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A Study of M Center Formation in Additively Colored KCl*

By

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With 11 Figures in the Text

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Additively colored crystals of KCl were cooled rapidly from a high temperature and then exposed to light absorbed by the F band. The rate of growth of the M band was initially low and increased markedly during the first part of the irradiation giving rise to what is called a "delay period" in the M center formation. During this delay period it was observed that 1. the quantum efficiency of F center fluorescence decreases by a factor of 3 or 4, and 2. the ability to convert F centers to F' centers is reduced by about a factor of 3. These effects are interpreted as arising because of an appreciable decrease in the average nearest neighbor F center separation during this period.

Results are also presented concerning the kinetics of M center formation, oscillator strengths of the M center transitions, the degree of polarization of the M center fluorescence, and the transfer of energy from an excited F center to an M center.

§ 1. Introduction

The centers which are formed in the alkali halides as a result of photo excitation of F centers near room temperature have been of interest to investigators ever since the M and R bands were first reported^{1, 2}. Various models for the M center have been suggested³⁻⁶ but the van Doorn-Haven model, which consists of two associated F centers in nearest neighbor positions with the axis through the two vacancies

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¹ MOLNAR, J. P.: Thesis, Mass. Inst. of Tech. 1940.

² PETROFF, ST.: Z. Physik **127**, 443 (1950).

³ SEITZ, F.: Rev. Mod. Phys. **18**, 384 (1946).

⁴ KNOX, R.: Phys. Rev. Letters **2**, 87 (1959).

⁵ DOORN, C. Z. VAN, and Y. HAVEN: Philips Res. Rep. **11**, 479 (1956).

⁶ DOORN, C. Z. VAN: Philips Res. Rep. **12**, 309 (1957).

oriented along one of the six [110] orientations, has received the most significant experimental support⁷⁻¹⁴.

Since the F center fluorescence was first observed by BOTDEN, VAN DOORN and HAVEN¹⁵, a number of investigators have studied the fluorescence of F and M centers. BECKER and PICK¹⁶ and VAN DOORN¹⁷ have shown that the quantum efficiency for F center emission is in the neighborhood of one. LAMBE and COMPTON¹⁸, VAN DOORN⁶ and KUWABARA and MISU¹⁹ have observed the fluorescence emission from M and R centers and have measured the degree of polarization of the luminescence. In view of the discrepancies in the degrees of polarization reported, it was thought worthwhile to repeat these measurements and at the same time to study changes in some of the properties of the crystal resulting from the growth of M centers.

§ 2. Experimental Procedure

The crystals used in these experiments were single crystals of KCl ($12 \times 12 \times 24$ mm), obtained from Harshaw Chemical Company, which were additively colored to contain F centers in the range of 0.2 to $5 \times 10^{17}/\text{cm}^3$. Crystals were cleaved from these blocks for use in the experiments; in all cases, these crystals were heated in a furnace at about 600° C from 45 to 75 secs depending on the thickness of the crystal, then cooled rapidly to room temperature in the dark by placing on a copper block, mounted in a dewar using a weak red light for illumination, and cooled to liquid oxygen or liquid nitrogen temperature.

Optical absorption spectra were taken at 90 or 77° K using a Zeiss PMQ II spectrophotometer or a Cary Model 14 spectrophotometer. Polarized light for optical absorption measurements was obtained through use of a Glan-Thompson or an Ahrens polarizing prism.

Emission spectra were taken at 90° K using the Zeiss monochromator (M), lead sulfide detector (D), and amplifying system according to the

⁷ DOORN, C.Z. VAN: Phys. Rev. Letters **4**, 236 (1960).

⁸ HOLTON, W.C., H. BLUM and C.P. SLICHTER: Phys. Rev. Letters **5**, 197 (1960).

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¹⁰ GROSS, H., and H.C. WOLF: Naturwissenschaften **8**, 299 (1961).

¹¹ OVERHAUSER, A.W., and H. RÜCHARDT: Phys. Rev. **112**, 722 (1958).

¹² JACOBS, G.: J. Chem. Phys. **27**, 217 (1957).

¹³ FARADAY, B. J., H. RABIN and W.D. COMPTON: Phys. Rev. Letters **7**, 57 (1961).

¹⁴ SONDER, E.: Phys. Rev. **125**, 1203 (1962).

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¹⁶ BECKER, K., and H. PICK: Nachr. Akad. Wiss. Göttingen **7**, 167 (1956).

