

Effect of X-Ray Intensity on the Production of Color Centers in NaCl and KCl

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The results of a study of the effect of irradiation intensity on the coloration of NaCl and KCl are reported. Three observations stand out: (1) The equilibrium established between F and complex centers shifts to favor F centers with increasing intensity of irradiation. Cycling of the irradiation intensity between low and high values produces reversible shifts in the relative density of F and complex centers. (2) The density of F centers produced by uv irradiation of a crystal following optical bleaching of a prior x irradiation increases with the intensity of the prior x irradiation. The density of uv-produced F centers could also be shifted in a reversible manner on cycling the intensity of x irradiation. (3) The intensity dependence of the F -center growth curves is present only at irradiation temperatures above 200°K. It is proposed that the intensity dependence of the F -center coloration arises from the establishment of a balance between two competing processes. It is proposed that the primary effect of x-ray photons is to disperse single vacancies in the crystal. Competing with this dispersal is the tendency of the anion vacancies to reaggregate by the diffusion of mobile vacancy units.

INTRODUCTION

THE production of F centers in the alkali halides by x-ray irradiation at room temperature shows several distinct growth stages. There is an initial rapid coloration which saturates; this stage is then followed by a much slower prolonged growth of the F band. The rapid growth of the F band has been attributed to the trapping of electrons at vacancies present in the crystal lattice at the start of irradiation. The slow prolonged growth is then due to the trapping of electrons at new vacancies produced by the radiation.^{1,2}

In a previous paper,³ which will be referred to as I, it was found that at room temperature the F -center density at which the rapid coloration saturates increases with the intensity of irradiation. The F -center density produced by a high-intensity x irradiation could be bleached by a subsequent low-intensity irradiation; the time rate of x-ray bleaching being approximately 30 times the initial rate of thermal bleaching at the same temperature. The M -center density produced by electron irradiation of KCl at room temperature has also been found to be intensity-dependent.⁴ The increase in F -center density with increased irradiation intensity is accompanied by a decrease in M -center density and a reduction in intensity produces the converse effect. Because of its possible clarification of the F -center production and bleaching processes, it was decided to study the effect of x-ray intensity on the room-temperature growth of all the prominent electron trapping centers in NaCl and KCl.

It has been proposed⁴ that F and M centers are in dynamic equilibrium during irradiation at room temperature. It was proposed that this equilibrium is maintained through the medium of some mobile entity which is responsible for the destruction of F centers and

the agglomeration of two F centers to form M centers. Etzel and Allard⁵ have found that uv photons can convert single anion vacancies to F centers. If aggregation of the vacancies has occurred, however, the uv colorability of the crystals is reduced although the aggregates can still be converted to F centers by x-ray photons. It may be possible then to use the uv colorability of a crystal as a measure of the state of aggregation of vacancies. The agglomeration of vacancies to form more complex centers upon a reduction of irradiation intensity may then be detected as a reduction in the uv colorability. Such a measurement would indicate whether the state of aggregation of the vacancies in a crystal changed upon reduction of the irradiation intensity or whether the change in the relative F - and M -center densities was due to a redistribution of electrons amongst the various vacancy units present in the crystal. Such a study of NaCl crystals is reported.

In order to investigate further the possibility of the existence of a mobile unit which influences the relative density of F and M centers, the intensity dependence of the coloration curves was studied between 85 and 308°K. Because of the low M -center densities produced at low temperatures of irradiation,^{6,7} the intensity dependence of this center was not extensively studied. It was assumed that the room-temperature results on the M center could be extended to low temperatures, i.e., changes in the growth of the F band with intensity of irradiation at low temperatures would be accompanied by corresponding changes in the growth of M centers.

EXPERIMENTAL

General

Platelets of Harshaw KCl and NaCl were irradiated with 50-kV x rays filtered through 1.1 mm of aluminum. The thickness of the crystals in the direction of x-ray

¹ R. B. Gordon and A. S. Nowick, *Phys. Rev.* **101**, 977 (1956); A. S. Nowick, *ibid.* **111**, 16 (1958).

² P. V. Mitchell, D. A. Wiegand, and R. Smoluchowski, *Phys. Rev.* **121**, 484 (1961).

³ P. G. Harrison, *J. Chem. Phys.* **37**, 388 (1962).

⁴ E. Sonder and W. A. Sibley, *Phys. Rev.* **129**, 1570 (1963).

⁵ H. W. Etzel and J. G. Allard, *Phys. Rev.* **116**, 885 (1959).

