Fussgänger *et al.*[7] compared their experimental value of ω_{eff}, 1.24×10^{13} rad/sec, with the observed frequency of the infrared resonance absorption 0.97×10^{13} rad/sec. This certainly is a logical comparison since the modes of vibration contributing to the infrared resonance have large atomic displacement amplitudes in the vicinity of the impurity. Our calculation shows that a point-ion model will not give an ω_{eff} in this general frequency region. A calculation consistent with an extended-ion model gives an ω_{eff} of 1.25×10^{13} rad/sec, in good agreement with the experimental value.

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Anion-Vacancy Processes Occurring after Room-Temperature *F*-Light Bleaching or Irradiation of NaCl

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The thermally activated processes occurring in the dark after room-temperature *F*-light bleaching of x- or γ-irradiated NaCl have been investigated. It has been shown that, near room temperature, the concentration of free-anion vacancies decays exponentially with time. The kinetics of the process has been studied by putting the crystal in the dark for a variable time after bleaching and then subjecting it to a short illumination or irradiation pulse which detects the disappearance of the vacancies. It has been observed that the decay in vacancy concentration is closely associated with a decrease in the F'-band intensity and with increases in the *F*- and *M*-band intensities. The experimental information has led to the conclusion that vacancies become trapped at F' centers according to a first-order reaction, giving rise to *F* and *M* centers through the mechanisms F'+anion vacancy → $2F$, and F' +anion vacancy → M, respectively. The activation energy for the trapping process has been found to be $E=0.48\pm0.06$ eV. These phenomena also occur after an x or γ irradiation, and are shown to provide a coherent picture of the previously reported anomalous coloring behavior appearing at the start of a new irradiation period.

I. INTRODUCTION

It has been shown recently that a thermally activated process takes place in the dark after *x* or γ irradiation of NaCl.[1–3] This process is responsible for the occurrence of anomalous regions of *F* coloring upon resumption of the irradiation.[3] It was attributed to the elimination of anion vacancies which remained free at the end of the prior irradiation. The decay in vacancy concentration follows first-order kinetics and was supposed to proceed via trapping at some lattice defects. Although the kinetic parameters for the decay, preexponential factor and activation energy were determined, it was not possible to elucidate the physical nature of the process and identify the defects responsible for the trapping of vacancies.

It is conceivable that the above process could also take place after effective *F*-light bleaching of the irradiated crystal with the advantage that the number of free-anion vacancies might be higher. Moreover, in this case, the kinetics of the various color centers can be more conveniently investigated in order to try to identify the physical nature of the processes. It is worth noting that although a certain amount of information is available on the evolution of a few color centers after bleaching and irradiation in a variety of alkali halides[4–14] a comprehensive investigation of the simultaneous behavior of all prominent centers (F, F', M, and V)[15] in the dark is lacking for NaCl.

The purpose of this paper is to show the existence of a thermally activated process, after *F*-light bleaching, whose kinetic behavior is similar to that observed after irradiation.[2,3] The concentration of free-anion vacancies decays with dark time following a first-order kinetics, whose rate coefficient agrees with that found after *x* or γ irradiation. The disappearance of free-anion vacancies in the dark has been detected through the initial *F*-center growth on reirradiation, as in previous work,[3] and through the change in *F*-center decay rate on subsequent *F*-light illumination. This method permits one to determine changes in free-anion-vacancy concentration without lowering temperature to the region where the α band is thermally stable[7] and so provides a very convenient tool to follow anion-vacancy processes at any temperature.

Furthermore, experiments now performed have provided definite evidence that the removal of vacancies takes place via trapping at F' centers and gives rise to *F*- and *M*-center formation through the mechanisms $F' + V \rightarrow 2F$ and $F' + V \rightarrow M$, respectively. The present data have yielded 0.48 eV as the activation energy for the $F' + V$ trapping process. This value is close to that found by Pick[16] (0.51 eV) for F' decay in NaCl and comparable to reported activation energies for optically induced $F \rightarrow M$ conversion in several alkali halides.[17] However, it should be stressed that we are not dealing here with processes occurring during irradiation or illumination but only with those occurring after the crystal is left in the dark.

Finally, as a consequence of this work, a more definite physical interpretation is given of the anomalous *F* coloring appearing after interruption of an *x* or γ irradiation.

II. EXPERIMENTAL

NaCl samples were cleaved from single-crystal blocks purchased from Harshaw Chemical Co. Sample thickness varied from 1 to 10 mm, the thicker crystals being used to enhance the changes in *F*, F', and *M* bands after bleaching or irradiation.

