

F-Aggregate Color Centers in KCl*

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(Received 13 February 1964)

The equilibrium which is established between F and F -aggregate centers in KCl by x rays has been studied at room temperature. It was found that the concentration of R centers was proportional to the product of the concentration of F and M centers, indicating that the R centers are composed of three F centers. The concentration of N_2 centers was proportional to the product of the concentration of F and R centers suggesting that the N_2 center is composed of four F centers. The concentration of N_1 centers was proportional to the concentration of M centers suggesting that the N_1 center is composed of two F centers. The deviation from linearity of the N_F^2 versus N_M curve is shown to arise from the presence of higher aggregate centers. Samples x irradiated at room temperature to establish an equilibrium among F and F -aggregated centers were cooled and the irradiation continued. The concentration of M centers decreased exponentially with irradiation time. The temperature dependence of this exponential decay time corresponded to an activation energy of 0.07 eV for temperatures above 100°K.

I. INTRODUCTION

ALTHOUGH the van Doorn-Haven¹ model of the M center—two nearest-neighbor F centers—is now well established,²⁻⁴ the mechanism of generation of M centers by x rays is not well understood. At low temperatures, the concentration of M centers N_M varies as $K_M N_F^2$, where N_F is the concentration of F centers. K_M is a statistical factor which may be approximately calculated assuming no diffusion of the F centers. At higher temperatures, the situation is more complicated. The M -center concentration is greater by a factor of the order of 500, a plot of N_M versus N_F^2 shows marked deviations from linearity, and sizeable concentrations of R and N centers appear.

Sonder and Sibley⁵ have proposed that the dynamic equilibrium which exists between the F and M centers during a room-temperature irradiation is accomplished by the simultaneous creation and destruction of F and M centers by the radiation. Thommen⁶ has demonstrated the temperature dependence of this equilibrium and has suggested that the curvature of the N_F^2 versus N_M plot at low concentrations of F centers results from vacancies initially present in the crystal. Harrison⁷ has proposed that a dynamic equilibrium exists among the F and all F -aggregate centers, i.e., M , R , and N centers.

In the presence of a dynamic equilibrium among F , M , R , and N centers, it should be possible to derive some information about the models of the more complex centers from the relative concentrations of these centers. Faraday *et al.*³ and Okuda and Asai⁸ have indicated

that the concentration of R centers varies approximately as the $\frac{2}{3}$ power of the M -center concentration, in support of van Doorn's⁹ model of the R center as being three F centers. The constant ratio between the peak heights of the R_1 and R_2 bands^{9,10} strongly suggests that both absorption bands arise from two distinct transitions of the same defect. Hattori¹¹ has studied photochemical and thermochemical reactions involving the N_1 and N_2 centers in additively colored KCl and finds that the two absorption bands probably arise from transitions of two distinct defects. It was suggested in this work that the N_2 band may arise from the same defect that gives the R centers. Very few results have been reported that can be used to verify Pick's suggestion that the two N bands arise from four associated F centers.¹²

In the present work, the absorption coefficient at the peak of the F , M , R_2 , N_1 , and N_2 bands in KCl was determined following x irradiation with various intensities and for various periods of time. The results and discussion are divided into three sections. Section A discusses the models of the R and N centers. Section B discusses the influence of R and N centers upon the equilibrium between F and M centers. Section C discusses the mechanism by which equilibrium of the M -center concentration is established.

II. EXPERIMENTAL TECHNIQUES

Samples of Harshaw KCl were cleaved into plates 0.12–0.60 mm thick and were irradiated with x rays from a tungsten target x-ray tube operated at 100-kV constant potential and 25-mA current. The uniformity of coloration was enhanced by filtering the x-ray beam with 0.004 in. of copper. The temperature of irradiation was 16°C unless otherwise specified. The x-ray intensity was altered by changing the distance from the sample

* This work was supported in part by a grant from the National Science Foundation.

¹ C. Z. van Doorn and Y. Haven, Philips Res. Rept. **11**, 479 (1956).

² C. Z. van Doorn, Phys. Rev. Letters **4**, 236 (1960).