⁶ W. H. Duerig and J. J. Markham, *Phys. Rev.* **88**, 1043 (1952).

⁷ B. J. Faraday, H. Rabin, and W. D. Compton, *Phys. Rev. Letters* **7**, 57 (1961).

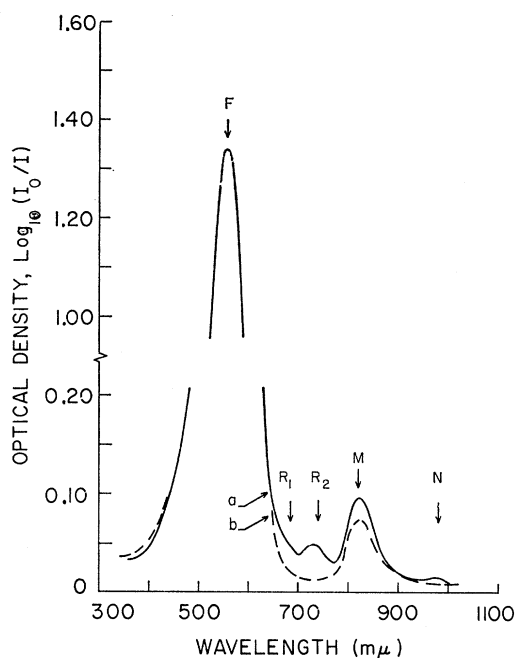


Fig. 1. Comparison of the optical absorption produced in KCl by two different intensities of irradiation. Crystal *a* was irradiated for 164 h at 5 mA. Crystal *b* was irradiated for 10 h at 50 mA. The two crystal thicknesses agreed within 0.02 mm.

passage was 0.75 mm or less. These crystals were cleaved from a large NaCl or KCl crystal and were used in the as cleaved condition. The results obtained with NaCl and KCl were very similar. The results on NaCl are reported, except in the section on the *F*, *M*, and *R* bands where the results for KCl are reported, as the bands of interest are better resolved in this case.

The x-ray tube current was varied between 1 and 50 mA; the x-ray intensity will be indicated by giving the tube current in mA. The x-ray generator contained both voltage and current regulating circuits. Unless specified otherwise all irradiations were performed at room temperature.

The density of *F* centers was calculated from the absorption by using Smakula's equation and an oscillator strength of 0.83.

Studies of *F*, *M*, *R*, and *N* Centers

The optical density of the KCl crystals used in these measurements was determined with a Cary model 14R spectrophotometer. The crystals were removed from the x-ray beam for approximately ten min during the measurement of optical density. It was found that the thermal and optical bleaching produced by the measurement operation was negligible.

In cases where the intensity of irradiation of the same crystal was varied, the x-ray irradiation after the change in intensity was of sufficient duration to bring the first stage *F*-center density to its quasiequilibrium value. It was found in I that the *F*-center density depended only

on the final "equilibrium" irradiation intensity and the total radiation dose.

The optical bleaching of the crystals and the associated measurements of optical density were made with the crystal in place in the spectrophotometer. The wavelength drum was set at 5580 Å and the slit width set at 3 mm. The small changes in *F*-center density produced by the optical bleaching were rapidly restored on reirradiation of the crystal.

Studies of the uv Colorability

NaCl crystals were irradiated with x rays until the first stage *F*-center density was brought to the saturation level. The crystals were then optically bleached with white light from a tungsten filament bulb. A glass heat filter was placed between the lamp and the crystals, and dry air was passed over the crystals to maintain them at room temperature. All coloration at wavelengths longer than 2800 Å could be bleached by this treatment in a period less than 1 h. After the optical bleaching the crystals were either annealed at 150°C or subjected to uv irradiation. A quartz envelope hydrogen arc lamp was used for the uv source. The crystals were placed 1 cm from the lamp and dry air at room temperature was blown over them. After the crystals had received the desired uv irradiation, they were x irradiated in whatever state the uv irradiation left them. Crystals reirradiated in this way were brought to an *F*-center