X irradiations were performed with a Siemens x-ray machine operating at 120 kV, and 13 mA, and with a 2-mm aluminum filter (dose rate $\simeq$ 300 R/min). An hexagonal arrangement of Co^{60} sources immersed in a water pool was used for γ irradiations (dose rate $\simeq$ 30.000 R/min). Absorption spectra were recorded with a Perkin-Elmer model 350 spectrophotometer. For optical bleaching, the irradiated crystal were illuminated with a 1000-W quartz-iodide lamp through a 10-cm distilled-water filter, to cut infrared radiation, and a CS4-71 Corning filter to select the *F*-band spectral range. During the dark time, samples were kept at a fixed temperature $\pm 0.5\,^\circ C$ by using a Medingen NBE ultrathermostat. For low-temperature work, a small cryostat which could be introduced in the spectrophotometer compartment was used. In most cases, sample temperatures quoted in the text were previously ascertained by embedding an iron-constantan thermocouple into a dummy sample. The photoconductivity during bleaching was measured with a Cary 31 vibrating-reed electrometer.

III. KINETICS OF VACANCY TRAPPING

A. Scheme of Experiments

Figure 1 shows a scheme of the experiments performed. First, samples are x or γ irradiated up to a given point in the initial stage. Then they are illuminated with *F* light to cause a fast appreciable decrease μ_1 in the *F*-center absorption coefficient and finally, after a certain time in the dark, they are given a new short irradiation, case (a); or a short light pulse, case (b). Essentially, the purpose of the first *F* bleaching is to provide a high concentration of free-anion vacancies at the start of the interruption (dark time). On the other hand, the change in *F*-center absorption coefficient μ_2, induced by the final short irradiation or illumination, is used to yield information on the thermally activated processes which have taken place during the dark time.

In case (a), if the irradiation is short enough compared to the half-life of the initial fast coloring, free-anion vacancies will mostly be turned into *F* centers and the increase in the absorption coefficient will be a measure of the vacancies which remain free at the start of the short irradiation.

In experiment (b), the efficiency of the *F*-center bleaching will depend on the concentration of free-anion vacancies which can act as traps for the photoelectrons and rebuild the *F* centers. Therefore, the *F*-center decrease induced by a short light pulse can be used also as a measure of the number of free vacancies existing at the end of the dark time.

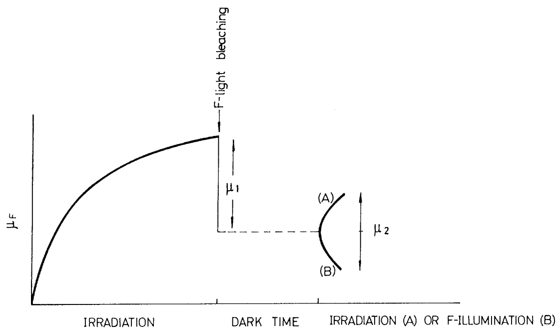

FIG. 1. Scheme of the experiments performed to detect and measure the trapping of free-anion vacancies after *F*-light bleaching. This bleaching causes a decrease μ_1 in the *F*-absorption coefficient. After a variable dark time, an additional short illumination or irradiation induces a new change μ_2 in the absorption coefficient which detects the trapped vacancies during that time.

These naive considerations are quantitatively substantiated in the Appendix where a more thorough justification of both experiments, (a) and (b), will be given. It will be there shown, in terms of simple but meaningful models for irradiation and bleaching, that the change in the absorption coefficient μ_2 induced by the final short irradiation or light pulse, is proportional to the decrease in free-vacancy concentration during the dark time.

It is to be expected that both experiments yield the same information, which should also be independent of such particulars as the energy of the ionizing radiation and the lasting of the first bleaching.

B. Experimental Results

Case (a)

NaCl samples were x irradiated at room temperature and at a dose rate $I \simeq 300$ R/min, then bleached, and finally reirradiated, after a variable dark time at 21 °C. The relative increase in absorption coefficient μ_2/μ_1 as a function of dark time τ is displayed in Fig. 2 for two different experiments. The initial x-irradiation time, F-bleaching time, and final short x-irradiation time were 15 and 20 min, 60 and 40 sec, and 2 and 4 min, respectively. In both cases, the production of F centers decreases with increasing τ up to ~ 60 min, where a steady level $(\mu_2/\mu_1)_\infty$ is reached. The differences $\Delta\mu = (\mu_2/\mu_1) - (\mu_2/\mu_1)_\infty$ relative to that steady level, plotted in the upper half of Fig. 2, follow an approximately exponential curve, whose half-life is ~ 14 min. It is clear that the dark-time behavior is independent of the initial x-ray dose, magnitude of the first bleaching, and dose of the final short irradiation. Completely similar results are found using Co^{60} γ rays instead of x rays.

