Color Centers in Additively Colored Alkali Halide Crystals Containing Alkaline Earth Ions

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The measurements of Pick on the absorption bands produced in additively colored crystals of KCl and NaCl containing additions of divalent ions are reviewed and an interpretation of the origin of these bands is presented. Specific models are given for the Z_1 , Z_2 , and Z_3 centers responsible for the absorption bands observed by Pick. These resemble models proposed by Pick, but differ in several essential points. It is concluded that the divalent ions remain atomically dispersed in KCl when the crystal is quenched to room temperature from elevated temperatures, whereas some of the divalent ions and their associated positive-ion vacancies migrate to F-centers during the quenching process in NaCl. The observations also suggest that the divalent ions are not very mobile in KCl until a temperature near 200°C is attained, although the pair consisting of a positive and a negative ion vacancy becomes significantly mobile in the vicinity of 100°C. A number of experiments are proposed which may provide a more stringent test of the models suggested.

I. INTRODUCTION

PICK,¹ Heiland and Kelting² have examined several novel absorption bands which are obtained in additively colored specimens of KCl and NaCl to which divalent ions, calcium, strontium, and barium have been introduced. The results appear to be capable of sufficiently straightforward interpretation to merit discussion at this time.

II. EXPERIMENTS ON KCI

The experimental facts for KCl, on which attention will be focused first because of the greater wealth of experimental material, are as follows:

(1) The crystals were prepared by adding between 2 and 60 times 10^{-4} mole fraction of alkaline earth chloride to the melt from which the specimens were grown. Pick, who made the most careful measurements on the absorption bands of the crystals, did not determine the amount of divalent salt in the crystals; however the measurements of Kelting and Witt³ on the equilibrium distribution of the divalent salts between liquid and solid indicate that only about one-tenth of the divalent salt in the melt appears in the solid when growth takes place at a rate of the order of 0.04 mm per minute or less, so that the mole fraction in the solid probably ranges between 10^{-5} and 3×10^{-4} in the various specimens investigated. The crystals were additively colored by heating them in potassium vapor, a density of color centers in the range from 0.3 to 1.0×10^{17} per cc being employed in the work. It may be observed that the density of alkaline earth ions should exceed this range in all cases if the divalent salt did not evaporate preferentially from the melt.

(2) If the additively colored KCl crystals are held well above 250°C and are then quenched, the normal F-band appears (Fig. 1), exactly as in a crystal which does not contain divalent salt. Pick states that the

F'-band can be produced in the normal wav⁴ by irradiating the crystal in the F-band at temperatures near -90° C where the *F*'-centers are stable.

(3) If the crystals are irradiated with wavelengths lying in the F-band when the crystal is at room temperature, some of the F-centers are converted into new centers, termed Z_1 . The Z_1 centers, which are not found in pure alkali halides, possess an absorption band which lies somewhat on the long wavelength side of the Fband (Fig. 1b, c). The two bands can be separated unambiguously only by cooling the crystal to low temperatures $(-215^{\circ}C)$ where both become relatively narrow. The entire F-band cannot be converted into the Z_1 band; a substantial portion of the former always persists. Irradiation of the crystal in the Z_1 -band at temperatures near room temperature or below does not alter this band; the Z_1 -centers appear to be stable and are not reconverted into F-centers. The quantum efficiency for conversion from the F-band to the Z_1 -band has apparently not been measured in additively colored crystals.

(4) If the crystal containing a mixture of F- and Z_1 -centers is heated to temperatures near 110°C, or somewhat above, the Z_1 -band vanishes and is replaced by a new band, Z_2 . In addition the intensity of the *F*-band increases, implying that some of the Z_1 -centers are reconverted into F-centers and others are converted into new centers, termed Z_2 .

(5) The process of generating Z_1 -centers can be repeated by irradiating in the F-band at room temperature after the Z_1 -centers have been converted into Fand Z_2 -centers by heating. A portion of these new Z_1 centers may then be converted into Z_2 -centers by heating near 110°C. Thus the density of Z_2 -centers may be built up in stages by reiteration of this procedure.

(6) The Z_2 -centers may be destroyed by heating the crystal above 200°C, in which case the F-band reemerges when the specimen is quenched.

 ¹ H. Pick, Ann. Physik 35, 73 (1939); Z. Physik 114, 127 (1939).
² G. Heiland and H. Kelting, Z. Physik 126, 689 (1949).
³ H. Kelting and H. Witt, Z. Physik 126, 697 (1949).