¹⁷ DOORN C.Z. VAN: Philips Res. Rep. **13**, 296 (1958).

¹⁸ LAMBE, J., and W.D. COMPTON: Phys. Rev. **106**, 684 (1957).

¹⁹ KUWABARA, G., and A. MISU: J. Phys. Soc. Japan **13**, 1038 (1958).

schematic arrangement shown in Fig. 1. The emission spectra data given here were measured with a slit width of 0.5 mm; measurements with a slit width of 0.1 mm decreased half widths of the F and M emission bands by about 10%, but no additional structure was observed. It was found that the sensitivity of the lead sulfide cell was approximately

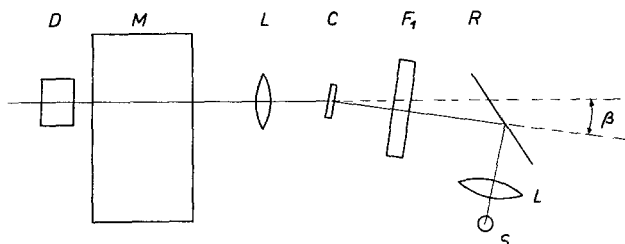


Fig. 1. Schematic Arrangement for measuring emission spectra. β is about 7°

constant over the wavelength range used; the emission spectra were not corrected for changes in the dispersion of the monochromator with wavelength. In obtaining the emission spectra crystals (C) were excited with either

a) 5461 Å light from an Osram HBO-200 high pressure mercury lamp (S) isolated with an F₁(543) filter combination consisting of a

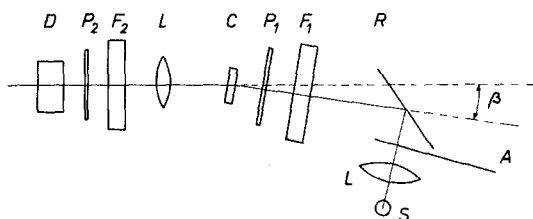


Fig. 2. Schematic arrangement for measuring degree of polarization. β is about 7°

543 m μ Schott Type AL interference filter, a Schott KG-3 (1 mm) filter, and a CuSO₄ solution (72% transmission at 546 m μ and 3.5% at 650 m μ), or

b) 800 m μ light using a 100 W filament lamp in conjunction with an

F₁(800) filter combination consisting of an 800 m μ Schott Type AL interference filter, two Schott RG-9 (3 mm) filters and one centimeter of water.

In order to be able to measure accurately changes in the intensity of the luminescence emission, the intensity of the exciting light was measured using the lead sulfide detector at the time of each emission spectrum measurement.

The measurements of the degree of polarization of luminescence were made at 90° K using the schematic arrangement shown in Fig. 2. The degree of polarization was measured for emission excited by

a) 543 m μ light obtained by using a 100 W filament lamp (S) in conjunction with the F₁(543) filter combination described above; the

associated F_2 filter combination consisted simply of the infrared polaroid analyser, P_2 ,

b) 800 $m\mu$ light obtained by using a 100 W filament lamp in conjunction with the $F_1(800)$ filter combination; the associated F_2 filter combination consisted of two Schott UG-8 (3 mm) filters.

For both types of excitations the polarizer (P_1) consisted of a polaroid film and the analyser of an infrared polaroid film. The Zeiss lead sulfide detector and amplifying system and an auxiliary chopper (A) were also used for the measurements.

The growths of the M and R bands were followed as a function of time of excitation of a crystal, at 0 or 30 °C, with nonpolarized light from two filament lamps each filtered by the $F_1(543)$ combination. The crystals were irradiated from both sides by equally intense beams; since the optical density of the crystals was between 0.5 and 0.6 at 0° C, this arrangement gave a fairly uniform intensity of light ($\pm 10\%$) through the crystal. The copper mounting block on the dewar was held at the desired temperature for 5 min before exciting the crystal in order to allow the crystal to come to temperature equilibrium.

M centers were preferentially oriented in a crystal by irradiating the crystal with 5461 Å light from an HBO-200 mercury lamp using the $F_1(543)$ filter combination and a Glan-Thompson or an Ahrens polarizing prism. The irradiation was carried out at about 170° K since at this temperature, the re-orientation rate is much greater than at 90° K.