Case (b)

Samples were γ irradiated for 10 min at room temperature and at a dose rate $I \simeq 30.000$ R/min, then bleached for 20 sec, and finally given a light pulse of 10 sec after a variable dark time. For this case, in order to obtain information on the temperature dependence of the dark process, several experiments were performed, keeping the samples at different constant temperatures while they were in the dark. However, in all cases, the initial as well as the final illumination were performed at room temperature. Figure 3 shows μ_2/μ_1 as a function of τ for three temperatures: 19, 34, and 47 °C. In all cases, the efficiency for F-center destruction by the final light pulse depends on τ. This dependence becomes progressively more abrupt on increasing temperature. A steady value for μ_2/μ_1 is always reached which is independent of temperature. By plotting the differences relative to that limiting value, Fig. 4, it can be concluded that the dependence on τ is roughly exponential. Also, the data are consistent with those obtained in experiment (a), and, as in that case, are not dependent on radiation dose, magnitude of the first bleaching, or width of the final light pulse.

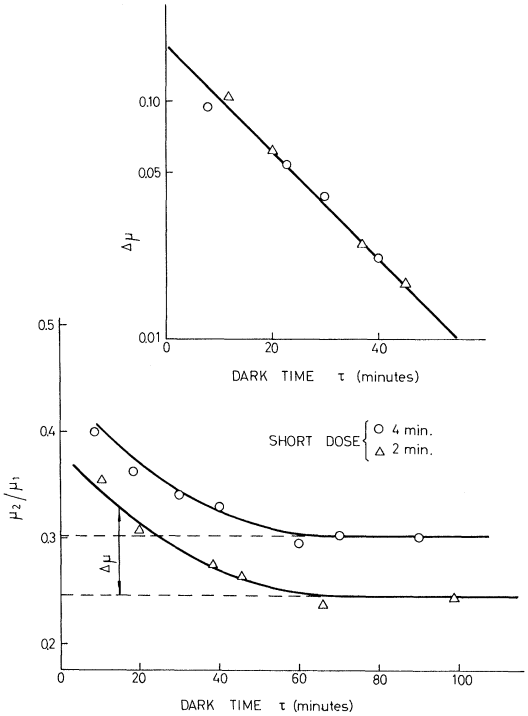

FIG. 2. Experimental data on the change μ_2 in the F-absorption coefficient (normalized by μ_1), induced by a short x irradiation, as a function of dark time. The results for two different experiments are shown. In the upper half of the figure, the differences $\Delta\mu$ with regard to the limiting steady value are analyzed in a semilog plot to check for an exponential dependence.

The results of both experiments, (a) and (b), support a first-order kinetics for the vacancy-trapping process occurring during the dark time. This conclusion, as well as the half-life time for the decay, agrees with the data obtained by Onaka *et al.*[7] by measuring α-band heights at low temperature after room-temperature F-light bleaching. Furthermore, it is noteworthy that the present data are also consistent with those obtained in a previous work[2,3] for the trapping of vacancies following the interruption of an x or γ irradiation. The decay was then found to be exponential, and the half-life ~ 13 min at room temperature (20 °C). This concordance proves the similarity of the processes occurring after irradiation and F-light bleaching.

IV. EVOLUTION OF ABSORPTION SPECTRUM IN THE DARK AFTER ROOM-TEMPERATURE *F*-LIGHT BLEACHING

After the room-temperature F-light illumination of NaCl is discontinued, the following effects are

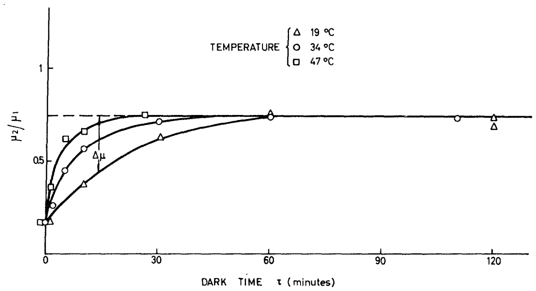

FIG. 3. Experimental data on the change μ_2 in the F-absorption coefficient (normalized by μ_1), induced by a short F illumination, as a function of the dark time. Results for three temperatures are shown.

observed: (i) The intensity of the M band experiences a slight additional increase; (ii) the F-band intensity also experiences an increase which is more apparent than that of the M band; and (iii) the spectral region between the F and M bands undergoes an over-all marked decrease.

Figure 5 illustrates these effects for a NaCl crystal which, after irradiation, has been bleached at room temperature for 30 sec with F light and then maintained for 1 h at 10 °C. All spectra have been taken at 135 °K. If the absorption measurements are performed at (or near) room temperature, the M-center increase is often masked by the overlapping of the nearby spectral region. Furthermore, for temperatures higher than ≃ 20 °C, M and F thermal decay disturbs the kinetics of both bands after bleaching.

