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The Equilibrium between *F*-Centers and Higher Aggregates in KCl*

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The conversion of *F*-centers to centers giving a broad absorption band at about 700 mμ has been found to be primarily thermal rather than optical. Evidence is presented to show that these centers are higher aggregates of *F*-centers and lattice vacancies, but are not colloidal. At temperatures between 300 and 500°C the *F*-centers are in equilibrium with the higher aggregates; the equilibrium was studied as a function of temperature and concentration. Absorption measurements at −195°C show that several species contribute to absorption in the band; some suggestions as to the likely nature of the centers are given.

I. INTRODUCTION

THE presence in alkali halides, colored by stoichiometric excess of alkali metal or by high energy radiation, of absorbing centers other than *F*- or *F'*-centers has been noted by several workers.[1–4] Except for the work of Glaser and Molnar, no experimental studies of the formation of the centers or of their possible structure have been reported. It has commonly been assumed that bands occurring at longer wave-lengths than the *F*-band are due to colloidal metal formed when additively colored crystals are cooled too slowly, and are thus undesirable from a theoretical standpoint, though the presence of a second metallic phase has not been demonstrated except in extreme cases.[5]

Molnar observed the development of a band (the *M*-band) at about 820 mμ in addition to the *F*-band and the *U*-band when KCl was colored by *x*-rays. This band and the *F*-band were interconvertible by irradiation with light of the wave-length absorbed by the respective bands, but during the interconversion some of the intensity of the *F*- and *M*-bands appeared as two new bands at about 675 and 730 mμ, called the *R*-bands.

Glaser studied the destruction of *F*-centers by irradiation with white light from an arc to obtain some type of aggregation of the centers, the assumption being that the process was made possible by the absorption of radiation in the visible region. Seitz suggests that the *M*-centers of Molnar are among the first products and may be an *F*-center attached to a pair of lattice vacancies; further that the *R*-centers may be first aggregates of *F*-centers such as F_2- or F_2^+-centers.

In the course of preparing KCl colored with stoichiometrically excess K for studies on the paramagnetism of color centers, it was found in this laboratory that at high concentrations of alkali metal (10^{18} to 10^{19} atoms/cc) in large crystals the formation of bands at wave-lengths greater than the *F*-bands could not be avoided even with the most rapid quenching experimentally possible. In the lower range of concentration, particularly when the crystals were smaller and thus more rapidly quenched, the bands were identical with the *R*- and *M*-bands. At concentrations around 10^{19}/cc the bands merged and increased to a prominence of the order of the *F*-band, having a maximum from 800 to 900 mμ. It was also desired to find a means of destroying *F*-centers by some process which could be conducted with the crystal in place upon a sensitive magnetic balance, and it was noted that irradiation with an arc light for a few minutes converted the *F*-band into the broad band.

The experiments reported here were undertaken to obtain information regarding the nature of the centers responsible for the broad band and their relationship with the *F*-, *M*-, and *R*-centers. For purposes of brevity the band will be referred to as the *R'*-band, and the centers as *R'*-centers, because of their absorption in the red. KCl colored with additional K was used in all cases

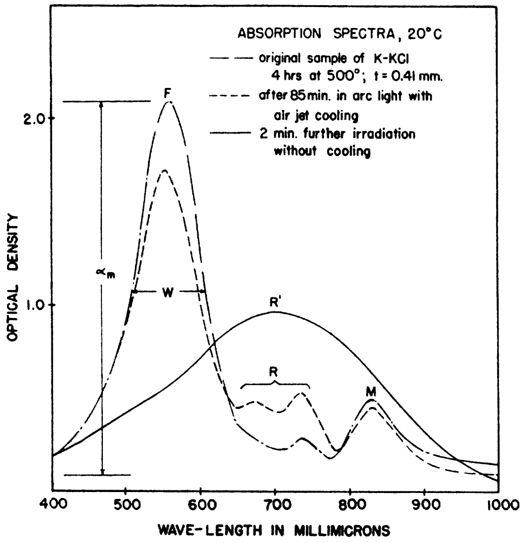

Fig. 1. Optical and thermal conversion of *F*-centers in KCl.

