

Effect of Plastic Deformation on the γ -Ray Coloration of NaCl Crystals*

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Measurements are made at room temperature of the growth of the F -band in NaCl crystals, under gamma irradiation in a Co^{60} source of constant intensity. Crystals of different origins, heat treatments, and states of deformation, are examined. While deformation has only a relatively small effect on the colorability in the early stage of F -band growth, the effect on the later stage is quite striking. The annealed crystals appear to saturate sharply at a value close to 10^{17} F -centers/cm³, except for a small linear increase with time, while the deformed crystals continue to show a high growth rate in the later stage of irradiation. Upon optical bleaching, the deformed crystals show K -bands, while undeformed crystals irradiated for the same time show no absorption maxima in the visible range. These and other observations confirm the concept advanced earlier that the first stage is due to vacancies and vacancy clusters present in the crystal prior to irradiation (which are determined by the impurity content of the crystal) while the second stage involves the generation of new vacancies at dislocations.

I. INTRODUCTION

IN a recent paper¹ (hereinafter referred to as I) it was shown that the growth of the F -band in NaCl crystals under x-irradiation at room temperature occurs in two stages. The first stage, which Gordon and Nowick called "rapid-type" coloring, was attributed by these authors to the generation of F -centers from vacancies or small vacancy clusters already present in the crystal prior to irradiation. The rapid-type coloring approaches a saturation density of F -centers of about 10^{17} /cm³ in the (Harshaw) crystals studied. The second stage, which was called "slow-type" coloring, involves a steady increase in F -center density up to values in excess of 10^{18} /cm³. Slow-type coloring is attributed to the generation of vacancies at dislocations and was found to be responsible for hardness changes in the crystals.

Although the separation into two stages seemed to be clearly indicated by the x-ray coloration experiments in I, these experiments were relatively complex in the following ways. (1) The complete x-ray spectrum from a copper-target tube operated at 39 kv was employed to produce the coloring. Because of the presence of a wide range of x-ray wavelengths with varying absorption coefficients, the crystals were not uniformly darkened by the radiation; rather the coloration was much stronger just below the surface on which the x-rays were incident. (2) Although the term "slow-type" coloration was used to describe the second stage, implying that longer irradiation times were required than for the first stage, this type of coloring was actually observed only near the surface of incidence of the x-radiation, where the high absorption of long wavelength x-rays gave a sufficient density of F -centers. Thus the second stage of coloration was really produced by different wavelength radiation from the first stage.

In view of these complexities, it was felt that the various experiments carried out in I should be repeated using radiation of sufficiently low absorption coefficient to color uniformly a crystal of reasonable thickness, yet of sufficient intensity to produce the slow-type coloration in reasonable times. The most satisfactory method for the attainment of these objectives seemed to be through the use of a strong Co^{60} gamma source. Such a source not only meets the above requirements but also gives almost monochromatic gamma radiation, at about 1.2 Mev.

The program of the present work is then to carry out experiments on the effects of heat treatment and deformation similar to those described in I but using the Co^{60} source. There are several ways in which the work has been made more extensive, however. First, in contrast to the earlier work, where all specimens came from the same large (Harshaw) crystal, specimens used here are from several different crystals which came from two different sources. Furthermore, the present work sets out to look for the effects of deformation on the second stage or slow-type coloration. While it had been found in I that rapid-type coloration was not very sensitive to deformation, it was predicted that slow-type coloration should be strongly dependent on the density of dislocations in the crystal (based on the mechanism proposed by Seitz² and others, whereby vacancies are generated by the action of excitons at dislocations). This prediction had not yet been checked. Finally, in addition to the measurements of the rate of F -band growth, the present work includes an examination of the optical absorption spectrum of heavily irradiated crystals both directly after irradiation and after optical bleaching.

II. SPECIMENS

All of the NaCl specimens used came from synthetic crystals from two sources. Most of the specimens were cleaved from two large crystals obtained from the

* Experiments conducted at the Brookhaven National Laboratory. This work was presented in part at the Color Center Symposium, Argonne National Laboratory, October, 1956, and in *Bull. Am. Phys. Soc. Ser. II*, **1**, 136 (1956).

¹ R. B. Gordon and A. S. Nowick, *Phys. Rev.* **101**, 977 (1956).

² F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

Harshaw Chemical Company. Since these two crystals were acquired at different times (about 18 months apart), it was expected that their properties were not necessarily the same. These crystals were consequently designated HAR-I and HAR-II. The other two crystals from which specimens were derived were prepared by the Crystal Branch of the U. S. Naval Research Laboratory and are designated NRL-I and NRL-II. A semi-quantitative spectrographic analysis of specimens taken from all four crystals was unable to distinguish any significant difference in impurity content of these crystals. In all cases the analysis showed traces of Si and Ca, and only faint traces of Al and possibly of Mg. In general, these crystals appeared to be substantially purer than the commercially obtained crystals which were examined several years ago.³

The samples used, which were cleaved from these crystals, ranged in thickness from 1.3 to 2.0 mm. Samples designated "as received" were irradiated after they were cleaved from the parent crystal, without further treatment.

All of the deformation experiments were carried out on specimens cleaved from the HAR-I crystal, and in fact, when no other designation is given it should be assumed that the specimens came from this crystal.

III. EXPERIMENTAL DETAILS

Annealing was carried out in a tubular electric furnace held at temperature by means of a suitable temperature controller. "Annealed" specimens were held at 600°C for 1 hr, and then either furnace-cooled (at a rate such that it took 90 min to reach 150°C) or air-cooled by removing the sample directly from the furnace. Low-temperature anneals after deformation were usually at 175°C for 1 hr. All anneals were in air.

Plastic deformation was carried out by compressing a crystal, several times larger than the size required, in a toolmaker's vise and then cleaving the necessary specimens from this deformed crystal.