§ 3. Experimental Results

3.1. Formation of M and R Centers

The growth of the M band (800 $m\mu$) at 0° C caused by 543 $m\mu$ excitation of the crystals containing 1.8×10^{17} , 0.70×10^{17} and 0.26×10^{17} F centers/cm³ is shown in curves *a*, *b*, and *c*, respectively, of Fig. 3. The growth of the R_2 band (730 $m\mu$) in these same crystals is shown by curves *a'*, *b'* and *c'*. The optical densities in Figs. 3 and 4 were measured at 77° K and are plotted as a function of time of excitation. Fig. 4 shows a similar plot of the growth of the M and R bands at 30° C as a function of time of excitation. Both sets of data, but especially that at 0° C, show a very small initial rate of formation of M centers; the rate of formation gradually increases and goes to a maximum value, which remains constant for a period of time, and then decreases and finally goes negative. Initially there appears to be an "induction period" or "delay period", similar to that observed by PETROFF², during which the rate of formation of M centers is very small. Since there is very little change in the optical absorption spectrum during this period, it will be assumed that the formation of M centers is not inhibited by a competing

reaction and therefore this period is not an "induction period" in the usual sense of the term. Consequently the term "delay period" will be used; an estimate of the delay period can be obtained by extrapolating

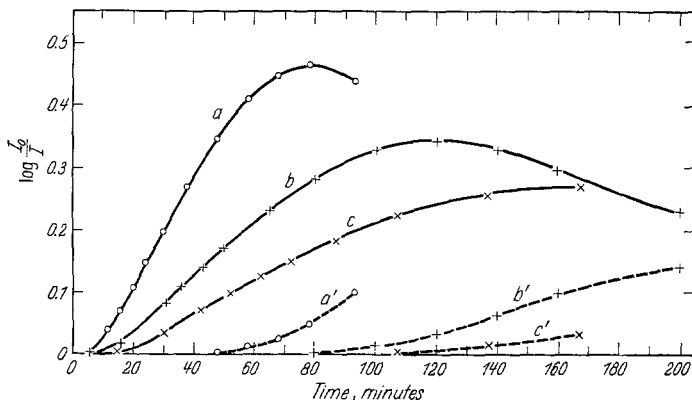


Fig. 3. The growth of the M band at 0° C caused by 543 m μ excitation of KCl containing a 1.8×10^{17} F/cm 3 ; b 0.7×10^{17} F/cm 3 ; c 0.26×10^{17} F/cm 3 . Curves a' , b' and c' show the growth of the R $_2$ band in these crystals

the linear part of the curve (maximum rate of growth) to the abscissa. The delay periods are listed in Table 1.

Also listed in Table 1 are some ratios which indicate the relative dependences of M and R center formation on temperature and F center concentration.

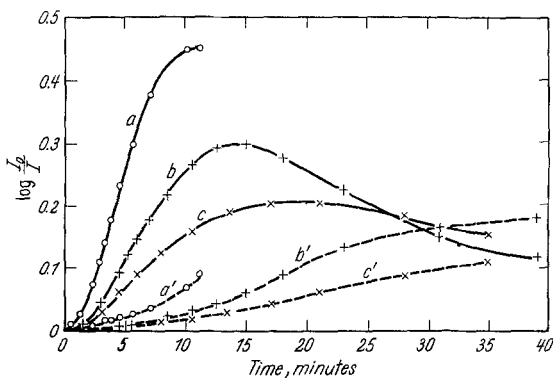


Fig. 4. The growth of the M band at 30° C caused by 543 m μ excitation of KCl containing a 1.8×10^{17} F/cm 3 ; b 0.7×10^{17} F/cm 3 ; c 0.26×10^{17} F/cm 3 . Curves a' , b' and c' show the growth of the R $_2$ band in these crystals

The ratio of the maximum optical density of the M band to the initial optical density of the F band ($\frac{M_{\max}}{F_0}$), depends on temperature and concentration; within the range of temperature and concentration studied, the maximum conversion of F to M centers is obtained at high F center concentration and low temperature. The ratio of the optical

density of the R $_2$ band (730 m μ) to that of the initial F band, at a given fractional conversion of F centers to M centers, show that R center formation is suppressed with respect to M center formation also at low temperature and high F center concentration.