⁴ See, for example, H. Pick, Ann. Physik **31**, 365 (1938); R. W. Pohl, Physik Z. **39**, 36 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chapter IV.

(7) When the crystal containing a mixture of Fand Z_2 -centers is irradiated near -90° C with light lying in either of these bands, both bands diminish in intensity. F'-centers and a new type of center, termed Z_3 , are generated. The absorption band associated with the Z_3 -center resembles the F'-band in the sense that it is very broad, even at low temperatures. However its peak lies on the short wavelength side of the F-band. Pick concludes from the general behavior of the Z_3 band that the Z_3 -center bears the same relation to Z_2 -center that the F'-center does to the F-center.

(8) Heiland and Kelting² have found that an additively colored crystal of KCl crystal containing calcium yields a broad "colloidal" band when annealed at 250 degrees for 90 minutes. Apparently the stoichiometric excess alkali metal and the calcium chloride will for a "colloidal" precipitate during this process.

(9) Harten⁵ has measured the photocurrents produced by x-rays in "pure" KCl, which contains of the order of 10-3 percent Ca and Ba, and in specimens containing of the order of 10¹⁸ Ca, Sr, or Ba atoms per cc. In all four cases the range of carriers, which are presumably principally electrons, seems to be dependent upon the density of foreign atoms below -180° C, as if the impurity had a cross section of about 10⁻¹⁵ cm² for capturing the electrons. The photocurrents rise above -180 °C, the temperature at which the rise occurs being dependent upon the nature of the divalent addition. In the case of the "pure" specimens and those containing Ca and Sr, the photocurrent near and above -100 °C seems to be independent of the impurity content, as if the electrons were captured by a trapping center other than the divalent impurity. The capture cross section of the impurities is then less than 10^{-16} cm². The photocurrents do not rise to the same extent in the crystals containing Ba; however, Harten concludes that the Ba forms aggregates in this case, in spite of rapid quenching from elevated temperatures.

(10) Hummel⁶ has found that crystals of KCl containing Ca darken more deeply under gamma-ray irradiation at room temperature than pure crystals do. The density of color centers increases with increasing concentration of the divalent impurity. Presumably the darkening is associated primarily with F-centers, since experiments described in the next section show that this is the case in NaCl containing divalent impurities.

III. AN INTERPRETATION OF THE EXPERIMENTS ON KCI

Pick¹ has given an interpretation⁷ of the centers responsible for the various bands described above. How-

FIG. 1. Absorption bands in additively colored KCl contain-ing $CaCl_2$ (after Pick). (a) The F-band, obtained by quenching to room temperature. The absorption spectrum was measured at -214°C to obtain resolution. These F-centers may be converted to normal F'-centers at -100°C by irradiating in the *F*-band. (b) The broad absorption band obtained by irradiating in the F-band near room temperature. This broad band contains both the F-band and the Z_1 -band, unresolved. (c) The specimen possessing the broad band shown in (b) at room temperature is cooled to liquid air temperature and the F-band and Z_1 -bands are resolved as shown. (d) The Z_2 -band is developed from the Z_1 -band by heating the specimen shown in (b) and (c) to the neighborhood of 110°C. The F-band is also enhanced relative to the value shown in (c). (d) was obtained from absorption measurements carried out at -125°C after heating to 110°C, in order to obtain better resolution of the Z_2 -band.



ever a somewhat different interpretation will be given here.

Following well-accepted arguments,^{8,9} we shall assume that the *F*-centers are to be associated with single electrons trapped in halogen-ion vacancies (Fig. 2(a)), whereas *F'*-centers are associated with pairs of electrons trapped in halogen-ion vacancies (Fig. 2(b)). Similarly we shall assume that the divalent ions enter the crystal substitutionally and are accompanied by positive-ion vacancies (Fig. 2(c)). The work of Etzel and

⁵ H. U. Harten, Gött. Nach., p. 15 (1950).

⁶ H. Hummel, thesis, Göttingen University (1950).