³ B. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters **7**, 57 (1961).

⁴ H. Seidel, Phys. Letters **7**, 27 (1963).

⁵ E. Sonder and W. A. Sibley, Phys. Rev. **129**, 1578 (1963).

⁶ K. Thommen, Phys. Letters **2**, 189 (1962).

⁷ P. G. Harrison, Phys. Rev. **131**, 2505 (1963).

⁸ A. Okuda and K. Asai, Bull. Inst. Chem. Res. Kyoto Univ. **40**, 81 (1962).

⁹ C. Z. van Doorn, Philips Res. Rept. **12**, 309 (1957).

¹⁰ R. Herman, M. C. Wallis, and R. F. Wallis, Phys. Rev. **103**, 87 (1956).

¹¹ S. Hattori, J. Phys. Soc. Japan **17**, 1454 (1962).

¹² H. Pick, Z. Physik **139**, 69 (1960).

to the x-ray tube. Optical absorption measurements were made at liquid nitrogen temperature with a Cary Model 14R spectrophotometer. Care was taken to prevent the exposure of the crystals to light while they were at room temperature. In all of the data presented, the concentration of F centers was determined by subtracting the absorption arising from the higher excited states of the M centers from the peak of the F band. The correction was evaluated using Delbecq's¹³ value of the oscillator strengths of the M_2 and M_2' bands and Okamoto's¹⁴ value of the half-widths of the M_2 and M_2' absorption bands. The correction was

$$(\alpha_F)_{\text{corrected}} = (\alpha_F)_{\text{measured}} - 0.65\alpha_M. \quad (1)$$

III. RESULTS AND DISCUSSION

A. R and N Centers

A plot of the absorption coefficient at the peak of the R_2 band versus the product of the absorption coefficients at the peak of the M and F bands is shown in Fig. 1 for two different x-ray intensities. Since the absorption coefficients are linearly related to the concentrations, a relation of the form

$$N_R = K_R N_M N_F \quad (2)$$

appears valid, with the constant K_R a function of the intensity of the x rays. In the presence of a dynamic equilibrium in which an F center is added to an M center to form an R center, the equilibrium reaction

would be expected to be of the form



This would predict a relation of the form of Eq. (2). Although three F centers might be combined by reactions other than that represented by Eq. (3), the joining of an F to an existing M center seems quite reasonable from a physical standpoint. The data of Fig. 1 strongly suggest, therefore, that the R centers are composed of three F centers, in agreement with van Doorn's suggestion.⁹

Figures 2, 3, and 4 present data concerning the N bands. The formation of an N center by attaching an F center to an existing R center, as suggested by Pick's model, would require an equilibrium reaction of the form



This leads to a relation of the form

$$N_N = K_N N_F N_R, \quad (5)$$

where N_N represents the concentration of N centers.

Figure 2 indicates that this is valid for the N_2 band but not for the N_1 band. Figure 3 is a plot of the absorption coefficients of the peak of the N_1 and N_2 bands as a function of the absorption coefficient at the peak of the R_2 band. The concentration of N_1 centers is clearly not proportional to the concentration of R centers. Although a linear relationship exists between the N_2 and R -center concentration, the fact that the curve does not pass through the origin implies that the bands do not arise from transitions in the same defect. The data given in Fig. 2 imply that the N_2 center consists of four aggregated F centers in agreement with the model suggested by Pick.¹²

The model of the N_1 center is not clear. Figure 4 suggests that the N_1 is closely related to the M center. It may consist of an M center perturbed by a nearest-neighbor positive ion vacancy or impurity. Since the

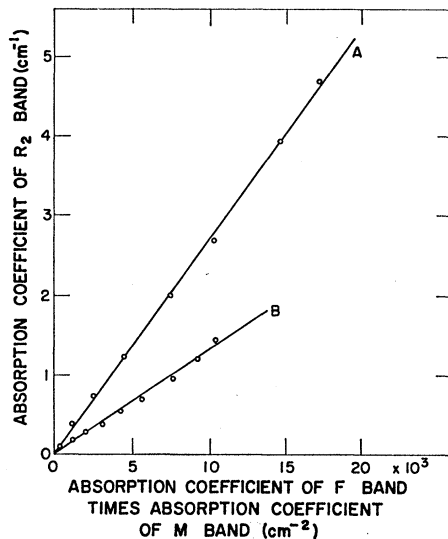


FIG. 1. Absorption coefficient at the peak of the R_2 band versus the product of the absorption coefficients at the peak of the F and M bands. X irradiated at 16°C. Measured at 77°K. X-ray intensity for curve B was 1.5 times the intensity for curve A.