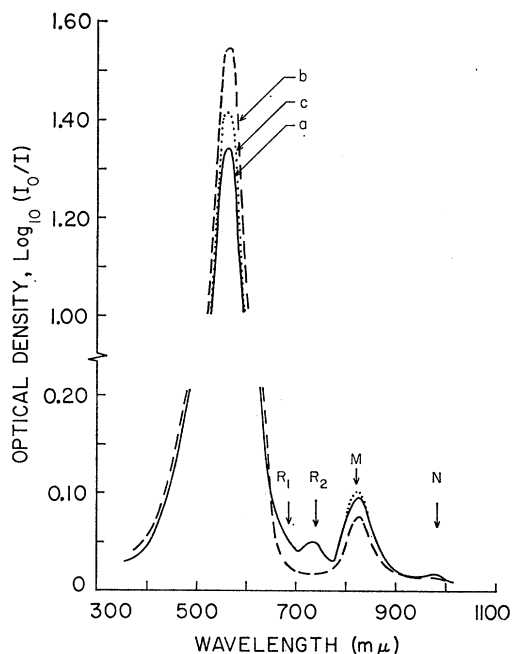


Fig. 2. The effect of variation of the intensity of irradiation of the same crystal on the optical absorption. Curve *a*, optical absorption after an initial irradiation at 5 mA for 164 h. Curve *b*, optical absorption after the crystal was subjected to an additional $\frac{1}{2}$ -h irradiation at 50 mA. Curve *c*, optical absorption after an additional 5 mA irradiation for 2 h.

density characteristic of the total dose of x rays and the intensity of the final x irradiation. The optical bleaching did not appreciably affect this level.

Low-Temperature Measurements

A standard optical cryostat was used for the measurements below room temperature. NaCl crystals were irradiated and the optical density measured through $\frac{1}{8}$ -in.-thick Corning 7940 fused silica windows in the cryostat. These windows reduced the x-ray intensity at the crystal by approximately a factor of three from that obtained during the room temperature irradiations. The optical density at the peak of the *F* band was measured by means of the interference filter technique described in I. The oven in the apparatus described there was replaced by the cryostat. At 85 and 200°K the interference filter used to measure the transmission of the crystal had its transmission peak at $4500 \pm 3 \text{ \AA}$. For irradiation temperatures above 200°K the filter used had a transmission peak at $4650 \pm 3 \text{ \AA}$. The temperature of the crystal during irradiation was measured with a copper constantan thermocouple in contact with the crystal.

RESULTS

Production of *F*, *M*, *R*, and *N* Centers

Figure 1 gives a comparison of the optical absorption produced in a KCl crystal irradiated with 5-mA x rays with that for 50-mA irradiation of another crystal. The

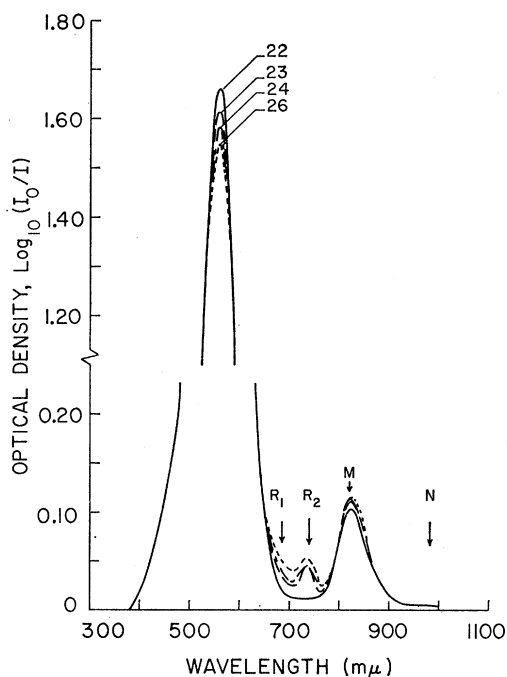


FIG. 3. Growth of the complex bands following a reduction of irradiation intensity. 22=optical density after a 15-h irradiation at 50 mA. 23=treatment 22+15 min at 5 mA. 24=treatment 22+30 min at 5 mA. 26=treatment 22+130 min at 5 mA.