Irradiation was carried out by lowering the specimens into one of the Co⁶⁰ gamma-ray sources at the Brookhaven National Laboratory. Since the same source was used for all experiments and the crystals were always placed in the same central area of the source, it follows that the gamma-ray dose rate was a constant (191 000 r/hr); therefore, in the presentation of the data, the total irradiation time is the most convenient measure of the total gamma-ray dose. Measurements of optical absorption following irradiation were made using a Beckman model DU spectrophotometer. All measurements were at room temperature.

Optical bleaching of previously irradiated crystals was carried out by placing the crystals within about one foot of a mercury arc lamp for a period of about two hours.

³ W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

IV. CALCULATIONS AND PRECISION

Since the gamma radiation colors the specimen crystals uniformly, the optical density for a given specimen thickness and the optical absorption coefficient (both measured at the maximum of the *F*-band) are proportional to the *F*-center density. Data for the *F*-band growth are reported here in terms of n_F , the number of *F*-centers/cm³. The latter quantity is calculated from the absorption coefficient using Smakula's equation⁴ with an oscillator strength, *f*, of 0.73. This value of *f* was used because it gave the simple relation: $n_F \times 10^{-17} = \log_{10}(I_0/I)$, between n_F and the optical density for a crystal thickness of 1.7 mm (which was taken as the "standard" specimen thickness in these experiments), and because it was not in disagreement with the rough value $f \sim 0.7$ proposed by Seitz.⁵ Since the curves in this paper were prepared, however, a measurement of the oscillator strength reported by Silsbee⁶ gave a value $f = 0.87$ for NaCl. In view of the fact that absolute values of n_F are not important in the present paper (except in order of magnitude) the data were not replotted in terms of the new *f*-value.⁷ Instead, one may use the relation

$$n_F(\text{true}) = 0.84n_F(\text{quoted}) \quad (1)$$

to convert the values of *F*-center density quoted in the figures below to the "true" *F*-center density, assuming $f = 0.87$ to be the true oscillator strength. Stated differently, all values quoted herein are too high by 16%.

For optical densities up to 2.0, the factor which limits the precision of the absorption coefficient is the measurement of the crystal thickness. Only those cleaved samples were selected for irradiation whose thickness was constant to 1.0, or at worst 1.5%; this condition was more difficult to attain in the case of the deformed crystals than for the undeformed ones. The irradiation time for each exposure could be measured to within 1 sec, so that errors in the time measurement offered no problem when irradiation times greater than 2 min were used.

The *F*-band growth curve was found to depend to some extent on the number of measurements made for a given total irradiation time, because of the slight thermal bleaching that took place during standing at room temperature. (It required a 15-min interruption of the irradiation in order to take a measurement.) Data were obtained to check the reproducibility of growth curves in relation to the number of interruptions made. As anticipated, it was found that for fewer interruptions a higher *F*-center density was obtained. For example, a 50-min irradiation with no interruptions

⁴ See K. Przibram, *Irradiation Colors and Luminescence* (Pergamon Press, London, 1956).

⁵ F. Seitz, Revs. Modern Phys. **18**, 384 (1946).

⁶ R. H. Silsbee, Phys. Rev. **103**, 1675 (1956).

⁷ It is also by no means certain the Silsbee's value is the correct one, in view of the recent measurements of C. J. Rauch and C. V. Heer, Phys. Rev. **105**, 914 (1957), which give a value $f \cong 0.7$ for NaCl.

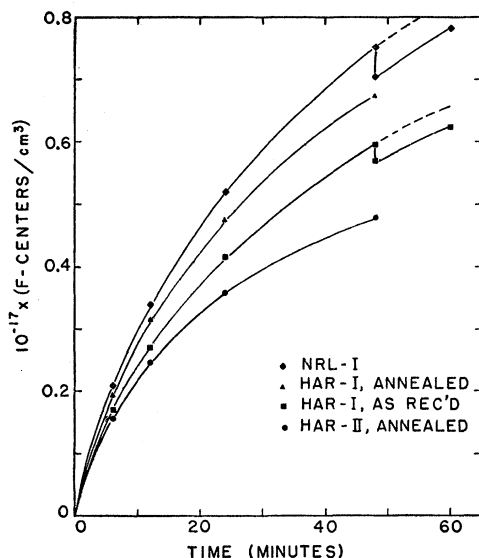


Fig. 1. The F -band growth curves in the early stage as a function of crystal origin and heat treatment.

gave, for the F -center density, a value which was 5% greater than that for an identical crystal irradiated for 50 min with four interruptions at earlier times. This observation is similar to the results of Platt and Markham.⁸ Such differences between growth curves will not play a role here, since in most cases growth curves are only compared when the specimens have had the same number of interruptions at the same set of values of the total irradiation time. Also, the decay of the F' -band will not affect the observations since measurements are always begun at least 8 min after stopping the irradiation, by which time F' -band decay is essentially complete.⁸

On the basis of the above considerations it may be concluded that a difference in the F -band growth curves of more than 2% is to be regarded as experimentally significant.

V. RESULTS

A. Experiments on Undeformed Crystals

The rate of F -band growth in the early stages was found to be sensitive to heat treatment. For example, a Harshaw crystal in the "as-received" condition colors more slowly than an annealed and furnace-cooled sample, as shown by the middle two curves of Fig. 1, in agreement with the results reported in I. (It is now known⁹ that Harshaw crystals are cooled extremely slowly, i.e., over a period of several days, after a final high temperature anneal; therefore, relative to the "as-received" crystals the laboratory-annealed specimens are, in effect, quenched, since they are cooled about fifty times faster.) The electrical conductivity

⁸ R. T. Platt, Jr., and J. J. Markham, *Phys. Rev.* **92**, 40 (1953).