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[1] R. Ottmer, Zeits. f. Physik **46**, 798 (1928).

[2] G. Glaser, Göttinger Nachrichten **3**, 31 (1937).

[3] J. P. Molnar, unpublished work described in reference 4; Phys. Rev. **59**(A), 944 (1941).

[4] F. Seitz, Rev. Mod. Phys. **18**, 384 (1946), reviews recent work on color centers in alkali halides, particularly the work of Molnar and Glaser.

[5] R. W. Pohl, *Optik* (Frederick Ungar, New York, 1943).

because more data is available on this system than on other alkali-halides; further high concentrations of color centers are more readily obtainable in well-formed crystals than in others investigated.

II. EXPERIMENTAL

(A) Preparation of Additively Colored Crystals

Single crystals of KCl, prepared commercially for optical use, were cleaved to the desired size, generally about 2.7×0.4×0.3 cm for use in magnetic studies. These were heated in closed bombs of $\frac{3}{8}$ in. copper pipe, with a small pellet of metallic K. The concentration of absorbed K depends upon the temperature.[6] Diffusion is quite slow, and at the lower temperatures several days were required to achieve a uniform color in large crystals. To obtain 10^{19} color centers/cc the bombs were heated at 675°C for 3 hours and for 5×10^{17}/cc, at 475°C for 72 hours. Following heating, the bombs were quenched in cold water; rapidity of quenching, as well as preservation of accurate dimensions of the crystals, was assisted by wrapping the crystals in thin copper foil, leaving the ends open, prior to placing in the bomb.

(B) Analytical Methods

The concentration of *F*-centers in crystals having less than 10^{18}/cc was obtained from absorption data, using the dispersion formula developed by Smakula[7]

$$n=(1.31\times10^{17}n')/[f(n'^2+2)^2]W_M W,$$

where n is the number of *F*-centers/cc, n' is the refractive index of the pure salt, α_M is the extinction coefficient at the center of the band in cm^{-1}, W is the width of the absorption curve, at half-maximum, in electron volts, and f is the oscillator strength for *F*-centers. In KCl, Kleinschrod[8] found $f=0.81$. A typical curve showing the *F*-band appears in Fig. 1.

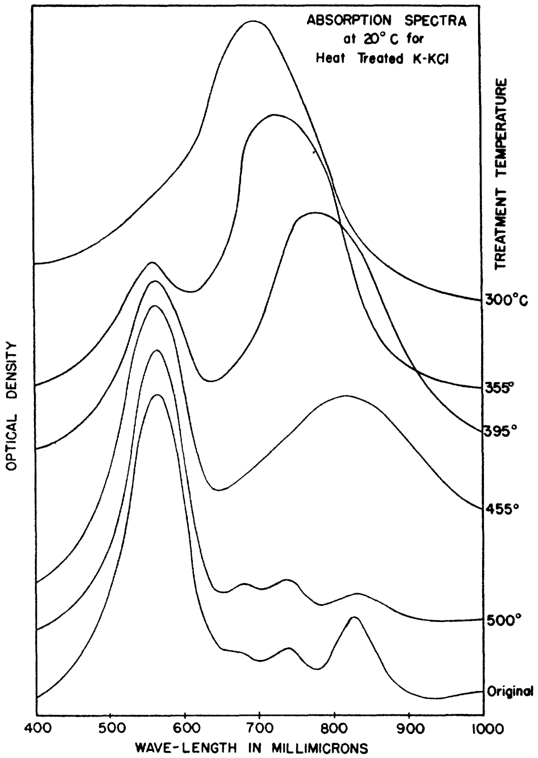

FIG. 2. Thermal equilibrium between *F*- and *R'*-centers.