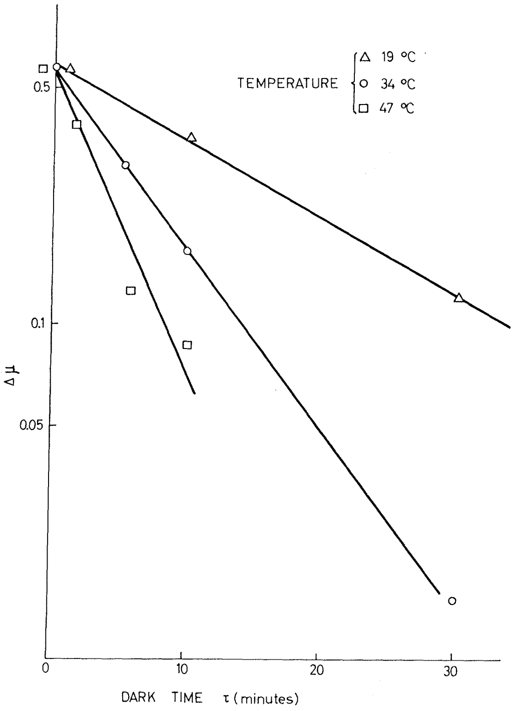

FIG. 4. Analysis of the data in Fig. 3 to check for an exponential dependence of the short-illumination-induced change $\Delta\mu$ in the F-absorption coefficient on the dark time.

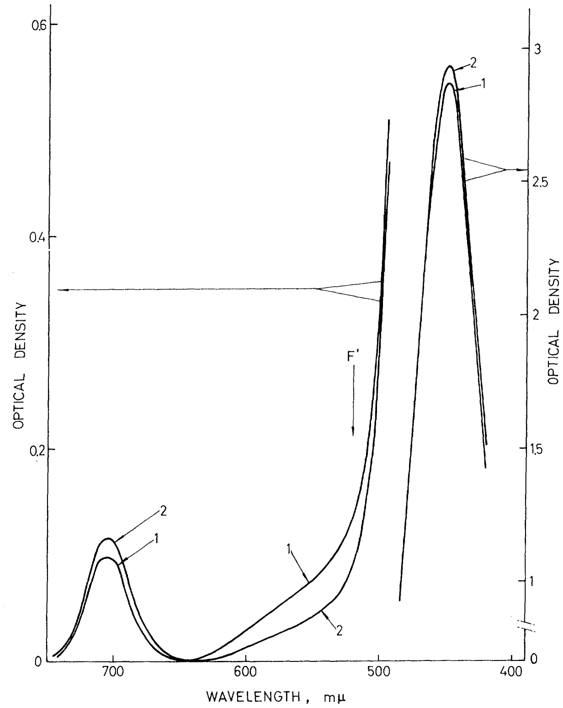

FIG. 5. Typical evolution of the absorption spectrum after F-light illumination. Curve 1 corresponds to immediately after ceasing the illumination. Curve 2 has been recorded after 50 min in the dark. Both spectra have been taken at 135 °K.

Subtraction of adequately scaled spectra immediately before and after F-light bleaching yields an F' band similar to that reported by Pick.[16] On the other hand, after a long enough time in the dark, the analysis of the spectrum yields essentially a pure F band. At the low doses used in this work, there is no indication of R bands.

The same effects listed above are observed when the bleaching is performed at low temperature (135 °K) and then the crystal is warmed up to near room temperature. They can also be produced by illumination with light in the F'-band spectral region. At room temperature the F- and M-band growth induced by F' light (550 mμ) is not very much enhanced with regard to the purely thermal behavior.

The kinetics of F' decay during the dark time has been investigated at various temperatures in the vicinity of room temperature. Figure 6 shows the experimental decay curves, corresponding to the absorption coefficient at 540 mμ, for three different temperatures. The curves are roughly ex-

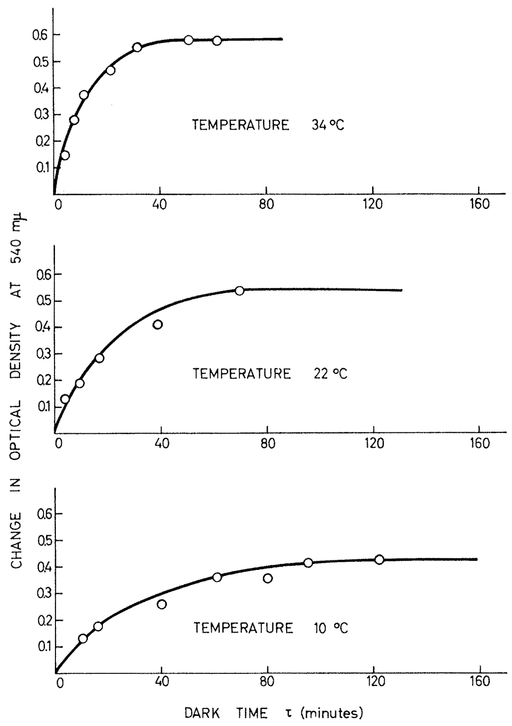

FIG. 6. Experimental decay curves in the dark for the absorption coefficient at 540 mμ (F' band).

ponential and the decay rates are comparable to those obtained for the trapping of vacancies, suggesting a close correlation between both processes.