⁹ D. B. Fischbach and A. S. Nowick, *J. Phys. Chem. Solids* **2**, 226 (1957).

of annealed as against as-received crystals shows the same behavior⁹; it has therefore been concluded^{1,9} that the lower rate of formation of F -centers and lower conductivity in the as-received crystal is due to the precipitation of divalent (and multivalent) cation impurities during the extremely slow cooling of these crystals. The presence of such impurities in solution is known to increase drastically both the colorability¹⁰ and the conductivity.²

The role of impurities is further illustrated by a comparison of growth curves obtained on crystals from different sources, shown in Fig. 1. The growth curve for a sample from crystal NRL-I falls above the pair of HAR-I curves, while that for NRL-II (not shown in the figure) falls only slightly below the curve for NRL-I. On the other hand, the curve for an *annealed* sample from the HAR-II crystal falls well below that for the *as-received* HAR-I. It was demonstrated in an additional run (not shown) that also for the HAR-II samples, the data for the as-received crystal falls well below that for the annealed sample (by 15%). Thus, regardless of heat treatment, all data from the batch of specimens taken from crystal HAR-I fall above data obtained from HAR-II samples. The results of Fig. 1 therefore indicate that the HAR-I crystal has a higher impurity content than HAR-II, and that the NRL crystals have still more impurities. The failure of the spectrographic analysis to distinguish between differences in purity of these crystals (see Sec. II) is not surprising, in view of the fact that it was only a semi-quantitative analysis.

The ratios between F -center densities in the various samples for which data are given in Fig. 1 is not substantially changed even after 20 hours of irradiation. The data for the early stages of F -center growth, shown in Fig. 1, therefore illustrate the significant differences between the various undeformed crystals examined.

One other feature is to be noted in Fig. 1. After 48 min of irradiation, some of the crystals were allowed to stand in the dark at room temperature for a period of two hours, during which time thermal bleaching took place to an extent shown in the figure as a vertical drop in F -center density. At the end of the two-hour period, irradiation was resumed. Figure 1 shows that upon re-irradiation the curve continues to increase at the same rate as before the thermal bleaching, i.e., it continues

TABLE I. Effect of re-irradiation of an As-received crystal after complete optical bleaching (n_F is F -center density on original irradiation, n_F' on re-irradiation).

Time (min)	n_F'/n_F
2	1.39
6	1.41
12	1.41
24	1.37
48	1.28
96	1.20

¹⁰ J. H. Schulman, *J. Phys. Chem.* **57**, 749 (1953).

parallel to the extrapolation of the original growth curve. It will be useful to recall this fact later on in this paper.

A preliminary experiment was also carried out on the effect of re-irradiation after optical bleaching of a HAR-I as-received crystal. This crystal was originally irradiated for 20 hours to a value $n_F = 1.03 \times 10^{17} \text{ cm}^{-3}$ and was then optically bleached until it was completely transparent in the visible range. It was then re-irradiated in steps up to 96 min at which time a value $n_F = 0.91 \times 10^{17} \text{ cm}^{-3}$ was attained. Table I shows the ratio of F -center density ($n_{F'}$) on re-irradiation to the corresponding value (n_F) upon the original irradiation, as a function of time. It is apparent that while the initial rate of coloration is 40% higher on re-irradiation, the discrepancy between the two coloration curves decreases as the irradiation time increases, suggesting that the two growth curves would have come together if the second irradiation had been carried far enough.

B. Effects of Deformation

1. F-Band Growth

All deformation studies were carried out on samples cleaved from the same large crystal (HAR-I). The early stage of F -band growth of an annealed crystal is not greatly affected by a deformation of about 4%. This is shown in Fig. 2, which compares the F -center growth curves of three samples for the first hour of irradiation. The data for the deformed crystal (No. 2) fall only 2 to 3% below that for the annealed crystal (No. 1). Crystal No. 3 was also deformed 3.7% but was given a subsequent low-temperature anneal at 175°C for 1 hour. Figure 2 shows that the data for this sample fall distinctly below the other two curves. These results agree qualitatively with those obtained with x-irradiation in I, except that the differences between the various curves

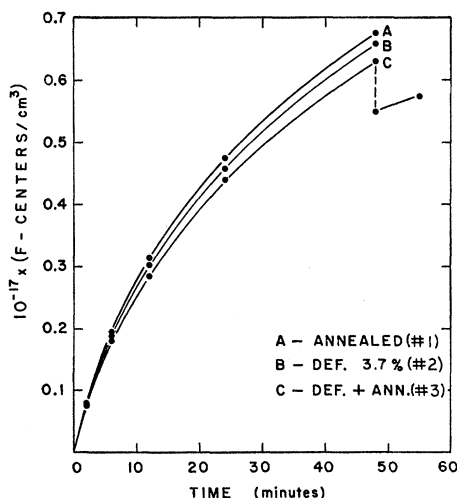


FIG. 2. Early stage of F -band growth for annealed and deformed crystals. Crystal No. 3 differs from No. 2 only in that the deformation is followed by an anneal for 1 hr at 175°C.

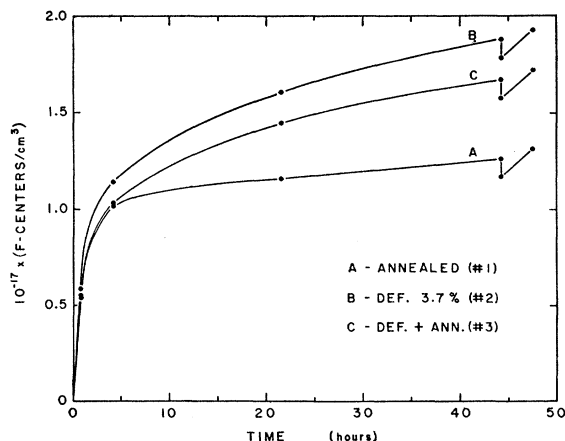


FIG. 3. The same F -band growth curves as in Fig. 2 carried out to a much longer irradiation time.

were somewhat larger in the previous work. Again the results may be related to impurity effects. The annealed crystal is presumed to be cooled sufficiently rapidly that divalent cation impurities remain in solution. Deformation, therefore, produces practically no effect. A low-temperature anneal subsequent to deformation begins to precipitate impurities out of solution, thus lowering the growth curve. The similar effect of deformation followed by low-temperature annealing on the ionic conductivity⁹ provides further support for this interpretation.