⁷ Pick has interpreted the Z_1 -center as the result of trapping an electron at a divalent ion with which a positive-ion vacancy is permanently associated; the Z_2 -center is interpreted as the result of combining an electron with an isolated divalent ion to which no vacancy is attached; the Z_3 -center is regarded as a Z_2 -center which has captured a second electron. At the time Pick's interpretation was offered, little direct information was available con-

cerning the mobility and energy of association of the various aggregates. The wartime research on skiatrons and the post-war studies of diffusion and ionic conductivity have made it possible to re-evaluate these models and offer the alternatives proposed in the text.

⁸ N. F. Mott and R. W. Gurney, reference 4.

⁹ F. Seitz, Revs. Modern Phys. 18, 384 (1946).

Maurer¹⁰ indicates that the energy of association of the positive divalent ions and the positive-ion vacancies is of the order of 0.3 ev, so that such association should be almost complete in the vicinity of room temperature.

Since the \overline{F} -centers appear in relatively pure form when the crystals of KCl are quenched from elevated temperatures, we may assume that the halogen-ion vacancies are atomically dispersed and are occupied

| + | - | + | - | + | + | - | + | - | + |
|---|----------------|-----|---|---|---|--------------|-------------|---|---|
| - | + | - | + | - | - | + | - | + | - |
| + | e | + | - | + | + | ee | + | - | + |
| - | + | - | + | - | - | + | - | + | - |
| + | - | + | - | + | + | | + | | + |
| | | (a) | | | | | (b) | | |
| + | - | + | - | + | + | - | + | - | + |
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| - | + | - | + | - | - | + | - | + | - |
| + | _ | + | - | + | + | - | + | - | + |
| | | (c) | | | | | (9) | | |
| + | - | + | - | + | + | _ | + | | + |
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| + | - | + | | + | + | | + | _ | + |

FIG. 2. (a) The conventional F-center consisting of an electron bound to a halogen-ion vacancy. (b) A representation of the conventional F'-center having two electrons bound to a halogen-ion vacancy. (c) The pair consisting of a divalent ion and an associated positive-ion vacancy. (d) The Z₁-center described in the text, consisting of an electron bound to a divalent ion in an otherwise perfect crystal. (e) The Z₂-center described in the text, obtained by combining a Z₁-center and a pair consisting of a positive- and a negative-ion vacancy. The electron is presumably shared by the divalent ion and the halogen-ion vacancy. (f) The Z₃-center, obtained at low temperatures when the Z₂-center from an F-center. If the Z₃-center retained its electrons at temperatures nearer room temperature, one might expect the positive-ion vacancy to migrate away, forming a new, neutral center. Presumably the electron evaporates first.

by electrons in exactly the same way as in an additively colored crystal which does not contain a significant quantity of alkaline earth metal.

It is simplest to assume that the divalent ions, with their associated vacancies, are also dispersed almost at random in the specimens of KCl. However, this assumption cannot be made without discussion. Mapother, Crooks, and Maurer¹¹ have given evidence to show that cadmium diffuses very rapidly in sodium chloride, as if the attached positive-ion vacancy imparted an unusually high mobility to it in the manner proposed for alloying agents in metals by Johnson and Wagner.¹² Although the measurements of Mapother, Crooks, and Maurer are only semi-quantitative, they are not inconsistent with the view that the time required for the divalent ion to jump from one lattice position to another, in such a way as to contribute to its diffusion, is nearly the same as the jump time for a free positiveion vacancy, that is about 10^{-2} sec at room temperature.¹³ Should the jump-time for the divalent ions be this small in KCl, any one divalent ion should be able to meet another, and in fact meet an F-center, in a time of the order of several hours. It is possible that Pick's experiments on KCl were carried out sufficiently rapidly that the divalent ions did not have time to combine with one another or with F-centers before the various stages of irradiation were set into effect. We shall see in Sec. IV that direct combination of the divalent ions and F-centers, through diffusion of the former and without the intervention of radiation, has probably been observed in NaCl. Apparently we must conclude that the divalent ions are more mobile in NaCl than in KCl. The same conclusion has been drawn independently by Burstein, Oberly, Henvis, and Davisson¹⁴ from a study of the temperature dependence of the change in absorption bands arising from additions of lead to NaCl and KCl. It is found that the bands change much more noticeably with time near room temperature in NaCl than in KCl, as if the lead may cluster in the course of several days in the former material, but not in the latter.