¹³ C. Delbecq, Z. Physik **171**, 560 (1963).

¹⁴ F. Okamoto, Phys. Rev. **124**, 1090 (1961).

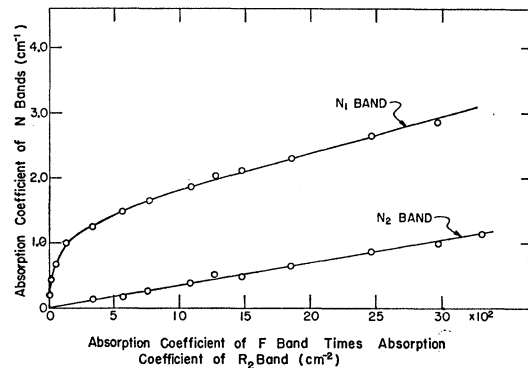


FIG. 2. Absorption coefficient at the peak of the N_1 and N_2 bands versus the product of the absorption coefficients at the peaks of the F and R_2 bands. X irradiated at 16°C. Measured at 77°K.

symmetry axis of this center is along $\langle 110 \rangle$, this is also consistent with the view that an M center might be involved in this defect.^{11,15}

B. Effects of Higher Aggregates on Equilibrium

The effect of higher order aggregate centers upon the F - M equilibrium can be seen from the following very simple approach. If it is assumed that F centers are formed at random, that the formation of an R center results from the addition of an F center to an existing M center, that the destruction of M and R centers does not contribute significantly to the concentration of F and M centers, respectively, and that all aggregation is stimulated by the x rays, the growth of the F , M , and R centers can be described by the relations

$$\dot{N}_F = \alpha_1 N_0 - \beta_1 N_F, \tag{6}$$

$$\dot{N}_M = \alpha_2 N_F - \beta_2 N_M, \tag{7}$$

$$\dot{N}_R = \alpha_3 N_M - \beta_3 N_R. \tag{8}$$

\dot{N}_i is the time rate of change of the concentration of centers of i th type, α and β are formation and destruction rates, respectively, and N_0 is the concentration of halide lattice sites in the crystal. Superimposing the experimentally observed relation given in Eq. (2) leads to

$$N_M + \left\{ \frac{\beta_1 + \beta_2 - \beta_3}{\alpha_3 - K_R \alpha_1 N_0} \right\} N_R = \left\{ \frac{K_R \alpha_2}{\alpha_3 - K_R \alpha_1 N_0} \right\} N_F^2, \tag{9}$$

which has the form

$$N_M + C_2 N_R = K' N_F^2. \tag{10}$$

Physically an equation of this form is quite reasonable since the formation of an R destroys an M center. Thus it is clear that N_M will cease to be proportional to N_F^2 when the concentration of the R centers becomes

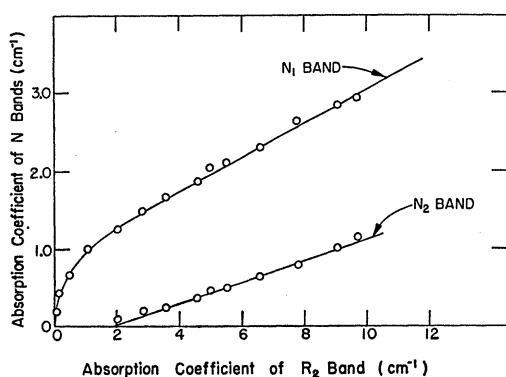


FIG. 3. Absorption coefficient at the peak of the N bands versus the absorption coefficient at the peak of the R_2 band. X irradiated at 16°C . Measured at 77°K .

