The Production of F', M, and R Centers in NaCl at Room Temperature*

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One may produce a variety of absorption centers to the long-wavelength side of the F band. The ones most carefully studied are the F', R_1, R_2, and M bands. In NaCl at room temperature, the R bands overlap and resemble the F' band; indeed, it is not possible to tell if the *erregt* state, so extensively studied by the workers in Göttingen, is due to R or F' centers. An experimental study of these bands has been made. It indicates that the F, F', and M band form during x-radiation. Since the lifetime of the F' band at 300°K is short, it dissociates during the course of the usual absorption measurement. To obtain reliable growth rate of the F band during x-radiation the contribution of the F' band must be taken into account. The R bands are formed primarily by optical bleaching of the F band. The experiments indicate that the "erregt" state at room temperature is due to the presence of the R bands.

I. INTRODUCTION

THE most prominent color center in pure alkali halides is the F center. Two types of absorption bands occur on the red side of it. One type is the F' band which is very broad and which occurs when an additional electron is trapped in an F center.[1] The second type, represented by the R_1, R_2, M, and N bands, is narrower. It is believed that the coagulation of vacancies is responsible for the second type of centers. Colloidal centers will not be considered in this paper. Generally the F' centers and the coagulation centers form at different temperatures and one may consider each independently. An exception occurs in NaCl where both types can be produced at room temperature. This crystal is of special importance since it has been studied extensively and may be obtained in both the natural and the synthetic form.

This paper describes experiments which distinguish between the two types. Actually a great deal of work has been done on these bands. Since this information will be needed in a latter part of the paper, it will be briefly reviewed in the next section. This will be followed by a description of the experiments and the presentation of data. Finally, some theoretical speculations will be made.

II. REVIEW OF INFORMATION ON R AND F' BANDS

The workers on the bands to the red of the F band can be divided into four groups. The first group explored the *unerregt* (unexcited) state and the *erregt* (excited) state (Fig. 1). Gyulai[2] and Smakula[3] fall in the first group. The second group worked at low temperatures and concerned themselves with the formation of F' centers in additively colored crystals. There seems to be little question that this work does not involve the R and M bands. Pick[4] by himself constitutes this group.

The third group recognized the presence of a structure different from the F' band. Examples of workers in this group are Ottmer,[5] Molnar,[6] Petroff,[7] Burstein and Oberly[8] as well as Delbecq, Pringsheim, Voreck, and Yuster.[9] The fourth group produced F' centers by means of x-radiation and used this band to explore the properties of other centers. Typical examples are Dorendorf,[10] Dutton and Maurer,[11] as well as Duerig.[12]

The effects of plastic deformation on these bands have been studied by Haberfeld.[13] These additional complications will not be considered.

Many years ago Gyulai exposed to F light a natural rock salt crystal which had been previously x-rayed. This work was done at room temperature. He observed that the F band shifted to the longer wavelengths and that there was a decrease in the maximum absorption. This effect could easily be explained on the assumption that some of the F centers were transformed to a broad band which peaks to the red of the F band. Shortly it will be seen that a combination of an F and an F' band gives an absorption curve which resembles those of Gyulai (Fig. 1). The following properties of the excited state have been indicated by the work of Gyulai and Smakula:

(1) Plots of the optical absorption and photoelectric response against wavelength give identical curves at