In this connection, it is interesting to note that the divalent ions may become at least partly immobilized at room temperature through relatively weak association. When two divalent ions, which have positive-ion vacancies attached, approach one another within the crystal, they will be subject to an electrostatic interaction which results from the dipole moment of the pair consisting of divalent ion and vacancy and to a repulsion which arises from the elastic distortion the pairs engender in the lattice. The electrostatic attraction reaches its maximum when the dipoles are antiparallel and the divalent ions are separated by the distance of the cubic unit cell, as in Fig. 3(a). It may be seen that a halogen ion lies between the divalent ions

¹⁰ H. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

¹¹ Mapother, Crooks, and Maurer, J. Chem. Phys. 18, 1231 (1950).

¹² R. P. Johnson, Phys. Rev. **56**, 814 (1939); C. Wagner, Z. physik. Chem. **38B**, 325 (1937).

¹⁴ This value of the jump-time is deduced from the experiments on the mobility of positive ion-vacancies in the alkali halides. See, for example, Etzel and Maurer (reference 8); C. Wagner and P. Hantelmann, J. Chem. Phys. 18, 72 (1950); H. Kelting and H. Witt (reference 3).

¹⁴ Burstein, Oberly, Henvis, and Davisson, Phys. Rev. 81, 459 (1951).

and between the positive ion vacancies which neighbor them. Presumably this configuration has a stability of the order of 0.3 ev for separation into divalent ionvacancy pairs. Actually, if such clusters have sufficient time to form, some of the divalent ions should have had sufficient time to migrate to the vicinity of F-centers, where we should expect the formation of a relatively stable unit consisting of an electron, a divalent ion, a negative-ion and a positive-ion vacancy—a unit which will presently be identified with the Z_2 -center. Since the F-band appears in unmolested form after the crystal is guenched to room temperature, we shall assume that the divalent ions in KCl do not diffuse rapidly and remain dispersed.

When the crystal containing F-centers is irradiated with light lying in the F-band at any temperature above 100°K, electrons are freed¹⁵ and wander about the lattice. They can be trapped by other centers, to form stable F'-centers⁴ if the temperature is not above 180°K. Apparently this process is strongly favored over any other in the low temperature region, so that F'-centers are formed in preference to centers involving electrons and divalent ions, perhaps because the dipole electrostatic field of the divalent ion and its associated positive-ion vacancy, which is relatively immobily bound to it at temperatures below 180°K, does not offer a stable state for the electron. On the other hand, the F'-center is thermally unstable at room temperature in KCl, so that the electron must wander until it meets a stable trap. The two possible traps are: (1) halogenion vacancies from which electrons have been ionized and (2) divalent ions which are either temporarily dissociated from their positive-ion vacancy or from which the positive-ion vacancy is ejected during the period of time which the electron spends in the vicinity of the divalent ion. An F-center will be reformed in the first case; we shall assume that the Z_1 -center is an isolated divalent ion which has captured an electron (Fig. 2(d)). It is evident that the Z_1 -center described here will not have a strong attraction for a positive-ion vacancy because it is electrically neutral.

The experiments show that the Z_1 -band of KCl cannot be bleached by irradiation in the Z_1 -band. We apparently must conclude that the thermal fluctuations available even at room temperature are not sufficient to free the electron from the first excited level before a transition occurs to the ground state. In other words, we must conclude that the thermal energy required for liberation of the electron in the first excited state of the Z_1 -center is at least three times as large as the value¹⁶ for the F-center (~ 0.075 ev), which exhibits similar behavior below 100°K. Although both centers are neutral, this difference in behavior is perhaps not difficult to understand: since the oscillator strength¹⁷



FIG. 3. (a) The weak aggregation of two pairs consisting of divalent-ions to which positive-ion vacancies are attached. It will be noted that the halogen ion lies midway between the two divalent ions and the two positive-ion vacancies. (b) The stable arrangement of the complex formed by combining a divalent ion to which a positive-ion vacancy is attached and a pair consisting of a positive- and a negative-ion vacancy.

for the transition from the ground state to the first excited state of the F-center is as large as 0.8, we may conclude that the charge distribution for the first excited state is not spread over an appreciably larger volume than that of the ground state. Hence the equilibrium nuclear configuration will be similar to the two states. On the other hand, we may expect the equilibrium nuclear configuration for the negative-ion vacancy from which the electron has escaped to be appreciably different from that for the first excited state, for the excess positive charge is no longer neutralized and the presence of the vacancy allows freedom for motion. It follows (Fig. 4(a)) that the thermal activation