The evolution of the F and M bands after bleaching has also been studied, but an adequate correction for the contribution of the F' band is then essential to yield quantitative results. On the other hand, for temperatures higher than ≃ 20 °C, the data are difficult to handle because of the increasingly important contribution of F and M thermal bleaching. Figure 7 shows the evolution of the F-, F'-, and M-band intensities during the dark time at 10 °C, after correcting the height of each band for the overlapping of nearby bands. For the half-widths we adopted, respectively, $W_F = 0.48$ eV, $W_{F'} = 2$ eV, $W_M = 0.2$ eV, but the time dependence was found to be quite insensitive to the less reliable of them, namely, $W_{F'}$. The three bands follow a parallel time dependence, indicating a close interrelationship among the centers. The same behavior is observed at other temperatures in the range 0–25 °C.

V. ACTIVATION ENERGY

From the above data, the activation energy for both F' and free-vacancy decay in the dark can be evaluated. In principle, the data for vacancy decay are more reliable since the magnitude of the observed effect is higher and the influence of the F-center thermal bleaching is not as disturbing as for the F' decay experiment. Assuming a purely first-order kinetics for the process, one can write

$$v = v_0 e^{-\chi\tau} ,$$

τ being the time in the dark and v_0 the vacancy concentration at $\tau = 0$. On the other hand, the decay constant χ should be of the form

$$\chi = \chi_0 e^{-E/kT} ,$$

where E is the activation energy and χ_0 the preexponential frequency factor.

Figure 8 shows the experimental χ values as a function of $1/kT$. Our data for F' decay, handled in the same way, are also included in the plot as well as the old Pick's values. It is very clear that all points can be approximated by an unique straight line. This result definitely proves that both processes, F' decay and vacancy trapping, represent complementary aspects of the same phenomenon. The best fit for the points in Fig. 8 corresponds to an activation energy $E = 0.48 \pm 0.06$ eV, which is close to, but somewhat lower than, that reported by Pick (0.51 eV). The preexponential frequency factor comes out to be $\chi_0 \approx 10^5$ sec^{-1}.

Although the vacancy behavior is qualitatively similar after bleaching or irradiation, the present values for E and χ_0 differ from those reported in a previous paper[3] ($E = 0.39$ eV and $\chi_0 \simeq 10^3$ sec^{-1}) by analyzing postirradiation data. This should be attributed to the relatively less accurate experimental procedure in the latter case, and to the limited temperature range in both cases so that a very pre-

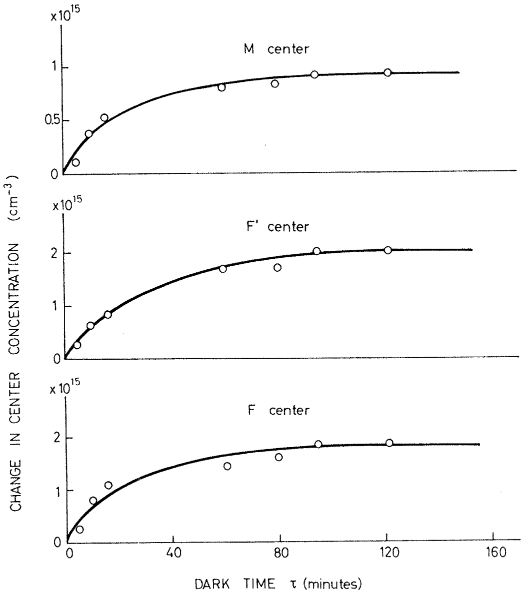

FIG. 7. Evolution of the three bands F, F', and M, as a function of the dark time at 10 °C.

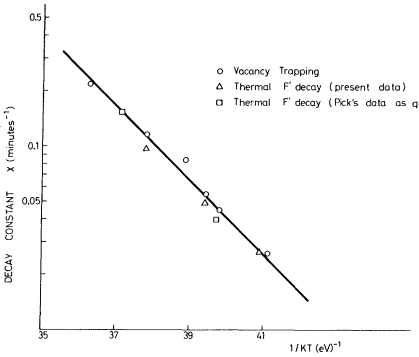

FIG. 8. Semilog plot for the dependence of the decay constant χ on $1/kT$.

cise value for the activation energy cannot be obtained.

VI. PHYSICAL MECHANISMS

The experimental results of Secs. III–V point to a $F' + V$ trapping mechanism. To account for the increase in F- and M-center concentration, one should propose that two different reactions[18,19]

$$F' + V \rightarrow 2F, \qquad (1a)$$

$$F' + V \rightarrow M \qquad (1b)$$

are simultaneously operating after room-temperature F-light bleaching.

The parallel behavior of F, F', and M bands after bleaching indicates that the rate of the reactions $F' + V \rightarrow 2F$ and $F' + V \rightarrow M$ is essentially controlled by the F' decay process, as long as the activation energy is too low in comparison to the value for the migration of free-anion vacancies. Moreover, it sounds reasonable that both reactions should proceed via a common intermediate center which very rapidly decomposes into a pair of F centers or collapses into an M center. The existence of this intermediate entity has been also postulated (and named F'_α) by Dudek and Grossweiner[20] in order to understand F-light bleaching behavior under short repetitive light pulses.