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[1] For reviews of this field, see R. W. Pohl, Proc. Phys. Soc. (London) **49** (extra part) 3 (1937) or Physik. Z. **39**, 36 (1938); F. Seitz, Revs. Modern Phys. **18**, 384 (1946); and N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford Press, New York, 1940), Chap. 4.
[2] Z. Gyulai, Z. Physik. **31**, 296 (1925); **33**, 251 (1925); and **39**, 636 (1926).
[3] A. Smakula, Z. Physik. **59**, 603 (1930).
[4] H. Pick, Ann. Physik **31**, 365 (1938); and **37**, 421 (1940).
[5] R. Ottmer, Z. Physik. **46**, 798 (1928).
[6] J. P. Molnar, thesis, Massachusetts Institute of Technology 1940 (unpublished).
[7] S. Petroff, Z. Physik. **127**, 443 (1950).
[8] E. Burstein and J. J. Oberly, Phys. Rev. **76**, 1254 (1950).
[9] Delbecq, Pringsheim, Voreck, and Yuster, U. S. Atomic Energy Commission Report A.E.C.U. 1533, 1950 (unpublished).
[10] H. Dorendorf, Z. Physik **129**, 317 (1951).
[11] D. Dutton and R. Maurer, Phys. Rev. **90**, 126 (1953).
[12] W. Duerig, thesis, University of Maryland, 1952 (unpublished).
[13] M. Haberfeld, Wien. Ber. IIa **142**, 135 (1933); see also K. Przibram, Z. Physik **102**, 331 (1936).

room temperature. This is true for both the *erregt* and *unerregt* states.

(2) The saturation excitation (reading at $\lambda = 630$ mμ) which occurs after a long irradiation is independent of the intensity of exciting F light, although the weaker sources take much longer.

(3) The amount of excitation decreases with temperature, reaching zero at 70°C.

(4) The quantum efficiency of excitation seems to depend on the intensity of F light, being higher for weaker sources.

(5) Some spontaneous (dark) bleaching of the erregt state occurs. This increases with temperature.

(6) In his work Smakula defined three maximum absorptions of the F band: k_0, the value after x-radiation; k_1, the value after the crystal has been re-exposed to F light; and finally, k_2, the maximum absorption after the excited state has been eliminated by red light. From these he was able to calculate the percentage of destroyed centers which can be restored by red light.[14] The percentage restoration is very small for synthetic crystals (less than 10 percent) and quite large (83 percent) for natural rock salt (see also reference 9).

Smakula carefully measured the shape of the *erregt* F band between 540 mμ and 660 mμ. Gyulai's measurements were made at selected points between 240 mμ to 700 mμ. They found no indication of any structure. This work was done at room temperature. We shall shortly see that in Smakula's work the absence of structure is an inconsistency which is hard to understand.

The workers in the third group above have modified and expanded Gyulai's and Smakula's work as follows:

(1) In NaCl at room temperature the M band appears at 720 mμ. Molnar has shown that by cooling the crystal to 90°K one may resolve the structure between the F and M bands into two distinct bands, R_1 and R_2. The structure between the F and M bands has been observed at room temperature by Ottmer[15] and by the group at the Argonne National Laboratory.[9]

(2) When irradiating additively colored KCl with F light, the red bands do not appear simultaneously. The M band appears first and is followed by the R bands.

(3) The M band appears during the x-raying.

(4) The Göttingen workers have been able to transform completely the *erregt* state to the *unerregt* state by exposing the crystal to red light. Gyulai's bleaching source emitted light between 700 and 1400 mμ; the sources of Ottmer and Smakula are not fully described. Molnar using a monochromatic source was able to bleach the M band but was unable to bleach the R bands.

[14] Actually a correction should be made to k_1 for the overlapping of the F and R bands.

[15] Ottmer did not have enough points to establish the R band (see reference 5, Fig. 8).

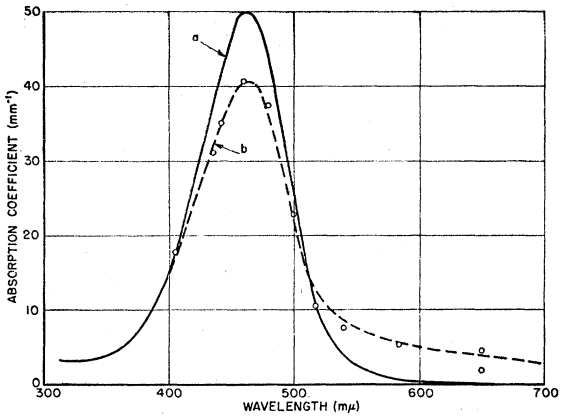

FIG. 1. Absorption curve for the *unerregt* (a) and *erregt* (b) state of the F band in NaCl. State (b) is formed from state (a) by the irradiation with F light. (Data taken from reference 2.)