FIG. 4. Schematic Franck-Condon diagram for the energy levels in an F-center and a Z_1 -center. The vertical axis represents energy and the horizontal the configurational coordinates of the nuclei near the centers. In both cases curve 1 represents the ground state, curve 2 represents the first excited state and 3 represents the ionization levels. The excited discrete levels between curves 2 and 3 are not shown. It is assumed that the coordinates for energy are nearly the same in states 1 and 2 for both centers because the charge distributions are not widely dissimilar. Moreover, it is assumed that the configurational coordinates are substantially different for the bound and ionized states (free halogen-ion vacancy) of the F-center because of the freedom of motion permitted by the presence of the vacancy. On the other hand, it is assumed that the configurational coordinates are not changed greatly near the Z_1 -center by freeing the electron because the ions are closely packed. The vertical arrows represent the thermal activation energies for the transition from the first excited state to the ionization levels in the two cases.

 ¹⁵ See, for example, G. Glaser and W. Lehfeldt, Gött. Nach. FGII, 91 (1936); H. Rögener, Gött. Nach. FGIII, 219 (1941).
¹⁶ See N. F. Mott and R. W. Gurney, reference 4, p. 136.
¹⁷ F. G. Kleinschrod, Ann. Physik 27, 97 (1936).

energy for freeing the electron from the excited state may be small. On the other hand, the equilibrium nuclear configuration for the ionized Z_1 -center (see Fig. 2(d)) cannot be very different from that for the ground state and first excited state (which are probably also similar) because the repulsive forces between closed shells will prevent the relatively close-packed array of atoms from shifting as much as would be the case for an ionized *F*-center (Fig. 4(b)).

It is interesting to note that the development of the Z_1 -band at the expense of the *F*-band becomes increasingly difficult as the former grows. This fact is possibly a consequence of the increase in concentration of halogen-ion vacancies, which have a large cross section¹⁸ for capture of electrons.

The positive-ion vacancies, which are released from the divalent ions when they capture electrons to form Z_1 -centers, and the halogen-ion vacancies, which are produced by ionization of the F-centers, should combine to form the mobile pairs which the writer¹⁹ has presumed play a very important role in the bleaching and coagulation of F-centers and in their generation by x-rays. If these were sufficiently mobile at room temperature to diffuse 10⁵ or 10⁶ atomic spacings in the times of interest in these experiments, we would expect both the F-band and the Z_1 -band to be modified by combination with negative-ion vacancies. In fact Scott and Bupp,20 studying additively colored crystals of KCl containing 5×10^{17} F-centers per cc, observed the formation of R- and M-centers when the crystals were irradiated rather heavily with an arc light for 85 minutes. The specimens were maintained at room temperature by air jet cooling. This result indicates that, at least in the pure crystal, the pairs should diffuse distances of interest to us in the course of 85 minutes at room temperature. It is possible that a small number of R- and M-centers were formed in Pick's experiments during the conversion from the F-band to the Z_1 -band, but were not investigated because they lie toward the red end of the spectrum. It is also possible that the vacancy pairs, produced by combination of the positiveand negative-ion vacancies, are captured by pairs formed of the divalent ions and their associated positive-ion vacancies. The concentration of the latter should exceed that of the F-centers and of the Z_1 centers. The center formed in this way is shown in Fig. 3(b). Simple calculations indicate that it should not have an energy of association larger than 0.5 ev. On the other hand, even this moderate inhibition may be sufficient to prevent the formation of R-centers and *M*-centers at room temperature in the time of observation.

The Z_1 -centers are transformed into Z_2 -centers when the crystal is heated above 110°C. The increase in temperature stimulates the mobility of the vacancies and hence the diffusion of ions. If the conversion $Z_1 \rightarrow Z_2$ were primarily the result of migration of the divalent ions, we would expect the *F*-band to be modified as a result of combination of *F*-centers and the divalent ions. Instead the *F*-band actually is enhanced, presumably because some of the Z_1 -centers lose electrons through thermal ionization, probably when positive ion vacancies are nearby, and these electrons are captured by the halogen-ion vacancies which were produced earlier, when the Z_1 -centers were formed by ionization of the *F*-centers.