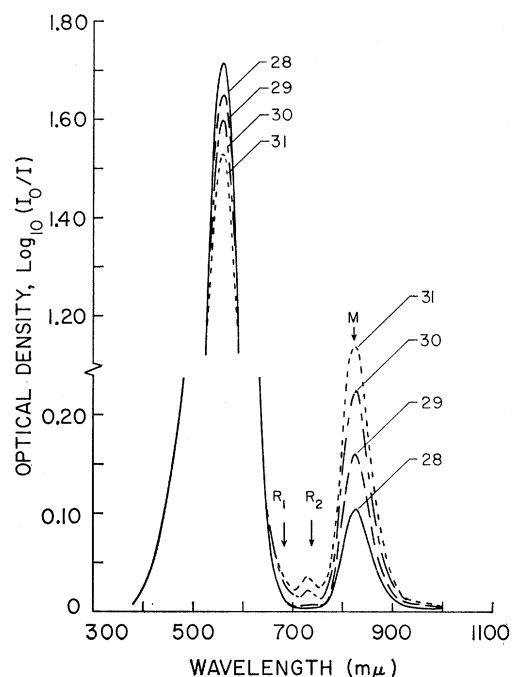


FIG. 4. Growth of the complex bands produced by optical bleaching of the *F* band. 28=optical density after irradiation equivalent to $16\frac{1}{2}$ h at 50 mA. 29=treatment 28+1 min optical bleach at 5580 Å. 30=treatment 28+2 min optical bleach at 5580 Å. 31=treatment 28+3 min optical bleach at 5580 Å.

two irradiations were of such duration that equal *F*-center densities were produced. The 5-mA irradiation (curve a) produced prominent *R*₂ and *M* bands along with weak *R*₁ and *N* bands in addition to the *F* band. The 50-mA irradiation (curve b) did not produce the *R*₁, *R*₂, and *N* bands, and examination of many crystals indicated that the *M* band produced by 50-mA irradiation was slightly less than that produced by 5-mA irradiation. Crystals were also irradiated with equal doses of 5- and 50-mA x rays. In this case the 5-mA irradiation again produced *R* and *N* bands while these bands were absent after the 50-mA irradiation.

Figure 2 shows the optical absorption produced in a KCl crystal subjected to various intensity irradiations. The initial 5-mA irradiation (curve a) produced *R*₂, *R*₁, *N*, *M*, and *F* bands. An increase in the intensity to 50 mA (curve b) removed the *R*₁, *R*₂, and *N* bands and reduced the *M*-band absorption while the *F* band increased in intensity. The absorption bands were restored approximately to their initial values upon reducing the intensity to 5 mA (curve c). The half-width of the *F* band was measured and no difference was found for any of the intensities of irradiation used. Therefore, the variation in absorption is primarily due to the "pure" *F* band⁸ and not to some other band appearing under it.

Another crystal was irradiated with 50-mA x rays for

⁸ J. D. Konitzer and J. J. Markham, *J. Chem. Phys.* **32**, 843 (1960); J. J. Markham and J. D. Konitzer, *ibid.* **34**, 1936 (1961).

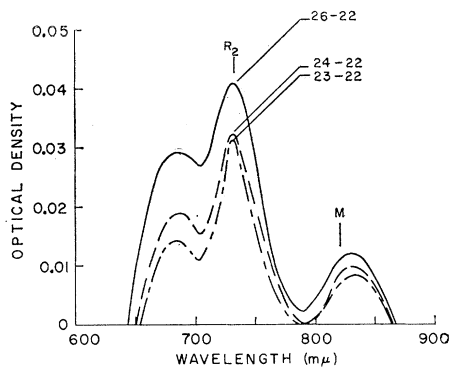


FIG. 5. Changes in optical density produced by the treatments of Fig. 3. 23-22, 24-22, and 26-22 give the optical absorption introduced by 15 min at 5 mA, 30 min at 5 mA, and 130 min at 5 mA, respectively.

16 h and then the x-ray intensity was reduced to 5 mA. The rate of change of the absorption bands produced by this treatment is shown in Fig. 3. This figure should be compared with Fig. 4, where a similar change in the absorption bands is produced by optical bleaching of the *F* band with 5580-Å light. Figures 5 and 6 give the changes in optical absorption between 6000 and 9600 Å produced by the treatments represented in Figs. 3 and 4.

UV Colorability

Figure 7 shows the optical absorption present in the uv region of the spectrum of a NaCl crystal after optical bleaching of the x-ray coloration. The absorption is characterized by two broad bands at approximately 1945 and 2230 Å. The height of the band at 1945 Å is greater following bleaching of a high-intensity x-ray

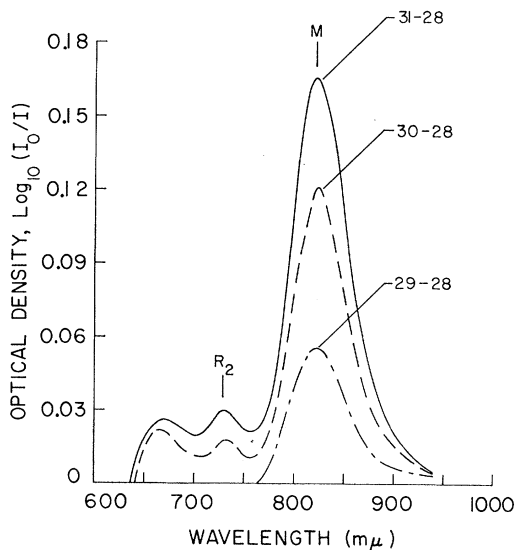


FIG. 6. Changes in optical density produced by the treatments of Fig. 4. 29-28, 30-28, and 31-28 give the optical absorption introduced by optical bleaching at 5580 Å for 1, 2, and 3 min, respectively.