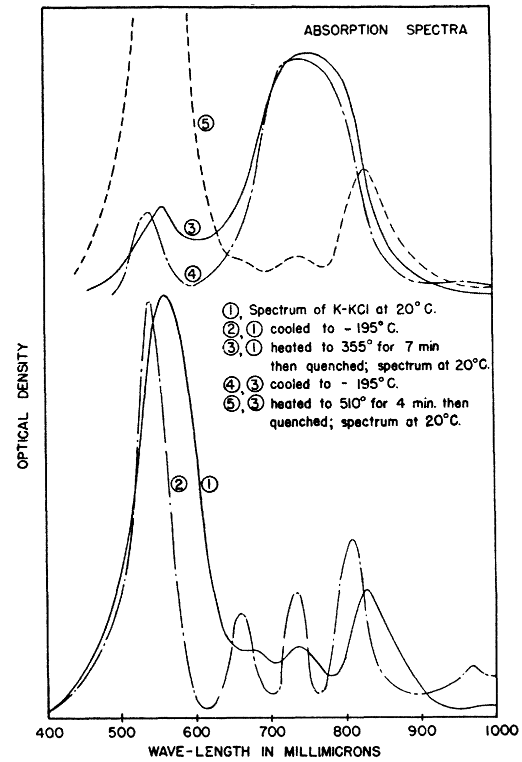

FIG. 3. Effect of low temperature on *R'*-, *R*-, and *M*-bands; thermal conversion of *R'*- to *F*-bands.

At higher concentrations, the absorption becomes so great in the *F*-band that it becomes impossible to cleave thin sections of accurately known thickness, and, though spectra were obtained for crystals having as high as 1.7×10^{19} centers/cc, by careful grinding or cutting of mounted crystals, it was necessary to use chemical analytical methods to determine concentration.

The chemical method consisted of measuring the change in *p*H occurring in 3 ml of boiled, slightly acidified water when a colored crystal weighing about 60 mg was dissolved. A Beckmann *p*H meter, having "micro" electrodes, was used. The probable error in concentrations measured in this way was about 10 percent, the error being due principally to variations within a given large crystal, and to some absorption of

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[6] R. W. Pohl, Proc. Phys. Soc. **49** (extra part), 3 (1937).

[7] A. Smakula, Zeits. f. Physik **59**, 603 (1930).

[8] F. G. Kleinschrod, Ann. d. Physik **27**, 97 (1936).

CO_2 during solution of the crystal. There is an uncertainty of at least this magnitude in the optical determination of the lower concentrations, so that in general the lack of exact analytical methods presents a serious obstacle to accurate quantitative studies upon color centers.

It must also be noted that while the optical method yields the concentration of *F*-centers as such, the chemical method yields the concentration of K in stoichiometric excess, whether in *F*- or in other centers. At concentrations around 10^{19}/cc, it was found that a considerable proportion of the K was present as *R*′-centers.

(C) Thermal and Optical Measurements

Absorption measurements were made by the Beckmann Spectrophotometer, Model DU. A special Dewar flask was designed for measurements at −195°C having a bottom section small enough to fit into the usual cell holder and silvered except for two small areas to permit passage of light. The top of the flask projected five inches above the cell compartment and was covered by a light-proof box so that the flask was free to move laterally. Room temperature measurements were made prior to addition of liquid N_2 with the crystal in place in the Dewar, then the measurements in liquid N_2 and finally the absorption of the N_2 and cell were measured in the range 400–1100 mμ. In every case the latter was negligible throughout the range.

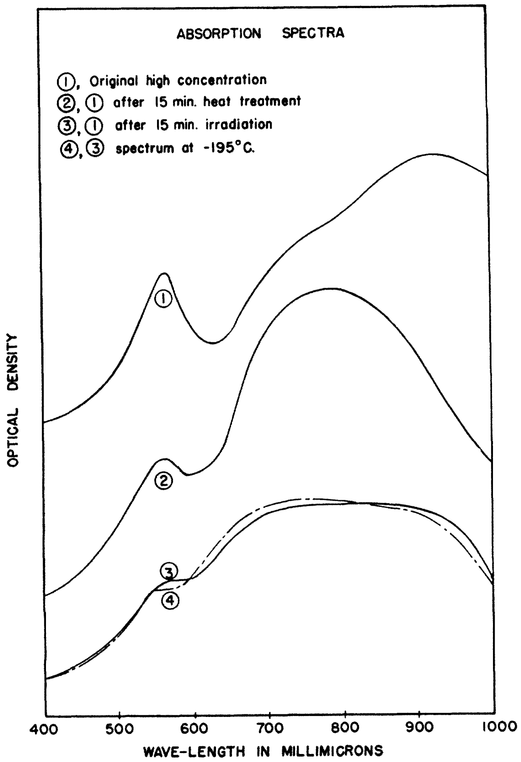

FIG. 5. Effects of concentration of the $F-R'$ equilibrium. Ordinates for curves 3 and 4 displaced downward one unit.