It seems reasonable to assume that the increase in temperature permits a fraction of the negative-ion vacancies which have combined with positive ion vacancies and formed pairs, to diffuse to these Z_1 -centers that have not decomposed and produce the center shown in Fig. 2(e). This is a neutral unit consisting of the pair of vacancies of opposite sign, the electron and the divalent ion. We shall identify this configuration with the Z_2 -center.

It is also possible that the electrons freed thermally from the Z_1 -centers generate Z_2 -centers by combining with the units shown in Fig. 3(b), which were produced during the transformation from the *F*-band to the Z_1 band by aggregation of the positive-negative-ion vacancy pairs and the divalent ions. A positive-ion vacancy would be ejected from the unit shown in Fig. 3(b) once it has captured an electron. The halogen-ion vacancy would then move nearer the divalent ion.

As mentioned previously, the Z_2 -center could be formed directly from the *F*-center by combination of this with a divalent ion which has migrated to an adjacent site with the aid of an associated positive-ion vacancy. If our identification of Z_1 and Z_2 are correct, we may conclude from the absence of Z_2 -centers in the freshly quenched specimen that the divalent ions are not very mobile in KCl, as was emphasized earlier.

Since the Z_2 -center possesses two vacancies, we

¹⁸ The cross section for capture of electrons by halogen-ion vacancies may be estimated in the following way. The experiments of Glaser and Lehfeldt and of Rögener (reference 12) on photoconductivity in colored alkali halides show that F-centers may capture electrons to form F'-centers. The cross section σ_I for this process may be determined from the relation $N_f \sigma_f = \beta/v(w/E)$ in which N_f is the density of F-centers, β is the mobility of the conduction electrons (assumed to be about 5 cm² per volt-sec in NaCl and KCl at room temperature), v is the velocity of thermal mo-tion of the electron (about 10^7 cm per sec at room temperature) and w/E is the ratio of Schubweg w to field strength E in the photoconductive experiments. This leads to values of σ_I of the order of 3×10^{-15} cm² in the range of temperature in which F'-centers are stable. The study of photoconductivity in the transition from F' to F-centers in a specimen having nearly equal densities of F- and F'-centers (see F. Domanic, reference 18) shows that near -120°C w/E is nearly equal to the value of this ratio for the photocurrent observed at the same temperature in the transition from F to F' in a specimen having an equal number of F-centers. This result implies that the cross section σ_v for capture of an electron by a halogen-ion vacancy is also of the order of 3×10^{-15} cm² near -120°C. The work of Domanic indicates that this cross section rises very rapidly in going to lower temperatures, becoming 20 times larger near liquid hydrogen temperatures. Presumably the highly excited states of the F-center become stable toward thermal dissociation at very low temperatures, so that the capture cross section attains a value near 6×10^{-14} cm².

¹⁹ See reference 9. Also G. J. Dienes, J. Chem. Phys. 16, 959 (1948).

²⁰ A. B. Scott and L. P. Bupp, Phys. Rev. 79, 341 (1950).

might expect it to have a low thermal activation energy for the freeing of an electron from the first excited state, as is the case for *F*-centers. The experiments indicate that the Z_2 -center, like the *F*-center and unlike the Z_1 -center, does bleach, at least in part, when irradiated with light absorbed in the Z_2 -band.

The isolated negative-ion vacancies become transformed into F- or Z_2 -centers during the thermal treatment near 110°C, so that they are not available to impede the formation of new Z_1 -centers when the crystal is irradiated in the F-band (or the Z_2 -band (?)) at room temperature, in agreement with observations.

We might expect the Z_2 -center to be able to hold a second electron if the *F*-center can. The close symmetry between the Z_3 -band and the *F'*-band suggests at once that the Z_3 -center is formed in this way (Fig. 2(f)). We shall return in the next section to the question of the tightness with which a Z_3 -center holds the positive-ion vacancy.

The interesting fact that the long wavelength limit of Z_3 -band lies on the high energy side of the Z_2 -band implies that the second electron in the Z_3 -center is about as tightly bound as the first, unlike the situation in the case of the F- and F'-center. This receives a fairly natural explanation in terms of the models proposed here. The negatively charged F'-center resembles the negative hydrogen ion, H⁻, very closely in the sense that the two electrons are bound to a more or less central field. On the other hand, the two electrons in the Z_3 -center make use of the attractive field of both the halogen-ion vacancy and the divalent-ion. One may regard the extra negative charge as arising from the positive-ion vacancy. The latter will attempt to shift away from the electron distribution-a possibility that has no analogue in the F'-center. As a result, the equilibrium configuration of the atoms in the Z_3 -center may correspond to an arrangement of the Z_2 -center of high energy. Hence the ionization energy of the Z_3 center may be relatively large.