Figure 2 also shows the effect of re-irradiation after thermal bleaching, when the crystals were allowed to stand at room temperature for two days, after 48 min of irradiation. To prevent confusion, the bleaching and re-irradiation effect is shown only in the figure for crystal No. 3. Actually, in all three cases the re-irradiation followed nearly parallel to the extrapolation of the original growth curve, in a manner similar to Fig. 1. The amount of thermal bleaching that took place differed for the three specimens, however. Whereas the drop in F -center density of crystal No. 2 on standing was as much as that of No. 3, crystal No. 1 showed a much larger decrease (about 1.6 times the decrease for crystal No. 3). This observation indicates that under the present conditions there is greater instability of F -centers in the annealed than in the cold-worked crystal, in contrast to the results that are usually reported.⁴

From the foregoing description of the results of Figs. 1 and 2, it appears that the growth curves for irradiation times less than 1 hour represent the first stage or "rapid-type" coloring defined in I. In order to attempt to obtain the second stage or "slow-type" coloring, which was predicted to be highly sensitive to the dislocation density, irradiation of the same crystals used for Fig. 2 was continued up to a total time of nearly 50 hours. Figure 3 shows the results of these long irradiations. The most striking feature of Fig. 3 is

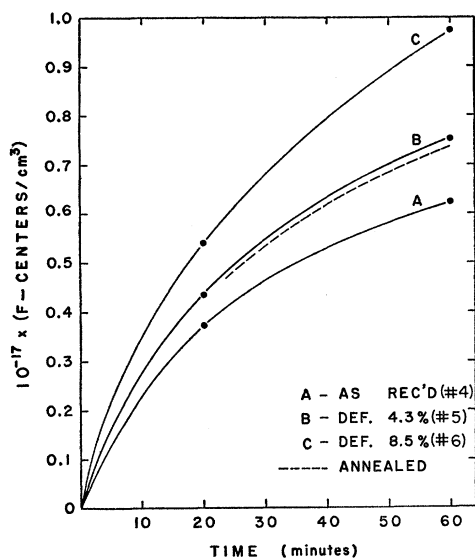


FIG. 4. Early stage of F -band growth for crystals No. 4, 5, and 6. The dashed curve shows the approximate position of the growth curve of an annealed crystal.

the distinct separation that has occurred between curves A and B , which in their initial stages were almost identical. Curve A appears to saturate sharply at a value close to 1.0×10^{17} F -centers/cm³, except for a small linear increase that seems to be superposed on the saturation value. Curves B and C , representing the two deformed samples, on the other hand, show no evidence for a saturation value for the F -center density below 2×10^{17} cm⁻³.

After irradiation for 44 hours, the specimens were partially thermally bleached by allowing them to stay in the dark at room temperature for two days. The decrease in F -center density as a result of this standing period is shown in Fig. 3 on each curve as a vertical drop. The results of re-irradiation for 3 hours after the standing period (the last point on all three curves of Fig. 3) show that a relatively short re-irradiation brings the F -center density to a point which lies on the extrapolation of the original curve. The difference between this result and that shown in Figs. 1 and 2, for the corresponding case of re-irradiation after thermal bleaching, is quite striking.

A second group of three samples, including an as-received crystal (No. 4), a crystal deformed 4.3% (No. 5), and one deformed 8.5% (No. 6), were irradiated concurrently. In contrast to the case of crystals No. 2 and 3, which were annealed prior to deformation, the present crystals No. 5 and No. 6 were deformed in the as-received condition. Figure 4 shows the early stage of F -center formation. In contrast to the case of Fig. 2, the specimen deformed about 4% (crystal No. 5) has undergone a substantial increase in colorability (from curve A to curve B) as a result of the deformation. The reason for this difference becomes apparent when

one inserts the dashed curve, which shows the approximate F -band growth curve for an annealed crystal, based on previous runs.¹¹ It is to be noted that, as in Fig. 2, the specimen deformed about 4% gives a growth curve very nearly the same as that of an annealed specimen. It may be concluded that deformation of this magnitude brings divalent and higher valency impurities into solution by dispersing any fine precipitate particles of these impurities that are present. In accordance with the earlier discussion, such precipitate particles must be present in the as-received crystals but apparently are not in the annealed crystals. Thus, when annealed crystals are deformed there is almost no change in the growth curve. On the other hand, deformation of an as-received crystal has almost the same effect on the growth curve as does annealing. These results and the interpretation advanced are in accord with I; however, the large difference between curves B and C of Fig. 4 is in contrast to I, where it was reported that a crystal deformed 8% showed a growth curve under x -irradiation indistinguishable from that of a crystal deformed 4%. It is also difficult to explain curve C of Fig. 4 if the only factor that controls colorability is the impurity content present in solution. This curve will therefore be given further consideration in the Discussion.

Data for the later stage of F -center growth for crystals 4, 5, and 6 are given in Fig. 5. As in Fig. 3, the undeformed specimen shows a curve which may be interpreted as a saturation of the first stage plus a linear slow-type coloration, while the two deformed crystals show much higher rates of F -band growth for long times of irradiation with no tendency toward saturation.

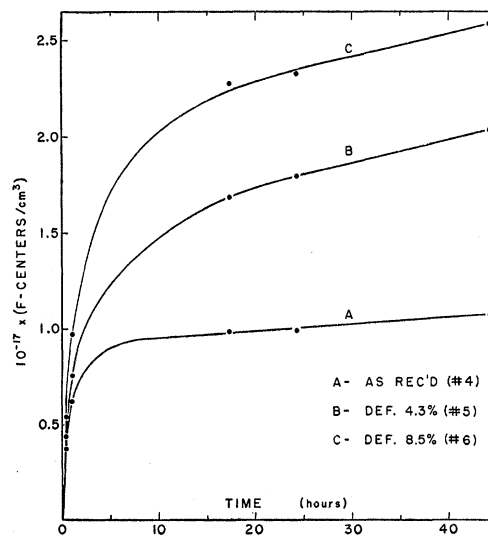


FIG. 5. The same F -band growth curves as in Fig. 4 carried out to a much longer irradiation time.