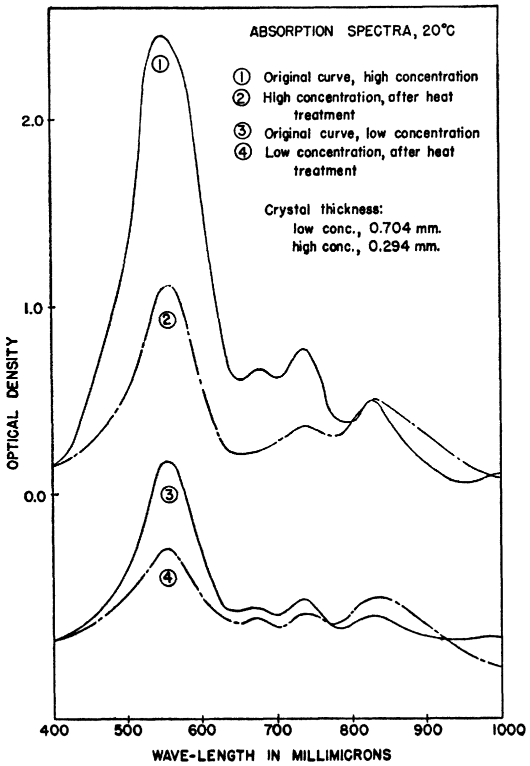

FIG. 4. Absorption spectra in densely colored crystals.

Heat treatments were carried out in air in a muffle furnace with automatic temperature control. Treatments carried out in vacuum as a check gave identical results. For these experiments it was not necessary to achieve very accurate control or measurement of temperature. Temperatures reported are accurate within about 5° below 400°C and about 10° above 400°C. Relative errors in absolute temperature are thus negligible compared to analytical errors.

III. DISCUSSION OF RESULTS

(A) Conversion of *F*- to *R*′-Centers by Irradiation

Glaser found that 20 minutes of arc light irradiation at room temperature was sufficient to destroy all *F*-centers in a particular sample of colored KCl. This effect could have been either optical or due to local increase in temperature, but the assumption has been that the mechanism has been dependent upon *F*-center ionization by irradiation, and Seitz[4] has offered an explanation of the conversion of *F*-centers into aggregates on this basis. An experiment was performed to determine whether the process is primarily thermal or optical. A small additively colored crystal containing about 6×10^{17} *F*-centers/cc was illuminated strongly with light from a carbon arc, but kept at about room temperature by means of a jet of air. The absorption spectrum was measured initially and at intervals during the irradiation. After 85 minutes the air jet was removed for 2 minutes further treatment. The absorption curves obtained after 85 minutes irradiation with the crystal at room temperature and after 2 minutes irradiation without cooling are compared in Fig. 1 with the curve for the original sample. The change from *F*- to *R*′-centers must occur almost entirely as a result of the increased mobility of centers, vacancies, or other defects with increasing temperature rather than as a result of illumination.

It is interesting to observe, however, that absorption of light at room temperature did result in a noticeable conversion of *F*- and *M*-centers to *R*-centers, in accordance with the work of Molnar.[3]

