Z_2$  center, respectively. The mass-action law applied in this case gives the following equilibrium condition:

$$x_F/x_{Z_2} = \frac{1}{2} K_0 x_c^{-1} \exp(-\Delta W/kT). \quad (3)$$

$x_c$  being the molar fraction of the complexes, and  $\Delta W$  the energy of association of a complex with an  $F$  center.  $K_0$  is an entropy factor, which takes into account the change of vibrational entropy due to reaction (2);  $\frac{1}{2}$  is the ratio between the configurational weights of the complex and the  $Z_2$  center in their ground state.

In order to compare Eq. (3) with the empirical relation (1), the temperature dependence of  $x_c$  must be taken into account. In principle  $x_c$  varies for two reasons: in the first place, reaction (2) occurs at the expense of a certain number of complexes, and secondly, there is a simultaneous equilibrium between the complexes and the dissociated divalent ions. However, the number of color centers taking part to reaction (2) is much smaller than the total amount of Sr present

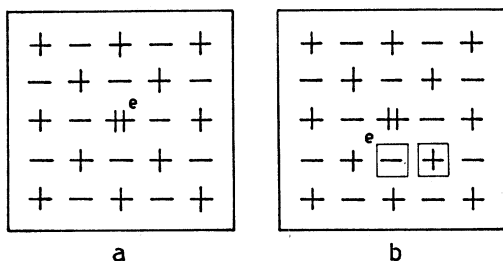


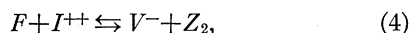
Fig. 3. Two models of the  $Z_2$  center according to H. Pick (a) and F. Seitz (b).

in the crystal: thus the first effect has a negligible influence on the concentration of complexes, which can be calculated by applying the mass-action law to the separate reaction of association between  $Sr^{++}$  and positive ion vacancies.<sup>10</sup> Taking for the association energy of the complex the theoretical value 0.39 eV,<sup>11</sup> it turns out that  $x_c$  is practically constant in the range of temperature of interest, the degree of association varying only from 0.90 to 0.97. Therefore Eqs. (3) and (1) are identical, and coincide numerically provided

$$\Delta W = 0.28 \text{ eV}, \quad K_0 = 2Ax_c \simeq 4.$$

These two figures are quite reasonable, even though the value of the association energy between an  $F$  center and a complex seems a little too large, since the two entities are neutral. However, it must be noticed that this value is an upper limit, owing to the slight temperature dependence of  $x_c$ .

Alternatively, one could try to explain the observed results on the basis of Pick's model. The simplest reaction which might be involved is



where the symbols stand for  $F$  center, divalent ion, negative ion vacancy, and  $Z_2$  center (Pick's model). In this case, the mass-action law reads:

$$x_F/x_{Z_2} = K_0'(x_-/x_{++}) \exp[(W_F - W_{Z_2})/kT]. \quad (5)$$

$x_{++}$  and  $x_-$  are the molar fraction of dissociated impurities and negative ion vacancies;  $W_F$  and  $W_{Z_2}$  the formation energies (absolute values) of the two centers in their ground state.  $K_0'$  is an entropy factor which takes into account the change of vibrational entropy due to the occurrence of reaction (4). Assuming as before that there is a separate equilibrium between divalent ions and positive ion vacancies, which is not appreciably changed by the occurrence of (4),<sup>12</sup> Eq. (5) changes to<sup>10</sup>:

$$x_F/x_{Z_2} = (12)^{\frac{1}{2}} K_0'' (\hat{x}_-/x_c^{\frac{1}{2}}) \times \exp[(W_F - W_{Z_2} + \frac{1}{2}W_c)/kT]. \quad (6)$$

<sup>10</sup> A. B. Lidiard, Phys. Rev. **94**, 29 (1954).

<sup>11</sup> F. Bassani and F. G. Fumi, Nuovo cimento **11**, 273 (1954).

<sup>12</sup> In this respect it should be noted that the maximum number of  $Z_2$  centers is always much smaller than the number of dissociated divalent ions, in the range of temperature of our experiments. For instance, in the case of crystal of Fig. 1,  $(x_{Z_2})_{\max} = 0.9 \times 10^{-6}$  molar fraction, whereas  $x_{++} = 0.8 \div 2 \times 10^{-5}$  molar fraction.

with  $x_c$  practically constant.  $W_c$  is the energy of association of a complex, and  $K_0''$  includes also the entropy factor of the reaction of association between impurities and positive ion vacancies.

The discussion of Eq. (6) is not as straightforward as that of Eq. (3), because very little is known about the concentration of negative ion vacancies in our crystals. However,  $x_-$  is presumably very small in the range of temperature considered,<sup>13</sup> except for the vacancies liberated in the course of the reaction itself. The number of such vacancies decreases with increasing temperature, owing to the rebuilding of the  $F$  band; furthermore, in any case  $x_- \ll x_c$ . Therefore, in order to fit the empirical Eq. (1), one should take:

$$(W_F - W_{Z_2}) < -0.28 \text{ eV} - \frac{1}{2}W_c \simeq -0.47 \text{ eV}; \quad K_0'' \gg A.$$

Actually, substituting reasonable values of the ratio  $x_-/x_c^{\frac{1}{2}}$ , one easily obtains  $K_0'' \approx 10^7 \div 10^9$ . A theoretical evaluation of  $K_0''$  is very difficult, involving an analysis of the normal modes of vibration of an imperfect crystal. However, factors of the order of unity are expected for most reactions. This should be especially true for a symmetrical reaction such as (4). In any case, a value of  $K_0''$  as large as the one obtained above seems rather unlikely. On the other hand, a value of  $-0.47$  eV for  $(W_F - W_{Z_2})$  implies that the ground state of the  $Z_2$  center is much lower than that of the  $F$  center. This seems rather difficult to justify; indeed, one would expect the opposite to be true, in view of the fact that the thermal ionization energies of the two centers in their excited states are nearly the same,<sup>3</sup> and that the optical excitation energy is greater for the  $F$  center.

In conclusion, our experimental results seem to agree much better with Seitz's model of the  $Z_2$  center, since only in this scheme do the measured quantities combine a simple meaning and reasonable values. In this respect, however, our conclusions do not fit the observations on the polarization of the  $Z_2$ -center luminescence, and the less clear results on the bleaching of the  $Z_2$  band with polarized light<sup>8</sup>: as is known, these experiments seem to postulate a  $Z_2$  center with a high degree of symmetry.<sup>14</sup> However, it must be noticed that Seitz's center, shown in Fig. 3(b), is not the only possible combination of an  $F$  center with a complex; centers with different symmetry, lying in the (100) as well as in the (110) plane, are also conceivable. The simultaneous existence of  $Z_2$  centers with different configurations, might be tentatively assumed to reconcile Seitz's model with the absence of polarized luminescence.

<sup>13</sup> Evidence for this is given by unpublished results, obtained in this Laboratory by D. W. Lynch, showing that no detectable  $\alpha$  band is present in uncolored KCl : Sr crystals quenched from various temperatures.

<sup>14</sup> However, dichroism was found in the  $Z_2$  band of NaCl after bleaching with polarized light: G. Remaut and W. Dekeyser, Physica **24**, 20 (1958).