¹¹ The exact curve for the annealed case cannot be given here since previous irradiations were carried out with a larger number of interruptions (see Sec. IV).

2. Absorption Spectra

In order to obtain a more complete picture of the effects of gamma irradiation, it seemed desirable to examine the complete optical absorption spectrum, rather than just the height of the *F*-band, in typical cases. Accordingly the absorption spectra were studied in some deformed and undeformed crystals which had been irradiated for relatively long periods of time. Figure 6 compares the absorption spectra for crystals 1 and 2 taken directly after 44 hours of irradiation plus 1 day of standing in the dark at room temperature, i.e., near the end of the growth curves shown in Fig. 3. It is difficult to tell by means of these room-temperature measurements whether the *F*-band is broader for the deformed crystal; if any broadening does exist it is just barely outside of experimental error. The peak position for the *F*-bands of the two crystals also may be said to be in agreement within experimental error. It is interesting to note that while the *F*-band in the deformed specimen is 1.6 times higher than that of the annealed specimen, the ratio of *M*-band heights is about a factor of 3. There is no evidence in Fig. 6 for the presence of the *R*-bands in either crystal, i.e., the absorption near 600 $m\mu$ (the approximate location of the overlapping *R*₁- and *R*₂-bands at room temperature in NaCl) can essentially be accounted for by the sum of contributions due to the *F*- and the *M*-bands.

A comparison was also made of the absorption spectra of deformed and undeformed crystals which were first irradiated for relatively long periods of time and then optically bleached. Figure 7 shows the results for crystals 4, 5, and 6 which were optically bleached after their growth curves (Fig. 5) were completed. There is no longer a maximum absorption at 465 $m\mu$ (the position of the *F*-band) for any of the three crystals. However, whereas crystal No. 4 has almost regained its full transparency after the bleaching, the other two crystals show a distinct maximum near 600 $m\mu$ which gives them a characteristic blue color.⁴ On the basis of a comparison of the present results with the bleaching experiments of others,⁸ this maximum is most reasonably ascribed to the (unresolved) *R*₁- and *R*₂-bands of NaCl. (The low-temperature measurements necessary to establish with certainty that the absorption near 600 $m\mu$ is really due

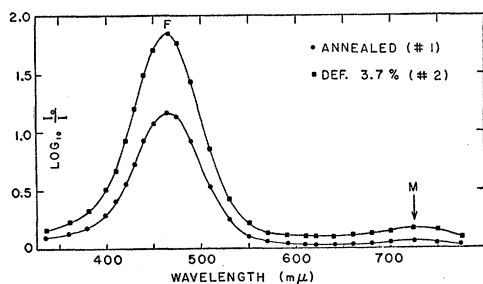


FIG. 6. Comparison of the absorption spectrum of crystals No. 1 and No. 2 after a 44-hr irradiation plus one day of resting at room temperature.

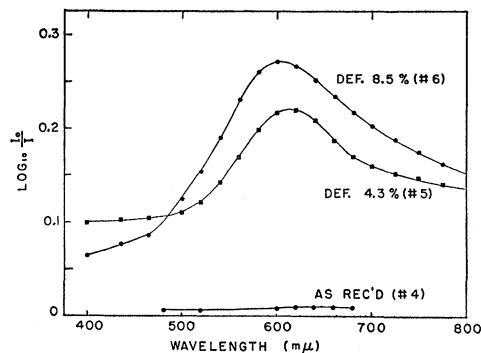


FIG. 7. Comparison of the absorption spectrum of crystals No. 4, 5, and 6 after optical bleaching following 44 hr of irradiation.

to *R*₁ and *R*₂ and not to a colloidal type band were not carried out, however.) The most striking feature of the results of Fig. 7 is that the magnitude of the *R*-band which is present after optical bleaching cannot be correlated with the height of the *F*-band before bleaching (Fig. 5). The height of the *F*-band of crystal No. 4 before bleaching, for example, was about 0.5 of that of crystal No. 5, and 0.4 of that of crystal No. 6; after bleaching, however, the *R*-band of crystal No. 4 is no more than 3% of that of the other two crystals.

VI. DISCUSSION

A. Comparison of the Two Stages

The present results agree, qualitatively, with those reported in I with regard to the effect of heat treatment, of deformation, and of deformation followed by low-temperature annealing, on the colorability in the early stage of *F*-band growth. The principal new results of the present work are related to the second stage (or "slow type") coloration, which had not been investigated systematically in I. In the light of this additional experimental evidence, it seems appropriate to reopen the question of whether or not there is a real difference between the two stages, which can be related to a difference in the mechanism of formation of *F*-centers. The present experiments show several types of evidence which point to the existence of a real distinction between the two stages. These will now be discussed in turn.

(1) The presence of a high dislocation density after cold working results in a greatly increased colorability only in the second stage. For example, whereas the early stage of coloration of a crystal that had been deformed about 4% parallels closely that of an annealed crystal, the later stage shows a much stronger increase on the part of the deformed crystal. This statement is best illustrated by a comparison of the behavior of crystals 1 and 2 in Figs. 2 and 3. It should be noted that the divergence of the growth curves for these two crystals in Fig. 3 is not proportional to n_F , since there was no anticipation of this divergence up to $n_F=0.7 \times 10^{17}/\text{cm}^3$.