¹⁵ W. D. Compton and C. C. Klick, Phys. Rev. **112**, 1620 (1958).

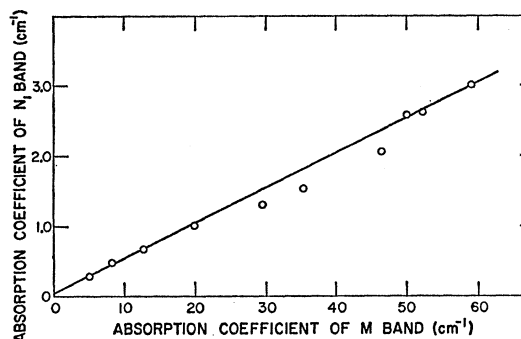


FIG. 4. Absorption coefficient at the peak of N_1 band versus absorption coefficient at the peak of the M band. X irradiated at 16°C . Measured at 77°K .

significant. Substitution of Eq. (2) into Eq. (10) indicates that an equivalent statement is that N_M will be proportional to N_F^2 only when $C_2 K_R N_F \ll 1$.

Utilizing Smakula's equation¹⁶ leads to an equation of the form

$$\alpha_M + C_2 \left\{ \frac{f_M W_R}{f_R W_M} \right\} \alpha_R = K' \left\{ C \frac{W_F^2 f_M}{W_M f_F^2} \right\} \alpha_F^2, \tag{11}$$

where α is the absorption coefficient at the peak of the absorption band in cm^{-1} , W is the full width at half-maximum of the absorption band in eV, f is the oscillator strength, and C is the constant $1.29 \times 10^{17} [n/(n^2+2)^2]$ for a crystal having index of refraction n . This is more simply written as

$$\alpha_M + C_3 \alpha_R = K'' \alpha_F^2, \tag{12}$$

where C_3 and K'' are constants obtained from Eq. (11).

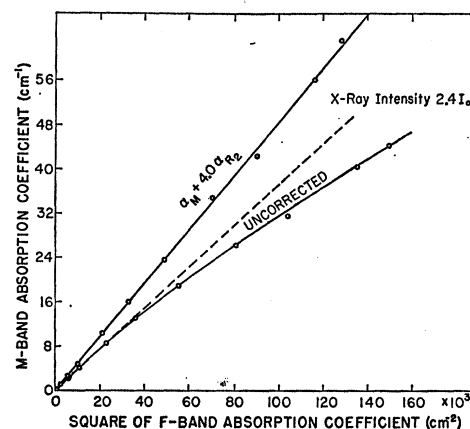


FIG. 5. Absorption coefficient at the peak of the M band versus the square of the absorption coefficient at the peak of the F band. X irradiated at 16°C . Measured at 77°K . Lower curve is uncorrected for R centers. Middle curve is a typical linear extrapolation of the uncorrected data. Upper curve is corrected for R centers.

¹⁶ See, for example, J. H. Schulman and W. D. Compton, in *Color Centers in Solids* (Pergamon Press, Ltd., London, 1962).

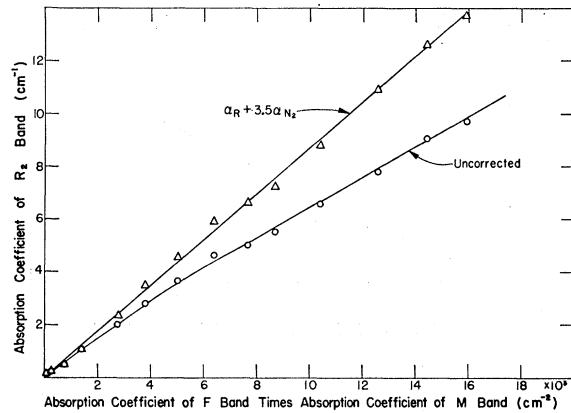


FIG. 6. Absorption coefficient at the peak of the R_2 band versus the product of the absorption coefficients at the peak of the F and M bands. X irradiated at 16°C . Measured at 77°K . Upper curve is corrected for N_2 centers. X-ray intensity is one-fourth that used for curve A of Fig. 1.