(B) Thermal Conversion

In order to determine whether increase in temperature alone, without the simultaneous absorption of light, was sufficient to bring about the $F-R'$ conversion, a number of samples, all from the same large crystal containing 5×10^{17} color centers/cc, were heated in the dark at several temperatures for varying times. After heating the samples were quenched on an Al block and their absorption spectra measured. Crystals heated at 125° showed a slow decrease in the *F*-band and corresponding increase in the *R*′-band, complete conversion being attained after 40 hours. At 300° the conversion was complete after 15 minutes. At still higher temperatures the conversion became very rapid but less complete; for example, at 455°, all crystals heated more than 2 minutes showed the same equilibrium curve for which conversion was about 40 percent complete, while at 500° there was little change in the original spectrum, except for a decrease in the *M*-band, for a crystal heated as long as 15 minutes. Equilibrium curves are shown in Fig. 2, in which the ordinates are displaced for clarity. The left intercept in each case represents about the same optical density; however, since the thicknesses of the crystals were not identical, the vertical location of the curves has no significance. It is evident that at this concentration *R*′-centers are the more stable form at temperatures below 300°C and *F*-centers above 500°C, while at intermediate temperatures they are clearly in thermal equilibrium. A pronounced shift of the maximum of the *R*′-band toward longer wave-lengths for higher treatment temperatures, indicates a change in the nature of, or relative abundance of, the absorbing centers.

It is doubtful if any existing analytical means will make possible a calculation of the equilibrium constant at the various temperatures, since the dispersion formula of Smakula[7] can be applied only to bands arising from a single absorbing species, and it will be shown presently that the *R*′-band arises from several species. It is also evident that as the nature of the *R*′-band is complex and variable with temperature, no single constant could describe numerically the state of equilibrium. However, it is of interest to note that in the case of the 300° sample of Fig. 2, the application of the dispersion formula, though not justified on theoretical grounds, yields the same concentration of absorbing centers, within 10 percent, as was found for *F*-centers in the original crystal. This result was confirmed in all similar cases where the formula was applied, and leads to some confidence in its use to estimate the concentration of excess K responsible for each type of band if not the concentration of centers as such.

The reversibility of the conversion was established by heating a crystal in which the *R*′-band was well developed (curve 3, Fig. 3) to 510° for 4 minutes and then quenching rapidly. Curve 5, Fig. 3, shows the reestablishment of the *F*- and *M*-bands and the marked reduction of the *R*′-band to the two *R*-bands.

(C) Low Temperature Absorption

Measurements of the absorption spectrum of several colored crystals at −195°C were made to determine whether a resolution of the *R*′-band into two or more bands occurred. Typical results are presented in Fig. 3. All data were obtained using the same crystal, whose original spectrum is given by curve 1. From the sharpening and displacement of the bands, shown in curve 2, with reduced temperature, it is apparent that the *R*- and *M*-bands of additively colored crystals, as well as *F*-bands,[6] are due to single absorbing species. Molnar[3] has observed this temperature effect on bands produced by x-rays. The definite appearance of a band at 980 mμ, which was occasionally observed as a broad low band at 1000 mμ at room temperature, is worthy of note. This band has been reported by Burstein and Oberly,[9] who have designated it the *N*-band. Curves 3 and 4 prove that the *R*′-band consists of a number of different absorbing species, probably not less than four or five and very likely several more, since at low temperature only a slight shift toward shorter wave-lengths is observed, the top of the curve remains more or less rounded, and the band is not appreciably narrowed. Such behavior is also to be expected of a colloidal system so that additional experiments were carried out to show whether or not the band was due to colloidal metal.

(D) Effects of Concentration

Although present experimental methods are insufficient to allow an exact study of the equilibrium between *F*- and *R*′-centers, a semiquantitative experiment was undertaken to establish the order of size (on the average) of the *R*′-centers. Two KCl crystals were prepared having *F*-center concentrations of 6.0×10^{17} and 7.8×10^{16} respectively as determined by application of the dispersion formula to the absorption curves (Fig. 4, curves 1 and 3). Both crystals had initially an appreciable development of *R*-, *M*-, and *N*-bands, though the appearance of the *R*-bands differed considerably. Both

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[9] E. Burstein and J. J. Oberly, Phys. Rev. **76**, 1254 (1949).

crystals were heated simultaneously at about 450°C for 12 minutes and quenched. Curves 2 and 4, Fig. 4, show the absorption following heating. The concentrations of *F*-centers were reduced to 2.6×10^{17} and 5.3×10^{16}/cc.