(2) Upon re-irradiation after partial thermal bleaching, a very different result is obtained in the two stages. In the early stage, coloration continues very nearly at the same rate as before bleaching (Figs. 1 and 2). In the later stage, the rate of coloration obtained immediately upon re-irradiation is much greater than the value just prior to bleaching, in such a way that the F -center density quickly rises to a value which lies on the extrapolation of the original growth curve (see Fig. 3).

(3) The rate of M -band formation that accompanies the second stage is higher than that which occurs during the early stage. This fact, which is indicated by a comparison of the absorption spectrum of crystals 1 and 2 in Fig. 6 was demonstrated even more strikingly by Mador *et al.*¹² In that work, unfiltered x-rays were used to irradiate the crystals and the slow-type coloration was obtained only near the surface of incidence of the x-rays. Mador *et al.* showed that the ratio of M -band to F -band heights was greatest just below this surface of incidence, where we now recognize that substantial second-stage coloration had taken place.

(4) The magnitude of the R -band, developed after optical bleaching, does not correlate with the height of the F -band prior to bleaching, but rather seems to be related to the F -centers formed during the second stage only. Thus, deformed crystals, such as crystals 5 and 6, which show a substantial second-stage coloration in 50 hr of irradiation, show an R -band after bleaching which is at least an order of magnitude stronger than that of crystal No. 4, which colored only very little in the second stage (compare Figs. 5 and 7).

These four types of evidence, which show the difference in character of the two stages of F -band formation, are not readily understood if one attempts an explanation in terms of a single mechanism of F -band formation. On the other hand, interpretation of the various differences in the two stages is given readily in terms of the two-mechanism hypothesis proposed in I, *viz.*, that in the first or rapid-type stage F -centers are being formed from vacancies and vacancy clusters already in the crystal prior to irradiation, while in the second (slow-type) stage high-energy photoelectrons produced by the radiation generate new vacancies at dislocations. Item (1) above is then immediately interpreted by noting that the dislocation density should then be important only in the second stage. In fact, it was the prediction of a strong sensitivity of stage 2 to dislocation density based on the mechanisms proposed in I that led to the present experiments.

The interpretation of item (2) above is also straightforward in terms of the two-mechanism hypothesis. When thermal bleaching, through standing in the dark, produces a decrease in the F -center concentration from n_{F1} to n_{F2} , the behavior on re-irradiation will be dependent on the mechanism of coloration. If coloration

involves only vacancies already present in the crystal prior to irradiation, then upon re-irradiation it is expected that the same rate of F -band growth will obtain as when the crystal first reached the level n_{F2} on the original growth curve. If, on the other hand, coloration involves the generation of new vacancies, one may predict on re-irradiation a very rapid growth rate from n_{F2} to n_{F1} followed by a continued gradual growth from there on. The latter prediction is based on the reasonable assumption that thermal bleaching involves no loss of excess vacancies from the crystal (allowing, however, for possible association). The data for stage 1 most closely matches the first of these predictions while that for stage 2 fits the second, in agreement with the respective mechanisms already suggested. Specifically, curves *A* in both Figs. 3 and 5 show that it requires about three hours to obtain saturation of the first stage coloration. Accordingly, re-irradiation for a period of three hours after thermal bleaching in the second stage should restore the proper saturation value, *i.e.*, return the F -center density to a value which lies on the extension of the original growth curve, as is actually observed in Fig. 3.

The behavior after partial thermal bleaching may also be compared with the behavior on re-irradiation after complete optical bleaching of an undeformed crystal that had first been irradiated for 20 hours (see Table I). The higher rate of F -band growth upon re-irradiation in this case cannot be accounted for if one assumes that the original irradiation produces no change in the defect pattern in the crystal. The origin of the higher rate of coloration on re-irradiation may be sought in two directions. First, the original 20-hr irradiation may have introduced an appreciable concentration of vacancies generated in the second stage. Second, it is quite unreasonable to expect that all of the $\sim 10^{17}$ vacancies/cm³ participating in the first stage are in the form of free vacancies. Rather, many if not most of them are probably originally in the form of clusters which are then broken up during irradiation. It then follows that re-irradiation takes place more rapidly because of the higher concentration of free vacancies than that which was present initially. The constant ratio of 1.4, for $n_{F'}/n_F$, over the first 24 minutes (see Table I) is in striking contrast to the increase in the ultraviolet colorability of NaCl crystals by two orders of magnitude, as a result of a prior x-ray irradiation by unfiltered (soft) x-rays.¹³ The latter irradiation undoubtedly involves an appreciable second-stage coloration.

The interpretation of item (3) listed above, concerning M -band formation in relation to the two stages, is not as clear as that of (1) and (2). It seems reasonable to suppose, however, that near dislocations various complex clusters may be generated together with single

¹² Mador, Wallis, Williams, and Herman, Phys. Rev. **96**, 617 (1954).

¹³ H. W. Etzel, Phys. Rev. **100**, 1643 (1955).

vacancies, and that among these will be the group of vacancies required to produce the M -band.⁵

Finally, it remains to consider item (4) which correlates R -band formation upon optical bleaching with the slow-type colorability. It might be argued, alternatively, inasmuch as the evidence quoted relates to a comparison between deformed crystals which show an R -band after bleaching, and annealed crystals which do not, that R -band formation might be related primarily to products of the deformation rather than to the slow-type coloration. Other evidence, however, clearly shows that R -band formation also takes place in annealed crystals which were heavily irradiated, i.e., into the second stage. For example, it was reported in I that a blue color after optical bleaching remained only in the region very near the surface where the greatest x-ray absorption had taken place. Further evidence that heavily irradiated annealed crystals are left with R -bands after optical bleaching has been presented by several workers.¹⁴⁻¹⁷ Especially worthy of note is an experiment described by Pringsheim.¹⁷ In this experiment it was shown that the initial x-ray colorability of natural rock salt is much less than that of Harshaw NaCl. To produce the same F -band in both required six times as much x-ray dosage for the natural rock salt as for the Harshaw crystal. Upon bleaching with F -light, the Harshaw crystal was observed to bleach the more rapidly of the two, leaving no residual electron bands. On the other hand, the rock salt crystal bleached relatively slowly with the formation of R , M , and N bands.¹⁸ This difference in the two crystals can be explained by recognizing that the natural rock salt crystal, which showed a lower initial colorability, had fewer vacancies in it prior to irradiation. Although the F -center density was made the same in both crystals, this was accomplished in the natural rock salt by the use of a much longer irradiation time, sufficient to produce a higher proportion of second-stage centers. The development of more complex electron centers upon bleaching is then in complete accord with the belief that these centers occur primarily following slow-type coloration.