Figure 5 clearly indicates that a value of C_3 can be found which satisfies Eq. (12). Within the accuracy of the measurements, C_3 was found to be independent of x-ray intensity.

It has been argued by Thommen⁶ that the deviation from linearity of the α_M versus α_F^2 at low density is a result of vacancies which are not generated by the x rays but are initially present in the crystal and are converted to F centers by simply trapping an electron. Figure 5 indicates, however, that for F -center densities as low as $4 \times 10^{16} \text{ cm}^{-3}$ the deviation from linearity of the observed curves is a result of the presence of R centers and not vacancies initially present in the crystal. Thommen's conclusion is based upon measurements at lower F -center concentrations, and does not necessarily conflict with the present interpretation.

The effect of the N_2 center concentration upon the M and R center equilibrium can be derived in a manner similar to that carried out for the effect of R centers on the F and M center equilibrium. Writing

$$\dot{N}_{N_2} = \alpha_4 N_R - \beta_4 N_{N_2}, \quad (13)$$

and superimposing Eq. (5), leads in a similar way to

$$\alpha_R + C_4 \alpha_{N_2} = K''' \alpha_F \alpha_M. \quad (14)$$

Figure 6 indicates that a value of C_4 can be found that satisfies Eq. (14). There is no need to apply this correction to the data of Fig. 1 since the higher x-ray intensity used in that measurement suppressed the concentration of N_2 centers.

These results clearly indicate that the dynamic equilibrium that exists in the presence of ionizing radiation is quite different from a chemical equilibrium. In the present circumstance, the concentration of one defect, e.g., the M centers, depends upon the concentration of a second type of defect, e.g., the R centers. Although this is quite obvious from the coupled nature

of Eqs. (6) through (8), it is important to realize that the equilibrium represented by Eqs. (3) and (4) are of limited validity. These equilibria are valid only so long as the concentration of the next higher order of aggregates is small.

C. Approach of the M -Center Concentration to Equilibrium

The results of Sonder and Sibley⁵ and Thommen⁶ indicate that equilibrium is rapidly re-established if the system is perturbed by a change in temperature or radiation intensity. These measurements were confined to near room temperature. In the present work, a crystal was irradiated at 16°C , cooled to some low temperature and again x irradiated. Since the concentration of M and R centers generated by a low-temperature irradiation is small compared to the concentration generated by the same irradiation at 16°C , it follows that the centers generated by x irradiation at room temperature are not in equilibrium when the sample is at a lower temperature. Figure 7 is an indication of the exponential decay of M centers that result from a second irradiation at 90°K . α_{M_0} is the absorption coefficient of M centers present prior to the x irradiation of 90°K .

At least two mechanisms by which M centers may be destroyed by x irradiation can be imagined.

(1) The x rays deposit energy at or near an M or R center. This energy has some probability of thermally dissociating the vacancies, thereby destroying the centers. The deposition of thermal energy could occur by (a) distribution of energy uniformly in a volume of the crystal, as a thermal spike resulting from the slowing down of a photoelectron; (b) distribution of energy among the defects as by electron-hole recombination at the defects.

(2) The x rays produce an interstitial ion or atom which moves to an M or R center thereby annihilating one of the vacancies and destroying the defect.

A simple calculation of the relaxation times that would be expected for each of these mechanisms can now be made.

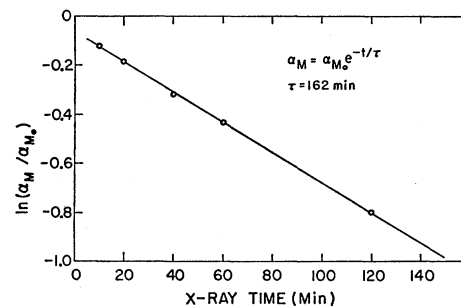


FIG. 7. Exponential decay of M centers at 90°K induced by a constant intensity x irradiation. M centers were initially generated at 16°C by x irradiation. $N_{F_0} \approx 9 \times 10^{17} \text{ cm}^{-3}$ and $N_{M_0} \approx 7.5 \times 10^{16} \text{ cm}^{-3}$.