We shall not review the work of Pick[4] since it has been described and interpreted in several places.[1,16] These data indicate that when the ratio of the concentration of F centers to negative-ion vacancies is not too small, free electrons attach themselves to F centers to produce F' centers. This occurs when additively colored crystals are first exposed to F light[4] or during x-radiation.[10–12,17] The F' band does not decay exponentially; nevertheless, Pick has measured a mean life. For NaCl at 20°C his value is 1000 sec (17 min) while at 40°C, his value is 200 sec (3 min). This indicates that the F' band bleaches in the dark at room temperature.

Finally, one should mention the work of Duerig who showed that the growth rate of the F band during x-radiation at 78°K is affected by the presence or absence of the F' band. Two distinct growth rates have been observed. These curves are not influenced by the x-raying interval.

III. EXPERIMENTAL PROCEDURE

The procedure is similar to the previous work of this laboratory.[18,19] The irradiation in the dark was made with 50-kv x-rays from a molybdenum target. The optical absorption measurements were made with a Beckman Model DU spectrophotometer and will be reported in terms of $\log_{10}(I_0/I)$, where I_0 is the light which is transmitted before coloration and I is the light transmitted after coloration. The room temperature runs were made with a simple holder designed in such a way that one can carefully position the crystal relative to the x-ray beam. Throughout these experiments Harshaw synthetic NaCl was used. The low-temperature measurements were made in the cell designed by Duerig and Mador.[18]

[16] For a recent reinterpretation of Pick's data, see J. J. Markham, Phys. Rev. 88, 500 (1952).

[17] Dutton, Heller, and Maurer, Phys. Rev. 84, 363 (1951).

[18] W. H. Duerig and I. L. Mador, Rev. Sci. Instr. 23, 421 (1952).

[19] W. H. Duerig and J. J. Markham, Phys. Rev. 88, 1043 (1952).

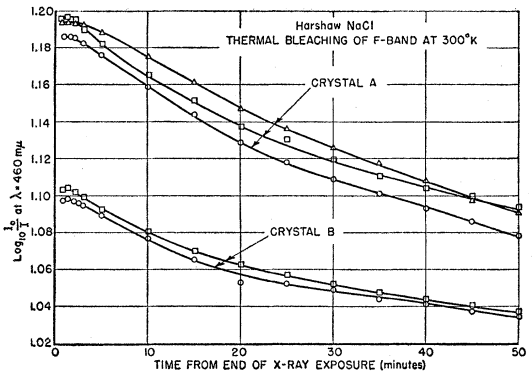

FIG. 2. Decay curves of the F band in NaCl at room temperature. The measurements were made at the band maximum.

IV. EXPERIMENTAL DATA

In this section data will be presented to show how the F' band forms during x-radiation at room temperature. This will be followed by curves which indicate the difference between the F' and R bands.

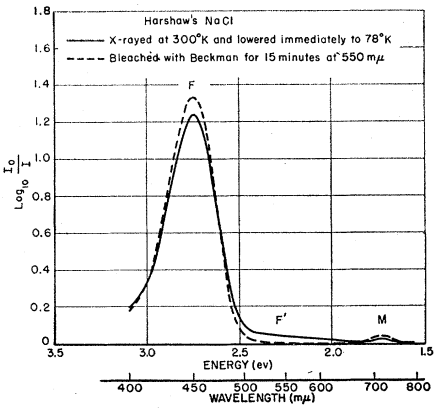

FIG. 3. Absorption spectra of NaCl x-rayed at room temperature. The measurements were made at 78°K.