Two interpretations may be given for the fact that the formation of R -bands on optical bleaching is a second-stage phenomenon. The first is in terms of the same suggestion as used above to explain the enhanced M -band after slow type coloration, *viz.*, the generation of various vacancy clusters near dislocations. (The R -bands also involve more than one vacancy.⁵) Such clusters may then serve as electron traps for electrons freed from F -centers by the F -light. This action would

then be analogous to that of electron traps generated by plastic flow as observed in additively and electrolytically colored crystals by Ueta and Känzig.¹⁹ A second interpretation is the generation of more stable V -type centers in the second stage of coloration, which therefore greatly lowers the electron-hole recombination probability. In this way it becomes more likely that electrons released from F -centers during bleaching will be trapped in appropriate clusters to form R -centers. This viewpoint is favored by Pringsheim¹⁷ to explain the slower bleaching of his natural rock salt crystal relative to the Harshaw crystal. If the first interpretation given above were correct, one would expect to find more rapid bleaching by F -light for the crystal in which R , M , and N centers form, i.e., the natural rock salt. Since the opposite is found it seems to favor the second interpretation. On the other hand, Pringsheim reports no evidence for a difference in the V -centers observed in the two crystals. His observations were, however, only down to 200 $m\mu$. Clearly, further experiments on the ultraviolet absorption spectra produced by irradiation in the first and second stages are required.

In view of the above discussion, it may be concluded that the present experiments support the hypothesis that there is a basic difference in mechanism between the two stages of F -band formation, as originally proposed in I. In view of this conclusion it seems desirable to attempt to separate out that part of the growth curve which is due to rapid-type coloration from the part due to slow-type coloration. To do this requires a knowledge of the saturation F -center density for the first stage. One method of carrying out such a separation is to use an appropriate theoretical or empirical equation for the early stage of F -center growth and to fit the data to this equation. There is, however, no simple expression that closely fits the actual growth curve of the F -band.⁴ An alternative procedure is to assume that the slow-type coloration always follows a linear growth law which, when extrapolated to zero time, gives the saturation value for the rapid-type stage of coloration. An examination of the results shows, however, that such an assumption would not be reasonable for the deformed crystals. For example, according to this scheme crystal No. 2, which parallels No. 1 so closely in the early stage (Fig. 2), would be given a much higher saturation value, based on a linear extrapolation of the long-time data in Fig. 3. It seems, therefore, that the slow-type coloration of a deformed crystal does not obey a linear growth law. The best procedure for obtaining saturation values for the rapid-type stage is based on the fact that practically all growth curves in the early stage are very nearly in a constant ratio (except for the most heavily deformed crystal, No. 6). Thus, if the saturation value for one curve is known, all the others may be obtained by the assumption that the saturation values are in proportion to the F -center

¹⁴ E. Burstein and J. J. Oberly, Phys. Rev. **76**, 1254 (1949).

¹⁵ Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 1564 (1950).

¹⁶ Herman, Wallis, and Wallis, Phys. Rev. **103**, 87 (1956).

¹⁷ P. Pringsheim, Z. Physik **144**, 31 (1956).

¹⁸ Bleaching by white light, as in the present experiments, eliminates the M -band, since the M -band is readily bleached by M -light.

¹⁹ M. Ueta and W. Känzig, Phys. Rev. **94**, 1390 (1954); **97**, 1591 (1955).

TABLE II. Estimates of saturation values of the rapid-type coloration in various crystals.

Crystal No.	Condition	n_F after 20 min (10^{17} cm^{-3})	n_F^0 (10^{17} cm^{-3})
1	Annealed	0.430	1.05
2	Def. 3.7%	0.412	1.01
3	Def. + Ann.	0.392	0.96
4	As rec'd	0.375	0.92
5	Def. 4.3%	0.436	1.08
6	Def. 8.5%	0.540	1.34
7 ^a	Annealed	0.445	1.09
8	As rec'd	0.370	0.91

^a Crystal 7 is from NRL-II. All others are from the HAR-I crystal.

concentration at some constant irradiation time, say 20 minutes. It also seems reasonable to obtain the saturation value for the *undeformed* crystals by a linear extrapolation of the second stage to zero time. In view of the low rate of growth in the second stage for the undeformed crystals, the error in saturation value obtained by this method should not be large. An estimated saturation value, n_F^0 , for the F -center density in the first stage, is therefore obtained by such an extrapolation for crystal No. 1 (Fig. 3). It is then assumed that the n_F^0 values for all other crystals examined are in proportion to the values of n_F obtained after an irradiation of 20 minutes. In this way, the results of Table II are obtained. This table includes the six crystals of Figs. 2-5 plus two more undeformed crystals (No. 7 and 8) which were studied in the early stage and then given an additional irradiation to a total of 20 hr to carry them into the second stage. Figure 8 shows a plot of $n_F - n_F^0$ vs irradiation time, where n_F is the total F -center density and n_F^0 the estimated saturation value.²⁰ It should be noted that the agreement between all four undeformed crystals is good in spite of the relatively wide range of n_F^0 values involved. Furthermore, as already indicated above, it is clear that the slow-type growth for the deformed crystals is not linear. This result is not unreasonable, since if the color centers are formed near dislocations, they could not be expected to increase in number indefinitely, due to interference effects (such as the formation of complex vacancy clusters). Whether the slow-type coloration for the undeformed crystals is also not linear cannot be determined from the present results.