(1a) X-ray energy distributed randomly throughout the crystal

Let N_0 equal the number of negative ion sites/cm³. N_E equals the number of lattice sites excited/time/cm³ by the x rays. p equals the probability an excitation of an M center will destroy it. If the number of M centers formed by the x rays at the low temperature are neglected, it follows that

$$-dN_M/dt = pN_E(N_M/N_0),$$

and

$$\tau = N_0/pN_E.$$

Thus, the relaxation time is a constant for a given irradiation intensity.

(1b) X-ray energy deposited preferentially at the defects

Let N_E equal the number of defects excited/time cm³ by the x rays. $P_F N_F$, $P_M N_M$, $P_I N_I$ equal the fraction of the excitations that occur at F , M or other unspecified defects, respectively. b equals the probability that excitation of an M center will destroy it. Again neglecting the M centers formed at the lower temperature by the irradiation, it follows that

$$-\frac{dN_M}{dt} = N_E \frac{b p_M N_M}{p_I N_I + p_F N_F + p_M N_M}.$$

It seems reasonable to assume $p_F \approx p_M$ since the cross sections for electron-hole capture should not differ markedly for the F and M centers. For $N_F \gg N_M$, as was the case during the experiment, it follows that

$$\tau = \tau_0 + C N_F, \tag{16}$$

where τ_0 and C are constants for a given crystal and for a fixed irradiation intensity.

(2) Motion of interstitial ions or atoms to defects

Let N_D equal the number of interstitials produced/time/cm³. $p_F N_F$, $p_M N_M$, f_I equal the fraction of interstitials which recombine with isolated F centers, the fraction which recombine with an F center that is part of an M center, and the fraction which are trapped in the lattice thereby generating a new stable F center, respectively.

Neglecting newly formed M centers, it follows that

$$-\frac{dN_M}{dt} = N_D \frac{p_M N_M}{f_I + p_F N_F + p_M N_M}.$$

Assuming $p_F \approx p_M$ and $N_F \gg N_M$, it is seen that

$$\tau = \tau_0' + C' N_F. \tag{17}$$

Figure 8 illustrates the dependence of the relaxation

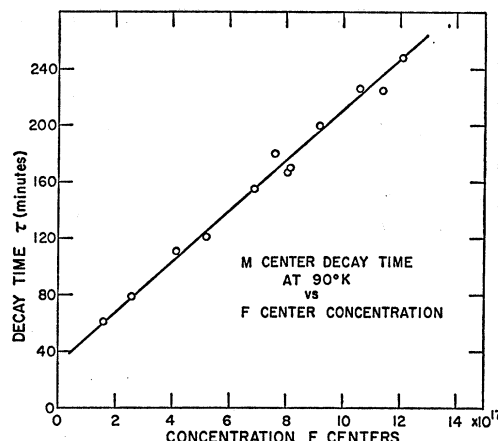


FIG. 8. Characteristic decay time of the concentration of M centers at 90°K versus the concentration of F centers initially present in the crystal. F and M centers were generated in an equilibrium concentration by x irradiation at 16°C prior to the x irradiation at 90°K.

time of the M -center concentration upon the initial concentration of F centers. In all cases, the F and M centers were generated in equilibrium by an x irradiation at 16°C. The relaxation time was determined by a second x irradiation at 90°K. A total of five crystals were used in obtaining the data shown in Fig. 8. If N_F is expressed in cm⁻³ these results may be represented by

$$\tau(90^\circ K) = 33 \text{ min} + 16.7 N_F \times 10^{-17} \text{ min}. \tag{18}$$

This result eliminates mechanism (1a) as a possibility. Mechanisms (1b) and (2) are both compatible with the results expressed by Eq. (18).