The effect of a concentration increase of approximately eightfold upon the number and distribution of the centers formed thermally is very pronounced. The relative decrease upon heating was much greater in the sample having the higher concentration, which shows that on the average more than one *F*-center is used in producing one *R*′-center. It is apparent also that centers absorbing at wave-lengths above 800 mμ are favored by increasing concentration.

An approximate calculation of the average size of the *R*′-centers, in terms of the number of *F*-centers contained, may be made by assuming the thermal equilibrium between *F*- and *R*′-centers to be expressed by the equation

$$nF=(F)_n,$$

where $(F)_n$ is that part of the *R*′-center composed of negative ion vacancies and an equivalent number of electrons. Leaving out of consideration the presence, either initially or at equilibrium, of *R*- and *M*-centers, the equilibrium concentrations of *R*′-centers for the two cases are $(1/n)(3.4\times10^{17})$ and $(1/n)(2.5\times10^{16})$. Since, at equilibrium, the concentration of *R*′-centers varies as the *n*th power of the concentration of *F*-centers, *n* may be evaluated from the two sets of equilibrium concentrations and turns out to be 1.7. The significance of this number is severely limited by the simplifying assumptions noted but indicates that *R*′-centers in this concentration range contain few (certainly less than 5) *F*-centers. At present no indication of the number of lattice vacancies also contained can be deduced, so that a large variety of *R*′-centers is possible.

Even without detailed calculation the absence of colloidal aggregates may be seen from these data. If they are colloidal, their equilibrium with the *F*-centers is heterogeneous, and the concentration of *F*-centers which may be in equilibrium is then dependent upon the temperature and the coexistence of the two phases, and independent of total concentration. Since at equilibrium at 450°, the *F*-center concentration of one sample was about 5 times that of the other, the possibility of a second phase and hence the existence of colloidal particles, at least for the lower concentration, is excluded. Observations made with the ultramicroscope also failed to show the presence of colloidal material.

Experiments at higher concentrations are severely limited by the difficulty of obtaining thin crystals of accurately known thickness. An inspection of curve 1 in Fig. 5, however, shows the marked increase in the *R*′-band in very thin section of crystal having an excess K concentration of 1.3×10^{19}/cc and rapidly quenched from 675°C. The effect of concentration in favoring the higher aggregates has reduced the *F*-band to a minor role, though the concentration of *F*-centers is still much higher than in the previous experiments. Also shown, curve 2, is the spectrum of the same crystal after heating 15 minutes at 300°. Complete equilibrium probably was not attained because of the extreme concentration, but the temperature shift of the maximum is apparent. Curve 3 shows the effect of arc-irradiation for 15 minutes and curve 4 illustrates the lack of resolution of the spectrum, even for this very broad band, at liquid N_2 temperature.

IV. CONCLUSION

We are now in a position to draw some tentative conclusions regarding the products of the thermal and optical destruction of *F*-centers in KCl, and to review the suggestions of Seitz[4] in view of the present experiments. It is immediately apparent that several processes are occurring simultaneously during either thermal, optical, or combined treatments, and that an isolation of effects by more refined experiments will be necessary before the properties and structure of the variety of centers produced may be known in the same way as those of the *F*-centers are known. Certain of these refinements are now being undertaken in this laboratory.

(a) Under irradiation with white light alone, the temperature remaining low, both *F*- and *M*-bands are somewhat unstable and *R*-bands are increased. This process may take place by ionization of *F*-centers and migration of electrons thus raised to the conduction level or by migration of positive vacancies which have sufficient mobility at room temperature to move several atomic spacings during the few minutes consumed in the process. If, as Seitz suggests, an *M*-center consists of a *F*-center combined with a pair of vacancies, and *R*-centers are F_2- or F_2^+-centers, the process could occur along these lines: an electron produced upon ionization of *F*-centers is trapped by a quartet of vacancies, and the weakening of the electrostatic bond between vacancies results in the loss of one or both of the positive ion vacancies. The loss of one would result in the center identified above as an *M*-center; if it were photoelectrically active, further illumination might result in its ionization and the reestablishment of a *F*-center. The loss of a second positive-ion vacancy would result in a F_2^+-center. Trapping of an electron by a F_2^+-center would result in a F_2-center; these latter two should be stable in the first excited level and thus not destroyed by irradiation. No migration of pairs is necessary for these occurrences if the initial presence of quartets of vacancies be assumed.