Harten's experiments on the photocurrents produced by x-rays in crystals which contain divalent impurities, but are not additively colored, seem to show that the center consisting of a divalent impurity and its associated positive-ion vacancy has a capture cross section less than 10^{-16} cm² near room temperature, although the value is near 10^{-15} cm² below -180 °C. In fact, the results suggest that the electrons are captured preferentially by centers other than the divalent impurities when the latter are present to concentrations of 10^{18} per cc or less, and do not form aggregates.

Hummel's observation that crystals containing divalent impurities darken more easily and more deeply than pure crystals implies that the divalent impurities may play an important role in the formation of Fcenters by irradiation. The precise nature of this role is obscure. However it is possible that the divalent ions with associated vacancies are excellent traps for the holes produced during irradiation, that the holes are immobilized by being captured at these units, and that the electrons are then captured preferentially at dislocations where they form F-centers by an as yet undisclosed process.²¹ This aspect of the present problem merits extended investigation.

The foregoing models suggest a number of critical experiments:

(1) One would expect the Z_2 -centers to be formed directly during a relatively slow cooling of the crystal to room temperature. The experiments of Heiland and Kelting referred to in Sec. II (paragraph 8) are not sufficiently refined to test this point, for they annealed the specimens so long that large aggregates were formed. This process has been observed in NaCl (see next section).

(2) It is possible that at least small components of the *R*- and *M*-bands are produced during conversion of the *F*-band into the Z_1 -band. It is also possible that Z_2 -centers will be formed in a second irradiation in the *F*-band, after a primary irradiation in which a "saturated" value of Z_1 -centers have been formed, provided sufficient time (an hour or a day) is allowed between the two irradiations to permit the positive- and negative-ion vacancies to combine and diffuse to divalent ions, where they form the units shown in Fig. 3(b).

(3) The Z_2 -centers should be a source of photoelectrons which, like the *F*-centers, become inefficient at temperatures near or below 100°K.

(4) In contrast, the Z_3 -centers should yield photoelectrons even near the absolute zero of temperature²² since the Z_3 -band, like the F'-band, should correspond to transitions from a discrete bound state to the ionization continuum.

(5) Electrons should be liberated when the Z_1 -band is converted into the *F*-band and Z_2 -band by warming the specimen to the vicinity of 110°C.

(6) For reasons which will become clear in the next section, we should expect to form Z_1 -centers by irradiation in the Z_2 -band at temperatures not so low that F'- and Z_3 -centers are formed. This process appears to be observed in specimens of NaCl analogous to those considered here.

(7) Evidently experiments on the diffusion of divalent ions, extending the work of Etzel and Maurer, would be highly informative.

(8) It would be highly desirable to investigate the V-centers which are formed when crystals containing divalent additions are irradiated with x-rays, for Hummel's observations suggest that divalent impurities may play an important role in the process of darkening with x-rays or other ionizing radiations.

²¹ F. Seitz, Phys. Rev. 79, 890 (1950).

²² The ability of F'-centers to produce photoelectrons even near 0°K has been demonstrated by F. Domanic, Ann. Physik **43**, 187 (1943).

IV. FURTHER EXPERIMENTAL RESULTS ON NaCl

Pick¹ has also described, in much less complete fashion, experimental results for additively colored NaCl containing strontium. The principal results are:

(1) The F-band does not appear alone when the crystal is quenched from elevated temperatures. Instead it is accompanied by a band, A, which can be bleached to yield both an increase in F-centers and additional centers which absorb in a region B between the F-band and the A-band. Pick identifies the A-band with the Z_2 -band in KCl and identifies the *B*-band with the Z_1 -band of KCl. This identification is in excellent agreement with the views put forth in the previous section if we assume that the divalent ions are appreciably more mobile in NaCl than in KCl, so that some of the F-centers combine with divalent ions, to which positive-ion vacancies are associated, during the quenching step. We saw previously that one might expect to form Z_2 -centers directly from F-centers by migration of the divalent ions if this migration is sufficiently rapid.