In accordance with reactions (1a) and (1b), the experimental changes Δf, $\Delta f'$, and Δm in the concentration of the F, F', and M centers after various times in the dark at 10 °C (Fig. 7) roughly obey a balance equation

$$\Delta f' = \tfrac{1}{2}\Delta f + \Delta m,$$

as it is shown in Fig. 9. This equation indicates that reactions (1a) and (1b) account for the change in concentration of the three centers without appreciable electron or anion-vacancy losses.

The efficiency of channels (1a) and (1b) for F' decay is about the same near room temperature. However, at least the reaction $F' + V \rightarrow M$ should be a function of temperature since some experiments performed at low temperature have indicated that the M-center formation is inhibited below ~ − 50 °C. At these temperatures, a relatively fast F' decay (not consistent with the activation energy) is observed, which leads exclusively to F-center production.

An increase in the F band following room- and liquid-nitrogen-temperature bleaching has been observed by Platt and Markham[4] and Itoh and Suita,[6] respectively. In both cases, an $F' \rightarrow V$ tunneling mechanism was proposed to be responsible for the observed increase. Also, Onaka *et al.*[7] have invoked reaction (1a) to account for α-band decay after bleaching. On the other hand, thermal increase in M-center concentration after optical bleaching has been recently observed by Schneider and Bailey[13] in NaCl, although they did not establish any connection with F' decay. In fact, our data on the $F' + V \rightarrow M$ process are at variance with the results by Rabin[8] and Hirai and Scott[10] on KCl which had been x irradiated, then bleached at low temperature, and finally warmed up. In these experiments, the F' decay and M growth do not occur in the same temperature range, indicating that their evolution is not correlated. It might be that in KCl, the thermal energy required for mechanism (1b) is not available at the temperature at which the F' center becomes unstable.

The data gathered in this work are insufficient to determine the mechanism whereby the excess electron of the F' center is transferred to the anion vacancy. In most cases, F' decay curves have been ascribed to thermal ionization of the center and therefore the activation energy corresponds to the depth of the F' energy level. For this parameter the near room-temperature data by Pick,[16] Onaka *et al.*,[7] and ourselves yield values relatively close to each other (around $E = 0.5$ eV), but the thermoluminescence experiment by Scaramelli[21]

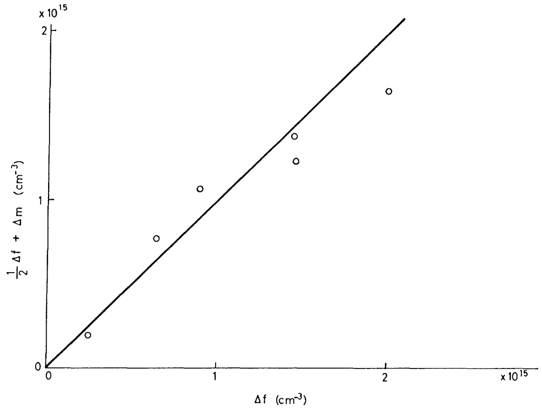

FIG. 9. Balance relationship between the decrease in F'-center concentration and the increase in F- and M-center concentrations during the dark time.

presents a peak at 340 °K (67 °C) and yields $E = 0.91$ eV. The reason for this large discrepancy is not clear, although it should be mentioned that F'-decay rates are not consistent with a single activation energy throughout the whole temperature range.[22,23] In view of the low value obtained in our experiment for the preexponential frequency factor, it seems plausible that Scaramelli's value should correspond to pure thermal ionization of the F' center, whereas our data (as well as Pick's) might be affected by some tunneling contribution.[6]

One might also consider that a Delbecq-type[24] mechanism $F + V \rightarrow M^+ \xrightarrow{e} M$ for vacancy trapping should be operative after bleaching. The occurrence of this (partly) thermally activated process has been often invoked in previous work. However, it is not consistent with our experiments since it should lead to a decrease in F-center concentration which is not observed, unless for temperatures slightly below room temperature, where thermal bleaching is negligible. On the other hand, the search for an M^+ band[13] has been fruitless. Moreover, one should expect that the efficiency of M-center formation by a short F-light flash after an interruption time was augmented with regard to the prior rate if the Delbecq mechanism was operative. The experimental results on the influence of an interruption on M-center formation rate by F light are shown in Fig. 10. At variance with those provisions, the rate decreases on increasing the dark time. On the contrary this result is consistent with mechanisms (1a) and (1b).

To summarize the above discussion, it can be stated that our data on the evolution of the F, F', and M bands after room-temperature F-light bleaching are consistent with a $F' + V$ trapping process leading either to F- or M-center formation.