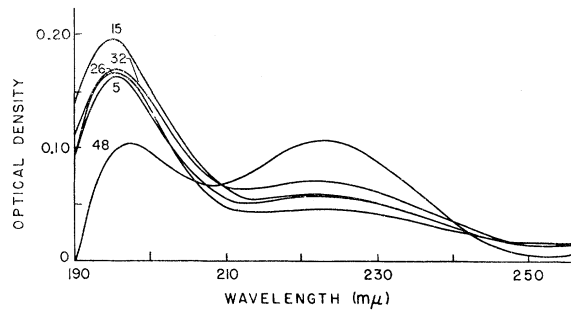


FIG. 7. Optical absorption in uv region produced by various treatments of NaCl crystal No. 2. 5=optical bleach after a 1-mA irradiation; the dose is equivalent to 4½ h at 50 mA. 15=optical bleach after 50-mA irradiation; dose equivalent to 5½ h at 50 mA. 26=optical bleach after 1-mA irradiation; dose equivalent to 7 h at 50 mA. 32=optical bleach after 50-mA irradiation; dose equivalent to 8 h at 50 mA. 48=optical bleach after 50-mA irradiation; dose equivalent to 13 h at 50 mA.

coloration than after bleaching of a low-intensity one. The height of this band during constant intensity irradiation decreases with increasing dose. The absorption band at 1945 Å could also be increased by annealing the crystal at 150°C. The band at 2230 Å only appears after prolonged x irradiation and slowly increases with radiation dose.

Figure 8 shows the effect of hydrogen lamp irradiation on the uv absorption of the crystal and the resulting growth of the *F* band. The uv irradiation reduces the band at 1945 Å and produces a shift in its peak position to longer wavelengths. The shift in peak position is believed to be due to the fact that the uv irradiation removes the optical absorption in a band peaking at 1920 Å (the *U* band). The presence of an absorption band at longer wavelengths which is relatively unaffected by the uv photons would cause the shift in peak position with uv irradiation.

A study of the *F*-center coloration with time under uv irradiation showed that the *F*-center density rose to a maximum and then decayed in agreement with prior results on Harshaw crystals.⁵ The maximum coloration produced by the uv irradiation depended on the prior treatment of the crystal; a summary of the results is given in Table I. This table shows that the uv coloration after irradiation at any particular x-ray intensity increases with x-ray dose regardless of the behavior of the 1945-Å band. Comparison of 15, 26, and 32 shows that the uv colorability is less after a low-intensity x irradiation than after a prior high-intensity irradiation. The reduction in uv colorability is then restored by a short irradiation of the crystal with high-intensity x rays.

Treatments 4, 12, 31, 44, and 62 show that while annealing of the crystal increases the 1945 Å absorption, it reduces the uv colorability of the crystal. This reduction in uv colorability may be restored by a subsequent x irradiation. (The low value of the 1945 Å band produced by treatment 31 is believed to be due to the fact

TABLE I. Comparison of O.D. at 1945 Å with maximum D.O. produced at *F* band by uv irradiation.

From Fig. 9	Treatment	O.D. at 1945 Å after optical bleaching	Maximum O.D. at <i>F</i> band produced by uv irradiation
5	O.B. after: 50 mA x rays followed by 18 h of 1-mA x rays	0.165	0.108
15	5+1 h at 50 mA	0.196	0.135
26	15+74 h at 1 mA	0.165	0.122
32	26+1 h at 50 mA	0.170	0.140
48	32+5 h at 50 mA	0.105	0.150

From Fig. 10	Treatment	O.D. at 1945 Å after optical bleaching	Maximum O.D. at <i>F</i> band produced by uv irradiation
4	O.B. after 3 h at 50 mA	0.165	0.110
12	4+3 h at 50 mA+O.B.+1 h at 150°C	0.210	0.100
31	12+1 h at 50 mA+O.B.	0.162	0.113
44	31+2 h at 50 mA+O.B.+19 h at 150°C	0.232	0.103
62	44+2 h at 50 mA+O.B.	0.204	0.120

O.B.=optical bleach
O.D.=optical density = $\log_{10} I_0/I_t$ where I_0 and I_t are the incident and transmitted intensities.

that the x irradiation had not produced saturation of the first-stage coloration.)