Table 1. Some Characteristics of M and R Center Formation in Additively Colored KCl Upon Excitation with 543 mμ Light at 0° and 30° C

	1.8 × 10 ¹⁷ F/cm ³		0.70 × 10 ¹⁷ F/cm ³		0.26 × 10 ¹⁷ F/cm ³	
	0° C	30° C	0° C	30° C	0° C	30° C
Delay Period	9 min	1.5 min	14 min	1.7 min	18 min	1.5 min
$\frac{M_{\max}}{F_0}$	0.38	0.34	0.37	0.31	0.33	0.26
$\left(\frac{R}{F_0}\right)_{M=0.25 F_0}$	0.00	0.022	0.00	0.026	0.004	0.048
$\left(\frac{R}{F_0}\right)_{M=0.33 F_0}$	0.008		0.011		0.041	

The fact that there is a delay period in the formation of M centers indicates that something unusual is occurring; however, if it is assumed that the maximum rate of growth of the M band (approximately linear parts of the curves in Figs. 1 and 2) characterizes the processes which are occurring in the formation of M centers then it is found that the rate of formation of M centers varies as the 1.28 power of the F center concentration at 0° C and as the 1.35 power at 30° C. If, in addition, it can be assumed that the rate determining step in the formation of M centers has a temperature dependence which is proportional to $\exp [E/kT]$, where E is the thermal activation energy of the process, then the values of the maximum rates of formation of M centers at the two temperatures yield an activation energy of 0.46 e.v.

Experiments were carried out in which the rate of formation of M centers at 0° C in a crystal containing 1.2×10^{17} F/cm³ was measured as a function of the intensity of the exciting light and it was found that the rate of formation varies as (intensity)^{1/3.7}. The maxima in the rates of M formation were used to calculate the rates of F center destruction (see Sect. 3.3 A) and Fig. 5 shows the variation of

$$\eta = \frac{\text{rate of F center destruction}}{\text{rate of photon absorption}}$$

with exciting light intensity. The data in Figs. 3 and 4 were obtained using an exciting light intensity of 4×10^{14} photons/sec absorbed in the crystal.

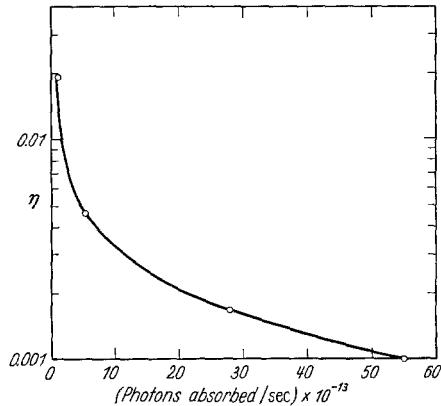


Fig. 5. The efficiency of F center destruction η , plotted as a function of the intensity of 543 mμ excitation of a crystal containing 1.2×10^{17} F/cm³ at 0° C

3.2. Fluorescence of KCl Containing F and M Centers

Fig. 6 shows the effect of excitation in the F band at 0° C on the fluorescence spectrum and intensity (measured at 90° K) of a quenched crystal of additively colored KCl containing 1.9×10^{17} F/cm³. Fig. 6A, curves *a*, *b* and *c* show that there is little change in the absorption spectrum as a result of 543 m μ light excitation for 1 and 3 min at 0° C. Fig. 6B, curves *a*, *b* and *c* show that although the corresponding emission spectra retain essentially the initial shape (peak at 1040 m μ ; one-half heights at 930 and 1180 m μ), the intensity drops by more than a factor

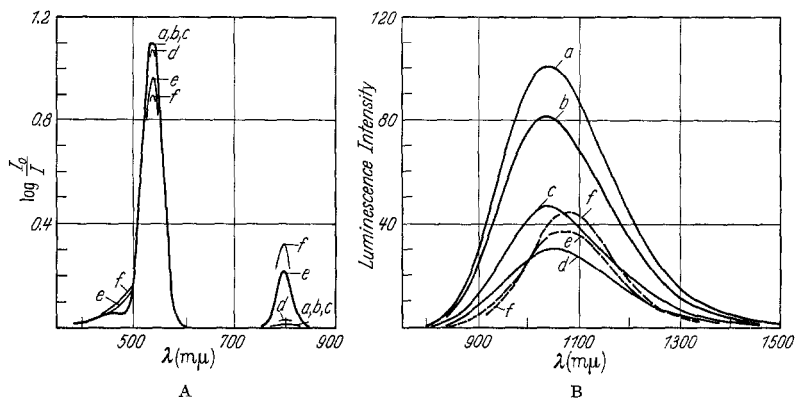


Fig. 6 A and B. The effect of 543 m μ excitation at 0° C on the optical absorption, A, and fluorescence, B, spectra of a KCl crystal containing 1.9×10^{17} F/cm³. (See text)