VII. COLOR-CENTER BEHAVIOR AFTER X OR γ IRRADIATION: ANOMALOUS COLORING

Qualitatively, the same evolution of the F-, F'-, and M-band intensities found after F-light bleaching (Fig. 5) is observed after x or γ irradiation, but the effects are less apparent because of the smaller magnitude of the F' band.[25] It should be mentioned that increases in the F- and M-band heights have been very clearly exhibited during the interruption of an irradiation sequence performed once the crystal had been continuously irradiated up to a high dose.[26] Since the kinetics of vacancy trapping has been also found to be analogous after irradiation or bleaching, one should conclude that the mechanisms $F' + V \rightarrow 2F$ and $F' + V \rightarrow M$ are operating after irradiation.

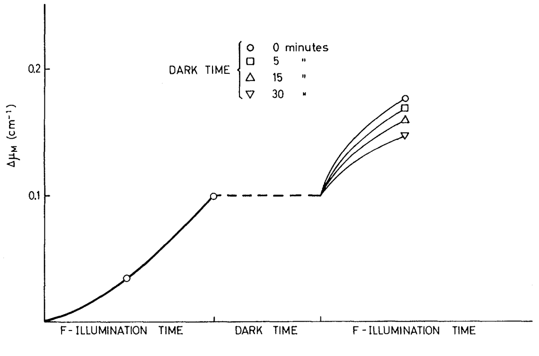

FIG. 10. Experimental data on the effect of a variable interruption on the M-center formation efficiency under F illumination.

Now, it is possible to get a new insight into the question of the anomalous coloring behavior appearing after an interruption of the irradiation. It should be recalled[3,26] that, initially, the F-center concentration decreases rapidly to a minimum and then undergoes a slower growth to the preinterruption level. Simultaneously with this slow F-center growth, the M band, which has been enhanced during the dark time, decreases to its former level. According to the scheme developed in this paper these effects can be visualized in the following way. During the interruption (dark time), the radiation-induced electronic equilibrium among F centers, F' centers, and vacancies is disturbed because of the removal of F' centers and vacancies through the mechanisms $F' + V \rightarrow 2F$ and $F' + V \rightarrow M$. The second reaction causes a net decrease in the total number of single-vacancy centers participating in the electron balance under irradiation. Consequently, an initial decrease in F-center concentration, in favor of F' centers and free vacancies, is produced, initially, on resuming irradiation. However, a slower radiation-induced $M \rightarrow F$ conversion superimposes on that effect, and is responsible for the slow evolution of the F and M bands to their preinterruption levels.

The dominant processes at each stage of the experiment are illustrated in Fig. 11, where thermal bleaching of the F and M bands has been ignored. Stage I corresponds to the dark time where the reactions $F' + V \rightarrow 2F$ and $F' + V \rightarrow M$ are operating. Stage II refers to the initial decrease in F-center concentration occurring upon resumption of the irradiation, when an $2F \rightarrow F' + V$ conversion is taking place. In stage III the radiation-induced $M \rightarrow F$ reaction has become dominant. After stage III, normal coloring behavior sets in.

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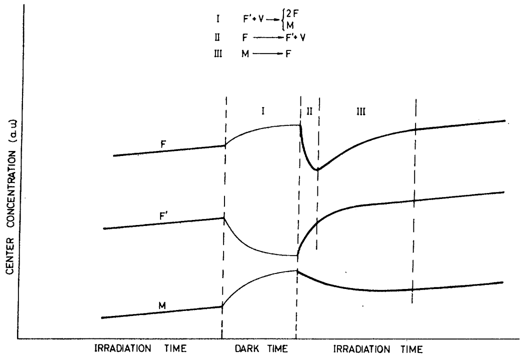

FIG. 11. Illustration showing the time dependence of the F-, F'-, and M-center concentrations, during an interruption of the irradiation and on subsequent reirradiation. The dominant processes occurring at the various stages of the experiment are indicated in the figure. Thermal bleaching effects on the F and M bands have been ignored.

APPENDIX

It will be shown here that (a) the increase in F coloring induced by a short irradiation, as well as (b) the change in F-decay rate induced by a short light pulse, after a certain dark time, are both proportional to the reduction in free-anion-vacancy concentration during this time.

In the case of the short irradiation, the problem can be dealt with in a rather simplified way. If we restrict ourselves to electronic processes, the rate equations should read

$$\begin{aligned} \frac{df}{dt} &= \alpha v - (\beta+\eta) f + \delta f' , \\ \frac{df'}{dt} &= \eta f - \delta f' , \qquad \text{(A1)} \\ \frac{dv}{dt} &= -\alpha v + \beta f , \end{aligned}$$

where α, β, η, and δ are adequate rate coefficients which depend on the equilibrium free-electron density and f, f', and v are, respectively, the F-center, the F'-center, and the vacancy concentration at time t. In fact, these equations are essentially the same ones which have been previously used to account for the anomalous F-coloring behavior appearing after an interruption of the irradiation, except for the inclusion in (A1) of the F'-center concentration as a part of the balance processes.