(b) With increasing temperature, even in the dark, the formation of the *R*′-centers becomes rapid, which strongly suggests that the process depends not on ionization but on migration of groups of vacancies (probably pairs at the lower temperatures). A pair combining with a *F*-center would yield the centers of the type produced by irradiation; however, because of the great variety of centers which now may result from the mobility of the negative vacancies (as members of pairs) the overlapping of absorption bands would lead to a broad band exhibiting the behavior of the R'-band. Among the R'-centers, particularly during early stages, will undoubtedly be found the R- and M-centers. There is no certainty that the R'-centers formed thermally are precisely the same as those formed by heating combined with irradiation; indeed Fig. 5 shows considerable difference in the R'-band formed thermally and that formed by irradiation of samples of the same colored crystal. The size of the R'-centers is probably not great, certainly not of colloidal size, and at temperatures above 300°C noticeable dissociation into F-centers and vacancies becomes apparent. At 510°, dissociation into F- and M-centers is virtually complete.

(c) The shift of maximum in the R'-band with variation in equilibrium temperature is undoubtedly related to the increasing mobility of negative-ion vacancies with temperature which should lead to the rapid formation of aggregates containing several F-centers by direct diffusion and combination.

Further experiments are being undertaken in this laboratory to establish more fully the structure and physical properties of the R-, M- and R'-centers.

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The Paramagnetism of Color Centers in KCl*

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Two methods for studying susceptibility changes occurring during thermal and optical alterations in color centers in KCl are described. The magnetic changes accompanying formation of R'-centers from F-centers, and upon completely destroying both F- and R'-centers, indicate that the moment of a F-center is that calculated for an s-electron, that R'-centers have a variable moment depending on the distribution of centers, but generally very nearly that of F-centers, and that irradiation during R'-center formation results in a destruction of paramagnetism.

I. INTRODUCTION

THE theory of color centers in alkali halides has been reviewed by Mott and Gurney[1] and by Seitz.[2] The interpretation of a variety of experiments on the optical and electrical properties of crystals colored both by radiation and by the addition of a stoichiometric excess of alkali metal has led to some quite definite ideas regarding the nature of the absorbing centers. A F-center is considered to consist of an electron trapped in a halide ion vacancy. Such trapped electrons behave optically very much as s-electrons, and since they are unpaired, the presence of F-centers should impart a small paramagnetic susceptibility to the over-all diamagnetism of the salt, given by

$$\kappa = n\beta^2/kT,$$

where n is the concentration of F-centers/cc, β is the Bohr magneton, and k is Boltzmann's constant. Jensen[3] succeeded in measuring the decrease in diamagnetism of a KBr crystal containing a small amount of KH when F-centers were produced by ultraviolet illumination; the agreement with the decrease calculated from this equation, was very good in view of the experimental difficulties involved. His experimental moment for a F-center was about 10 percent below that for an unpaired s-electron in a free atom but it is doubtful whether the difference is significant.

In order to provide further confirmation of the theory of F-centers and to permit a study of the magnetic changes accompanying the formation and destruction of other color centers in alkali halides,[4] methods have been developed for the measurement of the small susceptibility changes occurring in additively colored crystals when subjected to thermal and optical treatments.

The expected change in volume susceptibility as a densely colored alkali halide, containing for example 10^{19} F-centers/cc, is de-colorized completely by prolonged heating in vacuum is about 2×10^{-8} c.g.s. unit; in the case of KCl this represents a 2 percent increase in diamagnetism. Although this change can be conveniently detected for samples which may remain in place during a magnetic transformation, for samples requiring removal from the magnetic balance for extended thermal treatment and later replacement upon the balance, the errors due to positioning in the field

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[1] Mott and Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940).

[2] F. Seitz, Rev. Mod. Phys. 18, 384 (1946).

[3] P. Jensen, Ann. d. Physik 34, 161 (1939).

[4] Such as R-, M-, and R'-centers, discussed by Scott and Bupp, Phys. Rev. 79, 341 (1950), preceding paper.