of two after 3 min of excitation. After excitation for 7 min, curve *d*, the F band shows a small decrease and the M band a small rise, and the emission band has decreased in intensity by a factor of three and has begun to shift somewhat to longer wavelength and to narrow. It will be noted that these marked changes in the intensity of emission have taken place within the delay period in which there is very little change in F center concentration and very little formation of M centers. Curve *e* shows an appreciable drop in absorption in the F band region and a substantial rise in the M band and a band, M_3 ,*²⁰ to the short wavelength side of the F band, and a small increase in the intensity of the emission and a continued narrowing and shifting of the emission to longer wavelength. Curve *f* shows a further decrease in the F band and increase in the M band and a corresponding increase in intensity and shift to longer wavelength of the emission spectrum; in this case the emission peak occurs at 1080 m μ (the half-heights at 990 and 1180 m μ) and the shape is close to

* The nomenclature of Okamoto, Reference 20, will be followed concerning the identification of the various M center transitions.

that of M emission*. Up to this point in the bleaching, there had been no detectable formation of other absorption bands out to $2.5\ \mu$, such as R or N bands.

These experiments have shown that a short excitation in the F band of a quenched crystal at 0°C results in a marked quenching of the F fluorescence, without any appreciable change in the absorption spectrum. These observations suggest that excitation of the F center results in the migration of the negative ion vacancy and that as a result of a number of excitations and migrations the F center, after being reformed, finds itself in the neighborhood of a defect which strongly quenches the F fluorescence without producing any appreciable effect on the shape of the absorption. There seems to be a high probability for the F centers to migrate into the neighborhood of these defects before producing M, R or N centers. Additional excitation at 0°C causes further quenching of the F fluorescence, in all probability not connected with the formation of M centers; however, the somewhat greater width of emission spectrum f than that observed with $800\ \mu$ excitation suggests the possibility that the F center emission is not completely quenched (see next section and Fig. 8).

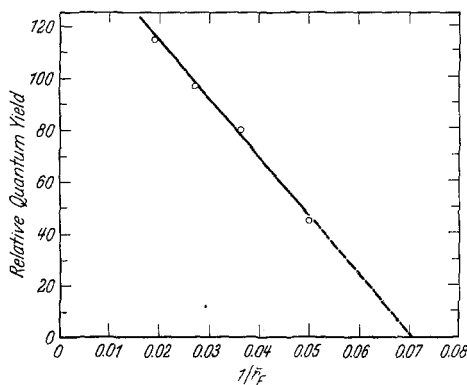


Fig. 7. Relative quantum yield of the F center fluorescence of freshly quenched crystals of various F center concentrations plotted vs $1/\bar{r}_F$ where \bar{r}_F is the mean separation between neighboring F centers

Fig. 7 shows the relative quantum yield of the F fluorescence of freshly quenched additively colored KCl plotted versus $1/\bar{r}_F$, where \bar{r}_F is the average number of negative ion lattice sites separating neighboring F centers and is calculated on the assumption that $f_F=0.8$. The data are similar to data obtained by LÜTY²¹ and show a strong decrease in the fluorescence efficiency with decreasing separation between F centers; this suggests that some kind of concentration quenching is taking place. Assuming that the extrapolation indicated by the dashed line is valid, complete quenching would occur at a concentration in which the average separation between neighboring F centers is 14 lattice spacings. The quenching of the luminescence of a given F center would be expected to

* Excitation of a KCl crystal containing both F and M centers with $800\ \mu$ light at 90°K gives an M emission with a peak at $1080\ \mu$ and half-heights at 998 and $1177\ \mu$, under the conditions of measurement employed here.

be caused primarily by the nearest F center and the average smallest separation between F centers would be considerably less than 14 lattice spacings.

3.3. Experiments with Crystals Containing F and Oriented M Centers

A. Oscillator Strengths of the M_1 and M_2 Transitions. Fig. 8A shows the optical absorption spectrum of a crystal containing F centers and oriented M centers. M centers were formed by excitation with 543 $m\mu$ light at 0° C and then oriented by excitation with [011] 5461 Å light at 170 to 200° K. The degree of orientation of the M centers is indicated