Assuming that the electronic processes represented in Eqs. (A1) are very fast in comparison to the rate for radiation-induced vacancy (or F-center) production, any point on the F-coloring curve corresponds to an electronic equilibrium where all derivatives are zero. Then it follows easily that at the start of the interruption $v_0/f_0 = \beta/\alpha$. During the interruption, a fraction of the free-anion vacancies is lost. On resuming the irradiation a new electronic balance will take place among a lower concentration of single-vacancy centers. Then, if the new irradiation is short enough to avoid competing processes contributing to the recovery of the F-center concentration, a new equilibrium is reached where $v_i/f_i = \beta/\alpha$. It is reasonable to assume that the ratio β/α should be independent of the free-electron density. Also, since this density is controlled by ionization of the perfect crystal and subsequent electron-hole recombination, it is to be expected that it should not be affected by the processes occurring during the interruption. Then, one obtains immediately by substraction

$$\Delta v/\Delta f = \beta/\alpha = \text{const} ,$$

i.e., the change in F-center absorption coefficient measures the change in vacancy concentration.

For case (b), where a light pulse is used to probe the vacancy concentration, a more sophisticated model should be used although the reasoning is essentially parallel to that for case (a). The rate equations are

$$\begin{aligned} \frac{df}{dt} &= \frac{f^*}{\tau_R} - K_F f - \rho\Sigma_F f + K_{F'} f' , \\ \frac{df^*}{dt} &= \rho\Sigma_V v + K_F f - f^*\left(\frac{1}{\tau_R} + \frac{1}{\tau_I}\right) , \\ \frac{df'}{dt} &= \rho\Sigma_F f - K_{F'} f , \qquad \text{(A2)} \\ \frac{d\rho}{dt} &= \frac{f^*}{\tau_I} + K_{F'} f' - \rho(\Sigma_V v + \Sigma_F f) , \\ \frac{dv}{dt} &= \frac{f}{\tau_I} - \rho\Sigma_V v , \end{aligned}$$

where f^* and ρ represent the excited F center and the free-electron concentration; τ_R and τ_I stand for the radiative and thermal ionization lifetimes of the excited F center, respectively; Σ_V and Σ_F are the cross sections for electron trapping by a vacancy and an F center, respectively (multiplied by the average thermal electron velocity); and K_F and $K_{F'}$ are the optically induced bleaching coefficients for F and F' centers, respectively.

In those equations, electronic processes are considered exclusively. Other processes, which lead to a net decrease in vacancy and electron concentration, are slower and can be considered as causing a drift in the electronic equilibrium. Under this approximation, one can assume that after an initial transient, any point in the F-bleaching curve corresponds to an equilibrium situation wherein all derivatives in Eqs. (A2) are zero. In accordance with photoconductivity measurements, the free-electron density ρ is very small relative to F- and F'-center concentrations ($\rho \lesssim 10^6$ cm^{-3} in our experiments) and therefore $v \simeq f'$ throughout the bleaching process.

In these conditions, one obtains after simple but lengthy algebra

$$v/f = f'/f = (K_F \Sigma_F \tau_R / K_{F'} \Sigma_V \tau_I)^{1/2}$$

for any value of the illumination time after the initial transient. The situation is, therefore, similar to that found under irradiation. During an interruption, anion vacancies are lost by trapping, and consequently, on resuming illumination, a new equilibrium is reached with the same value for the ratio v/f but a lower concentration of vacancies (filled or not). It follows immediately that $\Delta v \sim \Delta f$, relating the change in vacancy concentration during the dark time to the fast decrease in F-center concentration upon resumption of the illumination.

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Infrared Study of the Lattice Vibrations in $LiTaO_3$

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Polarized infrared reflectivity measurements have been made on single-crystal $LiTaO_3$ in the frequency range 20 – 10 000 cm^{-1} at 300 °K. Kramers-Kronig and classical-oscillator dispersion-theory analyses of these data have yielded values for the frequency, strength, and linewidth of the infrared-active transverse optic modes and longitudinal optic modes. Analysis of the far-infrared interference spectrum yields values of 41 and 40 for the ordinary and extraordinary clamped dielectric constants, as well as values for their temperature dependence and dispersion. A calculation is made of the spontaneous polarization in $LiTaO_3$ and $LiNbO_3$ using the x-ray ion displacements.

I. INTRODUCTION

$LiTaO_3$ is an optically uniaxial trigonal crystal belonging to the point group $3m$. It was found to be ferroelectric by Matthias and Remeika[1] and to exhibit large electrooptic effects by Lenzo *et al.*[2] The ferroelectric transition temperature is approximately 900 °K. With the production of high-quality single crystals of $LiTaO_3$,[3] there has been increased interest in the material for use in