Low-Temperature Measurements

In Fig. 9 the *F*-center density is plotted against the relative number of absorbed photons at irradiation temperatures between 85 and 308°K. At any point on the coloring curves a change in irradiation intensity at 85 and 200°K produced no change in the number of *F* centers formed per photon absorbed. At 273 and 308°K a similar change in irradiation intensity produced large changes in the growth curves. At the higher temperatures a reduction in x-ray intensity produced bleaching

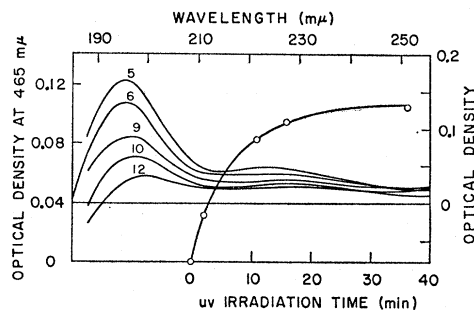


FIG. 8. Change in absorption in the uv region of the spectrum produced by uv irradiation of crystal No. 2. The corresponding growth of the *F* band is also shown. 5=optical bleach following 1-mA x irradiation (see Fig. 7). 6=optical density after 2-min uv irradiation. 9=optical density after 11-min uv irradiation. 10=optical density after 16-min uv irradiation. 12=optical density after 36-min uv irradiation.

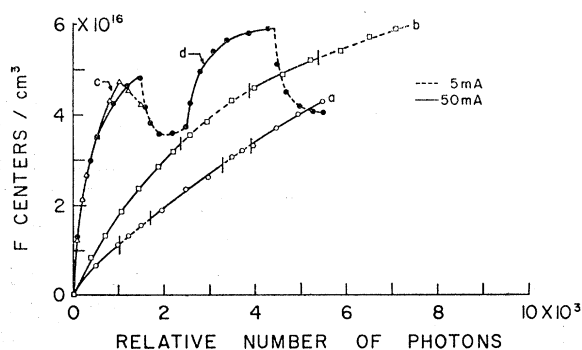


FIG. 9. Growth of the *F* band of NaCl produced by x irradiation at low temperatures. a=irradiation at 85°K, b=irradiation at 200°K, c=irradiation at 273°K, d=irradiation at 308°K.

of some of the *F* centers produced by the higher intensity irradiations. Measurements at 253°K also indicate that irradiation at this temperature produces the same general effect as is obtained at higher temperatures.

Figure 10 shows the effect of warming the crystal from 200 to 308°K after irradiation at 200°K. The warming process required 6 h and produced a decay in the *F*-center density that was approximately exponential with time. After this decay a relatively stable *F*-center density was achieved. This density was approximately 40% greater than the coloration that could be produced by irradiation at 308°K. Commencement of irradiation at this point produced x-ray bleaching at a rate approximating that found for first-stage centers in I. This similarity in the bleaching rates indicates that the centers formed at 200°K behave in the same general manner as those formed at higher temperatures. After the crystal was warmed to 308°K, it exhibited the usual variation in *F*-center density with changes in intensity. Thus, the lack of an intensity dependence at low temperatures is actually due to the temperature of irradiation and not to any peculiarity of the irradiation conditions.

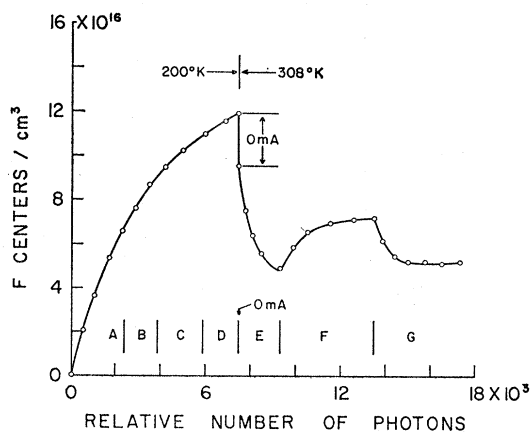


FIG. 10. *F* band produced at 200°K and the effect of warming to 308°K and then continuing the irradiation. A=50 mA, B=5 mA, C=50 mA, D=5 mA, E=5 mA, F=50 mA, G=5 mA.