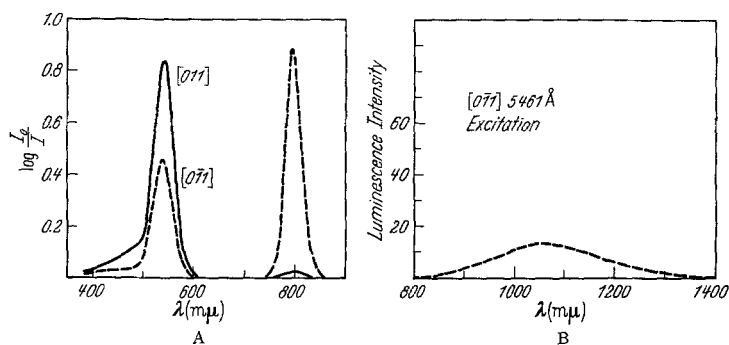


Fig. 8A and B. Part A shows the $[0\bar{1}1]$ and $[011]$ optical absorption spectra of a crystal containing F centers and oriented M centers. Part B shows the emission spectrum of this crystal when excited with $[011]$ 5461 Å light at 90° K. The initial F center concentration was 1.2×10^{17} F/cm³

by the ratio of the intensities of the 800 $m\mu$ bands in the two spectra; ratios of up to 50 have been obtained*. It is apparent that the M_1 transition (800 $m\mu$) is very anisotropic; and, since the excitation occurred at 5461 Å, it is also apparent that the M_2 transition (546 $m\mu$) is very anisotropic. Since there is no evidence for other centers in this crystal than F and M centers, it is believed that the absorption band between 500 and 600 $m\mu$ in the $[0\bar{1}1]$ spectrum is the F band; in fact the peak and half-height positions of this band are the same as for an F band in a well quenched crystal. Thus, it is possible to determine the fraction of F centers which were used to form M centers and, making certain assumptions, to calculate the oscillator strengths of the M transitions relative to that of the F band. The difference of the two spectra in Fig. 8A gives the anisotropic absorption spectrum of oriented M centers; the most prominent transitions are the M_1 (801 $m\mu$), M_2 (546 $m\mu$) and M_3 (~ 490 $m\mu$) transitions. The M_2 and M_3 transitions overlap and a somewhat arbitrary decomposition into two bands gives the following relative oscillator

* It was not observed that this ratio depends appreciably on the initial F center concentration; see Reference 20.

strengths: $f_{M_2}/f_{M_1}=0.86$ and $f_{M_3}/f_{M_1}=0.53$. In order to relate the oscillator strengths of the M transitions to that of the F center, the following assumptions have been made:

1. The M center consists of two nearest neighbor F centers, ($M \equiv F_2$) as first suggested by VAN DOORN and HAVEN⁵.
2. All of the F centers which disappear are converted into M centers. The fact that no other absorption bands are formed supports this assumption.

From the data of Fig. 8A, it is calculated that the ratio f_{M_1}/f_F measured with $[0\bar{1}1]$ light is $(f_{M_1}/f_F)_{[0\bar{1}1]}=1.3$. In the case of randomly oriented M centers $f_{M_1}/f_F=1.3/3=0.43$; if the van Doorn-Haven model of the M center is correct, then the two electrons are equivalent and on the basis of the oscillator strength per electron $f_{M_1}/f_F=0.21$. The relative oscillator strengths per electron of the M transitions of randomly oriented M centers are given in Table 2. The M'_2 and M'_3 transitions have not been studied in this work but OKAMOTO'S²⁰ results indicate that they have the same strengths as the M_2 and M_3 transitions respectively; on this basis these five M transitions account for 80% of the oscillator strength of the F band which has disappeared.

FARADAY, RABIN and COMPTON¹³ have shown that, in KCl and KBr crystals X-rayed at 77° and 4° K, the concentration of M centers is proportional to the square of the F center concentration. Assuming that each negative ion site is equally probable as the site of an F center (this almost requires an interstitialcy mechanism for F center production) they have shown that the M center concentration is given by $[M]=K[F]^2/[N]$, where $[N]$ is the concentration of negative ion sites. The assumption that the α center (or F center) cannot move from the site at which it was formed, requires that $K=6$ and using this value they have calculated that $f_{M_1}/f_F=0.69$. However, if it is assumed that $f_{M_1}/f_F=0.43$, as found in the present work, then the constant K has the value 9.6. This larger value of K , which is approximately the same at 4 and 77° K, implies that either an α or an F center which is a next nearest neighbor to an F center has an appreciable probability of moving during its lifetime into the nearest neighbor shell of the F center and forming an M center. This motion does not take place as a result of thermal vibrations characteristic of $T < 77^\circ$ K but is probably induced by the thermal spike associated with 1. the formation of the vacancy (as a result of formation of an interstitial) by the ionizing radiation, 2. the trapping

Table 2. Oscillator Strengths Per Electron of Some M Transitions Relative to that of the F Band

f_{M_1}	f_{M_2}	f_{M_3}
0.21 f_F	0.18 f_F	0.11 f_F

²⁰ OKAMOTO, F.: Phys. Rev. **124**, 1090 (1961).

and de-excitation of an exciton at an α or an F center, 3. the annihilation of an electron and a hole in the vicinity of an α or an F center, or with much less probability, 4. the trapping of an electron at an α center.