Figure 2 shows the dark bleaching rate of the F band at room temperature. A pair of crystals cleaved from the same block of NaCl were x-rayed for four minutes and allowed to bleach in the dark. The geometry was such that the faces exposed to the rays were adjacent before cleavage, i.e., a cleaved pair. Between runs the crystals were heated to 350°C for an hour and a half. This seemed to remove all the coloration.

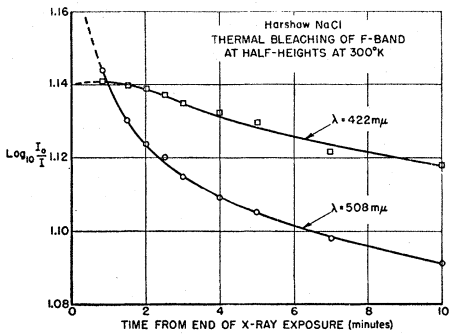

FIG. 4. Decay curve of the F band. The measurements were made at the half-heights.

A definite plateau in the decay curve appears after approximately two minutes. After the irradiation, the concentration of F centers seems to increase for the first minute and then decreases. This would occur if F' centers are formed during x-raying and dissociate in the first minute or two after the exposure. Pick's lifetime measurements show that our time interval is of the right order of magnitude although a little shorter than might be expected.

To show the presence of the F' band, the crystal was x-rayed at 300°K and immediately cooled to 78°K. To achieve this, the crystal was mounted in our low-temperature cell and x-rayed. The moment the x-raying stopped, the cell was filled with liquid nitrogen. Since the lifetime depends critically on the temperature, it was hoped that the crystals would be cooled with sufficient rapidity to trap some of the F' centers. The results of our attempts are shown in Fig. 3. Curve A, obtained immediately after cooling to 78°K, shows the F, F' and M bands. No resolved structure was observed in the F' region. On bleaching the F' band, the F band increased, a typical F' behavior.

An alternative way to show the presence of the F' band is to measure the thermal decay at 422 mμ and 508 mμ. These are the room-temperature wavelengths of the half-heights of the F band. At 422 mμ the F and F' bands overlap very little, if at all, and one essentially measures the half-height of the F band. If the F-center concentration increases, the absorption at 422 mμ would increase. At 508 mμ one measures the half-height of the F band superimposed on the F' band. If the F' band decreases and the F band increases or stays stationary, the absorption here should look quite different from that at 422 mμ. Figure 4 gives the results of the measurements and indicates significant differences in the behavior at the two half-heights. The rapid initial bleaching is believed to be due to the decay of the F' band. The small difference in the absorption after 10 minutes is due to limitations in the experimental technique.

The previous data show that the F' band forms during x-raying. No evidence of the two R bands was found. As stated above, Molnar (his Fig. 29) has shown that these bands form if one excites the F centers with light at room temperature. For this reason the data in Fig. 5 were obtained. A crystal was first colored by x-rays at 300°K and then bleached with F light from the Beckman. (At 460 mμ the band pass is about 30 mμ under bleaching conditions.) After this bleaching, the crystal was again exposed to x-rays and bleached so as to enhance the unresolved structure which appears between the F and M bands.

On cooling the crystal to 78°K, this structure was

resolved into the R_1 and R_2 bands. A comparison of Fig. 3 and Fig. 5 shows the difference between the two types of structure and indicates that the maximums shown in Figs. 2 and 4 are caused by the thermal dissociation of F' centers.

The growth rates of the F band during x-radiation were also studied. The data are not complete; nevertheless, some phenomena have been established. Samples of the data are presented in Fig. 6. The rates were obtained under the following conditions:

(1) The crystal was x-rayed for 25 minutes. For the first 9 minutes the absorption was measured every minute while for the last 16 minutes it was measured every 2 minutes. An absorption measurement indicates that the x-raying was interrupted for about 10 minutes during which time there was a short exposure in the Beckman to F light. A definite change in slope was observed when the x-raying interval was lengthened.

(2) The rate was obtained by taking absorption measurements every 4 minutes. In this case the growth-rate curve lies higher.