DISCUSSION

Equilibrium Between F and Complex Centers

The data of Figs. 1 through 4 indicate that during irradiation F centers are not only in equilibrium with M centers but with all the complex centers. The equilibrium shifts to produce F centers and bleach complex centers with increasing intensity of irradiation, while with decreasing intensity the opposite is true.

The density of F and complex centers characteristic of the intensity of the final irradiation intensity is quickly established after a change in intensity. The rapid establishment of equilibrium indicates that vacancies present at the initiation of irradiation are primarily involved. It was found in I that F centers associated with vacancies present at the initiation of irradiation quickly reached the F -center density characteristic of the intensity of the final x irradiation. The centers associated with new vacancies produced by the x rays required much longer to reach the equilibrium density characteristic of the final irradiation intensity.

X-ray bleaching produces growth of a broad band to the red side of the F band. This band, perhaps the R' band, produces a 10-Å shift to the red in the position of the M band between curves 26 and 22. It also appears to shift the position of the R bands, however, this has not been extensively investigated. This broad band is removed upon increasing the x-ray intensity to 50 mA. This indicates that the complex centers removed by the 50-mA irradiation are not converted into higher aggregates.

Figures 5 and 6 show that bleaching of the F band with 5580-Å light produces an initial growth of the M band which is followed by growth of the more complex centers, while x-ray bleaching produces simultaneous growth of all the complex bands. This difference in bleaching behavior may be qualitatively understood by a consideration of the different effect of the two types of bleaching irradiation and the proposal that a reduction in irradiation intensity produces $F \rightarrow M$ aggregation. Optical bleaching into the F band will initially produce electrons, anion vacancies, and F' centers. M centers may then be formed by the combination of an anion vacancy and an F' center. R centers would then be formed as the second step in the recombination process, i.e., the union of an anion vacancy and an M' center. During x irradiation vacancies will exist in various charge states and states of recombination. A reduction in irradiation intensity allows precipitation of some of the anion vacancies associated with F centers. These excess vacancies may combine with F' , M' , and other primed type centers with approximately equal probabilities. Therefore, simultaneous growth of all the complex centers will be produced by x-ray bleaching because of the presence of many different charged vacancy units, while during the initial stages of optical bleaching only anion vacancies and F' centers will have an appreciable concentration. The difference in bleaching behavior is

thus a strong indication that vacancy aggregation does occur during the formation of complex centers after a reduction in irradiation intensity.

An estimate was made of the number of negative-ion vacancies associated with the growth of the complex centers after a reduction in irradiation intensity. The density of the various centers was estimated by means of Smakula's equation and an oscillator strength of 0.4. The density of negative-ion vacancies in the centers was estimated by using Pick's models⁹ for the complex centers. It was found that the number of negative-ion vacancies appearing in the complex centers was approximately equal to the number associated with the bleaching of the F band. This calculation must be viewed with skepticism, however, as neither the oscillator strengths nor the models for the various centers are firmly established.

Vacancy Aggregation

Table I illustrates that while the 1945-Å absorption possesses an intensity dependence, the uv colorability is not determined by the absorption in this band alone. The uv colorability continuously increases with x-ray dose while the 1945-Å absorption decreases. The uv colorability decreases upon heat treatment even though the density at 1945 Å increases. It may be concluded from these measurements that the increase in uv colorability with the intensity of the prior x irradiation is not primarily due to an increased absorption in the uv region of the spectrum.

On the basis of Etzel and Allard's result that the density of F centers produced by uv irradiation decreased as vacancy aggregation occurred, the data of Table I indicate that vacancy aggregation occurs upon a reduction in x-ray intensity. The vacancy aggregates may then be broken up by a short high-intensity x irradiation. The rapid change in the state of vacancy dispersion with changes in irradiation intensity indicates that initially present vacancies are also involved in these processes.

The exact form of the aggregates produced by a reduction in irradiation intensity cannot be determined from these measurements. However, it must be concluded that the change in the density of F and complex centers upon a reduction in irradiation intensity is accompanied by vacancy aggregation. It seems probable that at least some of the vacancy aggregation is responsible for the observed growth of the complex centers. This result supports the proposal that the equilibrium between F and M centers is maintained by some mobile entity which can alter the state of vacancy aggregation in the crystal. The motion of this entity must allow the transfer of vacancies from an isolated state to an aggregated state and vice versa.