B. Emission Excited by $[0\bar{1}1]$ 5461 Å Light. Excitation of the crystal, having the absorption spectrum shown in Fig. 8A, with $[0\bar{1}1]$ 5461 Å light produces an emission having the spectral distribution shown in Fig. 8B; the intensity scale is the same as that used in Fig. 6B, and the intensity of this spectrum is to be compared with the intensities of those shown in Fig. 6B. Because of the very high degree of orientation of the M centers, it is believed that the excitation is taking place almost totally by absorption in the F band and therefore it is assumed that this emission is characteristic of these F centers. The data shows that the efficiency of F emission is one-sixth of that obtained in the freshly quenched crystal and that the shape of the emission has also changed; the emission is somewhat broader and shifted to longer wavelength. In addition, the emission is isotropic and therefore is not characteristic of M centers so that, at least in this crystal containing oriented M centers, there is no efficient transfer of energy from excited F centers to M centers and consequent M emission as has been suggested by LAMBE and COMPTON¹⁸. It was not possible to obtain an accurate emission spectrum or degree of polarization with $[011]$ 5461 Å excitation of this crystal since the light intensity required for the measurements was so great as to cause appreciable re-orientation; however, excitation of the 800 m μ transition at 90° K causes re-orientation with an extremely low efficiency so that in this case it was possible to measure the degree of polarization. It was found that the degree of polarization upon exciting with $[0\bar{1}1]$ 800 m μ light was $P(800, [0\bar{1}1]) \equiv \frac{I_{||} - I_{\perp}}{I_{||} + I_{\perp}} = 0.95$; if the emission from the small fraction of M centers not in the $[0\bar{1}1]$ orientation is taken into account, this value becomes about 0.98. Consequently, the M fluorescence at least for 800 m μ excitation, has a degree of polarization of essentially 1.

This series of experiments involving oriented M centers was also carried out with a crystal initially containing 5×10^{17} F/cm³ and the same behavior was observed.

3.4. Degree of Polarization of F and M Fluorescence

The degree of polarization of the luminescence measured at 90° K with 543 m μ excitation is zero within experimental error, $P(543, [100]) = P(543, [110]) = 0$, for a crystal in the state indicated by curves *a*, *b* and *c* of Fig. 4; however, as the M band grows the emission becomes more anisotropic and with the crystal in the state indicated by curve *f* the values $P(543, [110]) = -0.30$, $P(543, [100]) = -0.13$, $P(800, [110]) =$

0.62 and $P(800, [100]) = 0.31$ were obtained. These results are in good agreement with those obtained by LAMBE and COMPTON¹⁸.

FEOFILOV²¹ has shown that for molecules of $D_{\infty h}$ symmetry, which are oriented with equal numbers in the six $\langle 110 \rangle$ directions and emit polarized luminescence with the electric vector parallel to the molecular axis, the degree of polarization $P(\alpha)$, is given by

$$\left. \begin{aligned} P_{\parallel}(\alpha) &= \frac{1}{8}(3 - \cos 4\alpha); & P_{\parallel}(100) &= \frac{1}{8}, & P_{\parallel}(110) &= \frac{3}{8} \\ P_{\perp}(\alpha) &= -\frac{1}{16}(3 - \cos 4\alpha); & P_{\perp}(100) &= -\frac{1}{8}, & P_{\perp}(110) &= -\frac{3}{8} \end{aligned} \right\} \quad (1)$$