We might expect to form F-centers and Z_1 -centers at room temperature by freeing electrons from Z_2 centers as a result of irradiation in the Z_2 -band. Once electrons have been freed from the Z_2 -centers, we should expect the positive-ion vacancy to carry the negative-ion vacancy away from the divalent ion since the energy of association of the pair of vacancies with the divalent ion must be very small compared with the energy of association of a pair of oppositely charged vacancies.23,24 Some of the isolated divalent ions may then capture photoelectrons and form Z_1 -centers. Similarly, the remaining free electrons may combine with the negative-ion vacancies of a fraction of the neutral pairs of vacancies to form F-centers and free positive-ion vacancies, which may eventually combine with the remaining isolated divalent ions. Since the vacancies should diffuse away from the Z_2 -center very soon after it is ionized, the Z_2 -center would not be regenerated as rapidly as the F-centers are regenerated by combination of free electrons and negative-ion vacancies, when Z_1 -centers are produced by irradiating in the F-band.

(2) As in KCl, the Z_1 -band cannot be bleached by irradiating the crystal with light in this band. It can be converted into the *F*-band and the Z_2 -band by warming the crystal.

(3) The F-band and Z_1 -band appear when clear NaCl which contains strontium, but does not contain excess sodium, is irradiated with x-rays. The F-centers are presumably formed by the same process as in pure alkali halides, that is by the freeing of vacancies from clusters, cracks, or dislocations and the trapping of electrons and holes in these vacancies. The crystals possessing strontium should exhibit the Z_1 -band, as observed, if the assignment of the previous section is correct, for some of the electrons will be trapped by isolated divalent ions which are dispersed in the crystal. We would not expect to find the Z_2 -band if the irradiation is not carried on at elevated temperatures, at least immediately after the irradiation, for the rapid alternation of charge on a Z_2 -center as it alternately captures electrons and holes would cause it to disintegrate by the same process that operates when Z_2 centers are converted into F- and Z_1 -centers by irradiation in the Z_2 -band.

It is interesting to note that F-centers are formed preferentially, relative to Z_1 -centers, during x-ray irradiation at room temperatures. This observation suggests that the divalent impurities with attached positive-ion vacancies do not have a large cross section for capturing electrons, in good agreement with Harten's observations. Thus the electrons prefer to wander until they find centers with a larger cross section. The latter presumably are the traps from which F-centers may be formed.

There is another interesting point to note: During irradiation of the crystal with light lying in the Z_2 band at room temperature, some of the electrons freed by the light must approach Z_2 -centers. Presumably the Z_3 -centers, which would be formed if the electrons were captured, are unstable at room temperature and the electron either is not captured or is released after capture. On the other hand, if the electron persisted sufficiently long for a positive-ion vacancy to be ejected, an entirely new center consisting of two electrons, a halogen-ion vacancy and a divalent ion would be produced (see caption to Fig. 2(f)). This would have certain similarities to the *R*-centers obtained⁹ during coagulation of F-centers and might be very stable. It would be interesting to see if it can be produced at temperatures somewhat below room temperatures where the positiveion vacancies have not lost their mobility and where the F'-centers of NaCl are stable. It is not improbable that the activation energy²⁴ required to free a positiveion vacancy from the Z_3 -center is sufficiently larger than the activation energy required to free the electron that the latter will occur preferentially at any temperature where the Z_3 -center is unstable; however, the alternative possibility exists.

The writer is indebted to Dr. Pick for extensive discussions of this topic, even though the latter has maintained a reserved attitude toward the views presented in this paper.

²³ The negative-ion vacancy should hold the positive-ion vacancy more tightly than the divalent ion. The energy of association of the latter with the positive-ion vacancy is about 0.3 ev (see Etzel and Maurer, reference 8). The energy of association of a positive- and negative-ion vacancy is probably nearer 1 ev (see Seitz, reference 7, and the calculations mentioned in reference 20).

²⁴ I am indebted to Dr. John Reitz of Los Alamos for a description of calculations of the binding energies of various clusters in NaCl and KCl, carried out by him and Dr. Gammel. These investigators have found that the binding energy of a pair of vacancies of opposite sign is 0.9 ev and the binding energy of a cadmium ion and a positive-ion vacancy in NaCl is 0.3 ev. On the other hand, this work shows that the activation energies required to dissociate these units may be appreciably larger than the energies of association. This suggests that the Z_3 -center will probably always dissociate by ejecting an electron.