The results on the effect of temperature of irradiation on the intensity dependence of the F -center growth

⁹ H. Pick, Z. Physik **159**, 69 (1960).

curves furnishes additional confirmation for the proposal that the equilibrium between F and complex centers is maintained by a mobile entity. At temperatures below 200°K this entity is no longer mobile and the intensity dependence of the growth curves disappears. The temperature at which the intensity dependence disappears is in the same neighborhood as that at which F to M conversion by optical and thermal means ceases.¹⁰⁻¹² This suggests that basically the same type of mechanism operates in the three cases.¹²

These results indicate that the intensity dependence of the F -center growth curves arises from the possibility of forming several different stable centers from anion vacancies. The distribution of the anion vacancies amongst the various possible centers is determined by the intensity and temperature of irradiation.

Possible Coloration Processes

Consideration of several experimental observations gives some indication of the types of processes that may predominate in determining the dependence of the coloration on the irradiation conditions.

(1) At any point on the coloring curves the number of F centers produced per absorbed x-ray photon is independent of irradiation intensity at temperatures below 200°K.

(2) The number of alpha centers produced per absorbed photon is also independent of intensity below 200°K.¹³

(3) At any point on the coloring curves obtained at temperatures above 200°K the number of F centers produced per x-ray photon absorbed increases with increasing intensity of irradiation.

(4) At temperatures near room temperature the density of F centers present during irradiation increases with decreasing temperature of irradiation.^{14,15} The opposite behavior is exhibited by M centers.¹⁵

(5) M centers can only be formed in appreciable quantities at temperatures above 200°K.¹²

(6) The formation of complex centers during irradiation is accompanied by an increase in the state of aggregation of single anion vacancies.

Items 1 and 2 indicate that below 200°K one of the primary effects of irradiation is to disperse single anion vacancies in the crystal. At any point on the growth curves the amount of dispersal produced is proportional to the irradiation intensity.

Items 3 and 4 show that above 200°K the ability of the x-ray photons to produce single vacancies, F centers, in the lattice increases with increasing intensity of irradiation and decreases with increasing temperature of irradiation.

Items 5 and 6 indicate that aggregation of vacancies is responsible for the growth of complex centers which occurs above 200°K.

It seems probable that the primary effect of radiation on the crystal does not change above 200°K. Thus, even above 200°K the x rays disperse vacancies at a rate that is proportional to the intensity of irradiation. The fact that this is not observed in a study of the F -center coloration curves may then be due to the aggregation of single vacancies which can occur in this temperature range. The actual F -center density observed is then due to the balance established between the dispersal of vacancies and their reaggregation. The time rate of dispersal of vacancies being proportional to the irradiation intensity while the rate of reaggregation increases with increasing temperature of irradiation. The dispersal may be by means of thermal spikes which occur in the neighborhood of aggregates.¹⁶ The re-aggregation may be accomplished by the diffusion of a mobile vacancy unit. The same general types of processes appear to predominate during all stages of irradiation.³

It should be pointed out that this aggregation occurs only during irradiation of the crystal. Appreciable reduction in F -center density does not occur while the crystal is held in the dark at constant temperature. This indicates that the charge state of the vacancy units may play an important role in the aggregation processes. This supports Lüty's¹¹ proposal that the $F \rightarrow M$ conversion is aided by the Coulomb attraction of oppositely charged vacancy units. In fact, it indicates that his proposal should be extended to all the vacancy aggregation which takes place.

The above considerations will not explain the shape of the coloring curves in a quantitative way. Many effects have been neglected. Several of the more important are (1) the effect of irradiation temperature on the dispersal of vacancies, (2) the effect of irradiation intensity on the aggregation of vacancies, (3) the effect of impurities, (4) the effect of the reduction in the number of anion vacancies available for further coloration as the F -center density increases. This effect has been considered extensively elsewhere.^{2,17} The only processes considered here are those that appear to predominate in determining the observed intensity and temperature dependencies.

¹⁰ F. Lüty, Z. Physik **165**, 17 (1961).

¹¹ T. Tomiki, J. Phys. Soc. Japan **15**, 488 (1960).

¹² H. Rabin, Phys. Rev. **129**, 129 (1963).

¹³ H. Rüdhardt, Z. Physik **140**, 574 (1955).

¹⁴ H. U. Harten, Z. Physik **126**, 619 (1949).

¹⁵ Result of K. Thomen as reported in Ref. 4.

¹⁶ J. J. Markham, Phys. Rev. **88**, 500 (1952).

¹⁷ J. H. O. Varley, J. Phys. Chem. Solids **23**, 985 (1962).