The interpretation of the F -band growth curve of the crystal deformed 8.5% (No. 6, Figs. 4 and 5) is still somewhat confused. This crystal shows values of n_F for irradiation times less than one hour that are distinctly greater than for annealed crystals and those deformed by about 4%. One could conclude either that this crystal shows a greater vacancy concentration prior to irradiation due to the generation of free vacancies during deformation, or that at least a large part of the

²⁰ The quantity $n_F - n_F^0$ only represents the second-stage coloration when the irradiation is carried out beyond saturation. Therefore no points are plotted in Fig. 8 for irradiation times less than 5 hours.

higher n_F value is due to a much stronger second stage than that of the other crystals. In terms of the latter explanation, the slow-type coloration in crystal No. 6 makes a substantial contribution during the first hour of irradiation, whereas for the other crystals the second-stage contribution in times less than 60 min is unimportant. On this basis, the value of n_F^0 given for crystal No. 6 in Table II may be too high, and therefore, the corresponding curve in Fig. 8 would require modification.

B. Energy to Form F-Centers

In view of the simple conditions, such as a source of constant γ -ray intensity and essentially monochromatic radiation, used in the present experiments, it seems worthwhile to calculate the coloration efficiencies in the two stages of F -band growth. As already shown, the rate of F -band growth depends on impurity content and heat treatment in the first stage and on dislocation density in the second stage. For purposes of calculation, let us take the case of an annealed HAR-I crystal; the energy to form F -centers at the start of irradiation and at the start of the second stage will be computed. The initial slope of the growth curve is difficult to obtain since there is a negative curvature even within the first 5 min of irradiation. Nevertheless, the curvature is not large, and an initial slope of 6×10^{13} F -centers/cm³ sec is obtained for crystal No. 1 (Fig. 2). For this same crystal, the second-stage slope is about 1.2×10^{11} F -centers/cm³ sec, or 500 times lower than the initial slope. For the present gamma radiation (mean energy = 1.2 Mev), 1 mr/hr = 447 photons/cm² sec.²¹ Also, the absorption coefficient for this radiation in NaCl is 0.123 cm⁻¹. Under the present conditions of irradiation (191 000 r/hr intensity) there are 10.5×10^9 photons/cm³ sec absorbed. The initial slope then gives 300 ev as the energy to form an F -center [after correction using Eq. (1)], while the energy for the second stage is 500 times larger. The value of 300 ev is distinctly lower than

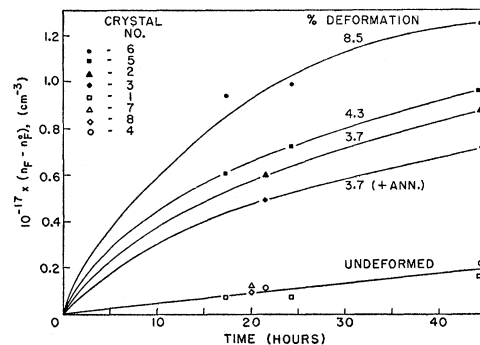


FIG. 8. Second-stage F -band growth of the various crystals studied, based on values of the first-stage saturation F -center density, n_F^0 , given in Table II.

²¹ R. Stephenson, *Introduction to Nuclear Engineering* (McGraw-Hill Book Company, Inc., New York, 1954), p. 184.

the value of about 2000 eV estimated by Schneider²² from earlier experiments of Leitner on the gamma-ray coloration of NaCl, but is high compared to energies (~ 20 – 40 eV) estimated for x-ray irradiated NaCl and KCl.

C. Effect of Plastic Deformation on Colorability

In 1950, Seitz²³ proposed the concept that plastic deformation of a crystal results in the generation of free vacancies through the movement of dislocations. He suggested that this concept could explain the fact, widely quoted in the early literature, that deformation enhances colorability. A brief review of the status of Seitz' concept will now be presented in the light of the present work. There appears to be no evidence in support of this concept in crystals deformed up to 4% at room temperature. There is possibly some evidence in favor of the concept that free vacancies (or simple clusters) are generated by deformation in the case of crystal No. 6 (deformed 8.5%), where the apparently high value of n_F^0 of this crystal (see Table II) may be due to this cause. On the other hand, the possibility that crystal No. 6 shows simply a very large second stage contribution has also been discussed as an alternative explanation for its enhanced colorability.

In any case, the present work and that in I establish two interpretations for the enhancement of colorability in deformed crystals other than the one proposed by Seitz. The first interpretation is in terms of the role of dislocations in greatly enhancing the slow-type colorability. The second is the dispersion of finely precipitated impurities through plastic deformation, which

occurs in the present experiments when an "as-received" crystal is deformed (see Fig. 4). This mechanism may be an important one for the natural rock salt crystals used in most of the early experiments on coloration. It is well known that annealing increases the colorability of these natural crystals, similarly to the present as-received crystals; it is therefore likely that deformation will also increase the colorability by taking precipitated impurities into solution.

Unfortunately, the older literature quoted by Seitz usually does not give sufficient information to determine whether the first stage or second stage is in question. However, in view of these two alternate interpretations which account essentially for all of the deformation effects observed in the present experiments, one can only conclude that evidence from coloration experiments in support of Seitz' concept is at present very meager. Chiarotti's²⁴ failure to find an α -band in deformed alkali halides also supports this conclusion.

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Note added in proof.—F. Seitz has pointed out to the writer that the concept of two stages of coloration had been suggested as early as 1946 (see reference 5, p. 403 ff.), although the role of impurities in the first stage and that of dislocations in the second stage were not recognized at that time.

²² E. E. Schneider, *Photographic Sensitivity* (Butterworths Scientific Publications, London, 1951), p. 13.

²³ F. Seitz, *Phys. Rev.* **80**, 239 (1950).

²⁴ G. Chiarotti, *Phys. Rev.* **107**, 381 (1957).