(3) The rate was obtained by taking absorption measurements every 12 minutes. The x-raying was interrupted every 4 minutes for 10 minutes.

(4) The rate was obtained by making measurements every 12 minutes; however, in this case the interruption period was shortened to 15 seconds.

Between runs the crystal was bleached by heating it to 350°C for 90 minutes. Preliminary tests indicate that after this treatment, the growth-rate curves were completely reproducible. The possibility exists that it is harder to color a fresh crystal than a heat-treated one. The number of heat treatments, however, does not seem to be important. During this test little was known about the presence of the F' band, so that its behavior was not taken into account.

Figure 6 indicates that the shape of the curve is affected by the x-raying period. The x-raying period has less effect if the interruptions are small (15 sec) than if they are large (10 min). The number of actual measurements on the Beckman does not seem to be important.

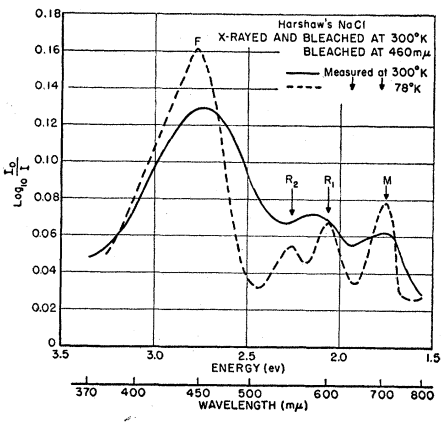

FIG. 5. Absorption spectra of NaCl with R bands. The R bands were produced by prolonged bleaching at room temperature. The measurements were made at 78°K and 300°K.

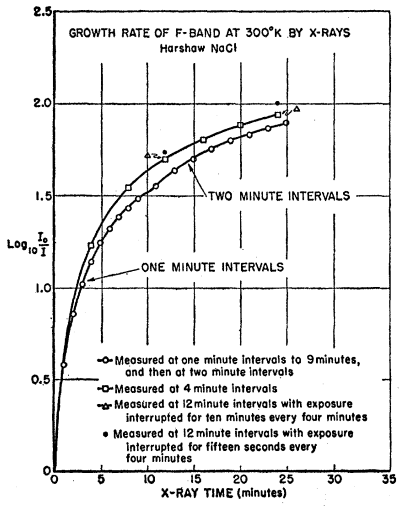

FIG. 6. Curves showing the rates of coloration of NaCl exposed to x-rays.

The data presented can be summarized as follows:

(1) x-raying NaCl at room temperature produces the F, F', and M bands. The F' band is thermally unstable and dissociates in a matter of minutes.

(2) The rate of growth of the F band in NaCl during x-raying at room temperature depends on the number and length of the interruptions of the x-ray beam. The number of optical measurements, if few, does not seem to be important.

(3) In agreement with Molnar's data, the optical bleaching of the F band creates R centers which, in contrast to the F' center, are stable at room temperature. The R structure can be resolved into two bands at 78°K.

V. SOME TENTATIVE INTERPRETATIONS

In this section we shall briefly speculate on what seems to be happening during these experiments. The curves shown in Fig. 2 illustrate the fact that the stability of the F band depends on the lifetime of all the centers formed during irradiation. If the F' centers were the only unstable imperfection, one would expect that there would simply be a rise in the number of F centers after the x-radiation stops. The fact that there is a plateau or maximum strongly suggests that two or more imperfection reactions occur. One is the creation of F centers by the thermal release of electrons from the F' center. The other is the annihilation of the F centers. This may be caused by the thermal dissociation of some of the F centers or the dissociation of some hole centers (i.e., color centers which are caused by the trapping of holes) followed by a capture of the electron trapped in the negative-ion vacancy.

The bleaching of a center may depend primarily on the concentration of other centers. Specifically in this case, the number of F centers produced depends on the concentration of F' centers but does not seem to be related to the F-center concentration. Thus one may not be able to explain the decay rate of a color center by a simple first or second-order reaction equation.