Mechanism (2) would be expected to have a temperature dependence that is determined by the activation energy for motion of an interstitial. Crawford¹⁷ has suggested that the temperature dependence of process (1b) would be determined by the difference in the energy of ionization of F' centers and the activation energy associated with the diffusion of holes. Figure 9 illustrates the data that were obtained for the temperature dependence. The ordinate is plotted as the logarithm of the relaxation time at a temperature T relative to that at 90°K in order to account for variations in the concentration of F centers among the various measurements. At temperatures below ~100°K, the temperature dependence is much less. Insufficient data were taken below this temperature to know whether a unique activation energy exists. The magnitude of the activation energy for temperatures above ~100°K cannot be reasonably used to decide between mechanisms (1b) and (2).

The concentration of R centers was observed to decay exponentially with time over the temperature

¹⁷ J. H. Crawford, Phys. Rev. Letters 12, 28 (1964).

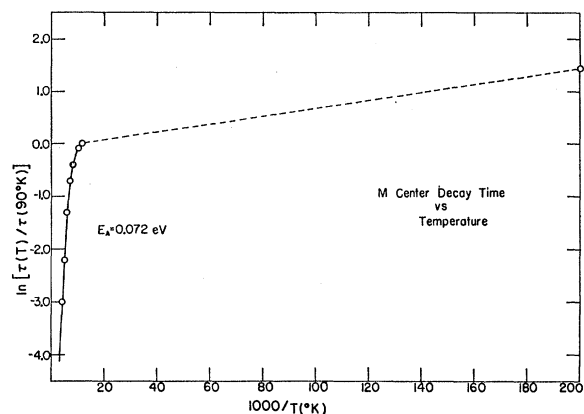


FIG. 9. Temperature dependence of the characteristic decay time of the concentration of M centers plotted as the logarithm of the decay time at a temperature T to the decay time at 90°K as a function of the reciprocal temperature.

range covered. At 90°K , $\tau_R/\tau_M \approx \frac{3}{4}$. The temperature dependence of τ_R was essentially the same as that of τ_M .

In an effort to provide a more sensitive test between these two mechanisms, F and M centers were generated at 16°C and optically oriented by irradiation at 200°K with F light polarized along $\langle 110 \rangle$. The absorption measured with $\langle 110 \rangle$ M -band light was a factor of 2 greater than with $\langle \bar{1}\bar{1}0 \rangle$ M -band light. A further x irradiation was now made. At 200°K , both components decayed with the same time constant which was equivalent to that observed for randomly oriented M centers. At 90°K , the M centers reoriented much more rapidly than they decayed; i.e., the difference between the two orientations decreased faster than the over-all decrease in the total number of M centers.

Although no absolute statements can be made concerning the mechanism by which equilibrium is estab-

lished, the following suggestions seem compatible with presently available data.

(a) The dominant mechanism establishing equilibrium apparently changes as the temperatures are increased above 100°K .

(b) The recombination of an interstitial with an M center, thereby destroying one of the F centers composing the M center, would not result in a change of the orientation of M centers. This fact suggests that interstitial recombination is the dominant mechanism above 100°K . The activation energy of 0.072 eV therefore represents some measure of the motion of the interstitial.

(c) The significant reorientation of M centers at 90°K suggests that below 100°K the predominant mechanism is a result of electron-hole recombination.

(d) Since the temperature dependence for the destruction of R and M centers is about the same, it is suggested that the same mechanisms operate for all of the aggregate centers.

Although these conclusions are reasonably consistent with the data, it must be noted that the calculation of Crawford would suggest that electron-hole recombination cannot be effective at quite low temperatures, for the F' center is stable¹⁸ and the hole has a negligible energy for diffusion at temperatures near 100°K .¹⁸

It should also be noted that the situation may be quite different if the entire irradiation is performed at temperatures near liquid helium. In this case, the interstitial and F center which are formed in pairs may remain near each other and annihilation can occur by a first-order rate process.¹⁹

¹⁸ C. Delbecq, W. Hayes, and P. Yuster, Phys. Rev. **121**, 1043 (1961).

¹⁹ C. C. Klick and D. A. Patterson, Phys. Rev. **130**, 2169 (1963).