In several respects the curves shown in Fig. 6 are not similar to Duerig's data at 78°K. At this temperature two growth-rate curves exist, one with and one without an F' band. The x-raying interval as well as the time when the F' band is bleached does not influence the rate. Further, from Duerig's data one would expect that the F concentration would be greater when there had been more F' bleaching. The fact that this is not true is another indication that the F centers are destroyed rapidly during the initial dark period. The change in slope shown in Fig. 6 is related to the F band bleaching as well as the F' band dissociation.

At present it would be premature to analyze our decay curves so as to establish a half-life for the F' band. If one associates the plateau of Fig. 2 with the half-life, then it is of the order of 2 minutes which is shorter than Pick's value of 17 minutes. One cannot be sure that this procedure is correct.

It is evident from these data that the growth rate of the F band in NaCl at room temperature is not only a function of total x-ray time, but it also depends on the length of interruption if the exposure is interrupted. One way to obtain a curve is to heat-treat the crystal after every irradiation, and take the absorption measurements about 2 minutes after the x-raying has stopped.

We do not know the answer to the question, "Did Gyulai and Smakula study F' centers or R centers?" The shape of the *erregt* state was measured carefully by Smakula (reference 3, Fig. 1) and the characteristic R bump is not in evidence. Perhaps Smakula's degree of excitation is too small to produce a measurable bump. Our guess is that Gyulai and Smakula actually studied R bands.

Now consider the bleaching properties of the R-bands. Some very puzzling and possibly contradictory information is available. Gyulai's papers indicate that optical and photoelectrical measurements of the shape of the absorption curve, *erregt* and *unerregt* give identical results. The photoconductivity data of Glaser and Lehfeld[20] support the idea that in NaCl at 300°K every photon absorbed in the F center yields a conduction electron. Hence, Gyulai's measurements indicate that every photon in the red tail of the *erregt* state also yields a conduction electron. This would imply some bleaching of the R bands except if the unlikely situation occurred where every electron released from an R center to the conduction band reformed another R center. As mentioned, Gyulai, Ottmer, and Smakula have been able to bleach the *erregt* F band producing an *unerregt* F band.

Molnar, on the other hand, has investigated the bleaching properties of the R bands in NaCl, KCl, KBr, and RbBr. He was unable to bleach the R bands although the M band readily bleaches. Molnar's results have led Seitz[1] to suggest that the R centers are molecules of the F center, i.e., F_2 or F_2^+. F_2 implies a cluster of two negative-ion vacancies combined with two electrons, while F_2^+ implies two negative-ion vacancies combined with one electron. The work of Gyulai, Ottmer, and Smakula suggest that further work is needed to establish this point. Perhaps the band width of the bleaching source affects the results.

Finally, one seems justified in concluding that two types of electron centers form to the red of the F band. One type, namely, the F' and the M, requires a presence of free electrons. The other type, R centers, requires, in addition, a concentration of excited F centers, which are produced by the F radiation. Why excited states are needed is not clear at present.

We may summarize our speculations as follows:

(1) The plateau in the decay curves is due to two competing reactions, one creating and one destroying F centers. There is no reason to believe that either rate is related to the concentration of F centers.

(2) The difference between the growth curves of NaCl at 300°K and the growth curves in KBr and KCl at 78° is due to a rapid bleaching in the dark immediately after the x-radiation stops.

(3) The formation of R centers seems to require a concentration of F centers in the excited state.

(4) The early Göttingen workers seemed to have been studying R and not F' centers.

(5) Contradictory information is available on the bleaching properties of the R bands which suggests the desirability of further experimental work. This is especially important in view of the present models of these centers.

The authors wish to thank Dr. I. L. Mador for his helpful discussions of the problems involved and Miss Doris Rubenfeld for the preparation of the figures.

[20] G. Glaser and W. Lehfeld, Nachr. Akad. Wiss. Göttingen, Math.-physik. **2**, 91 (1936–37). See also Seitz, reference 1, Fig. 6.