where α is the angle between the electric vector of the exciting light and the $[001]$ direction, see Fig. 9, and the \parallel (\perp) indicates that the polarization of the transition being excited is parallel (perpendicular) to the molecular axis. The agreement between the experimental and theoretical results suggests that the M center does, to a first approximation, fit the above described model with the M_1 transition ($800 \text{ m}\mu$) permitted for exciting light with the electric vector parallel to the molecular axis (∞ -fold axis) and with the M_2 ($546 \text{ m}\mu$) and M'_2 ($538 \text{ m}\mu$) transitions not being quite degenerate* and permitted for light with electric vector perpendicular to the molecular axis. The experimental values are much closer to the theoretical values in the case of $800 \text{ m}\mu$, or parallel, excitation than in the case of $543 \text{ m}\mu$, or perpendicular, excitation; however, when the partially quenched isotropic F center luminescence (see previous section and Fig. 8B) is taken into account, the experimental values become $P(543, [110]) = -0.38$ and $P(543, [100]) = -0.18$. These latter figures agree very well with the theoretical values and with the results of KUWABARA¹⁹ who measured these values at 25°C where the efficiency of F center fluorescence is essentially zero. These results on the degree of polarization of the emission upon excitation of the M_1 , M_2 and M'_2 transitions prove that these transitions are very anisotropic and that the M center has D_{2h} symmetry with the M_2 and M'_2 transitions nearly degenerate.

The above discussion is based on equal populations of M centers in the six $\langle 110 \rangle$ orientations but one must consider why such a distribution obtains. It is reasonable to assume that the initial formation of M centers does not lead to the preferential population of any of the $\langle 110 \rangle$ directions; however, excitation of an anisotropic M transition under the proper conditions of temperature, etc., will cause preferential excitation and re-orientation of M centers having certain orientations even if the exciting

* In a KCl crystal the symmetry would be D_{2h} and the M_2 and M'_2 transitions would not be expected to be degenerate since the transition moments are oriented along the inequivalent $\langle 110 \rangle$ and $\langle 100 \rangle$ directions respectively.

²¹ FEOFILOV, P. P.: Dokl. Akad. Nauk. SSSR. **92**, 743 (1953).

light is non-polarized. The M centers were formed by excitation with 543 m μ non-polarized light at 0° C and consequently the M₂ and M₂' transitions are excited in addition to the F transition. If it is assumed that a) the M₂ and M₂' transitions have equal oscillator strengths²⁰ under 543 m μ excitation, b) the probability of re-orientation subsequent to excitation is independent of which transition is excited, and c) a re-orienting M center will find itself after re-orientation with a probability of $\frac{1}{6}$ in any given $\langle 110 \rangle$ orientation, then it can be readily shown that the steady state population distribution is given by $n_1 = n_2$, $n_3 = n_4 = n_5 = n_6$, and $n_1 = \frac{3}{2} n_3$ where n_i indicates the number of centers having the orientation i (see Fig. 9). For M centers having this population distribution, the degrees of polarization of the luminescence would be expected to be given by

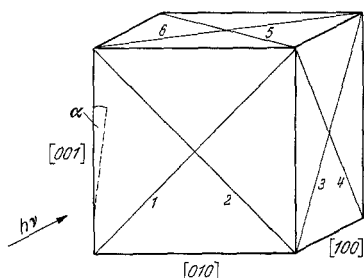


Fig. 9. Diagram showing the six possible $\langle 110 \rangle$ M center orientations. The direction of propagation of the exciting light is along $[100]$.

and

$$\left. \begin{aligned} P_{\parallel}(\alpha) &= \frac{1}{4}(2 - \cos 4\alpha); \\ P_{\parallel}(100) &= \frac{1}{4}, \quad P_{\parallel}(110) = \frac{3}{4} \\ P_{\perp}(\alpha) &= -\frac{1}{8}(2 - \cos 4\alpha), \end{aligned} \right\} \quad (2)$$

instead of (1). It is found that after excitation of a crystal containing F and M centers at about 170° K with a non-polarized and approximately parallel beam of 5461 Å light the population distribution is changed as indicated by the degree of polarization of the fluorescence, measured at 90° K, $P(800, [110]) = 0.77$ and $P(800, [100]) = 0.18$. Thus the experimental values are in approximate agreement with (2) and the change in population distribution can be understood on the basis of excitation of both M₂ and M₂' transitions.

These results obtained upon irradiation with 5461 Å light at 170° K make it necessary to consider why a similar crystal irradiated at 0° C does not produce the same population distribution instead of the apparently random distribution which is observed. Perhaps the most obvious possible explanation is that the M center can spontaneously change its orientation at 0° C; however this is not the case. Another possible explanation is that the M transitions are considerably less anisotropic at 0° C than 77° K. Careful measurements of the anisotropic absorption spectra of a crystal containing very well oriented M centers have shown that the area under the M₁ band and the area under the overlapping M₂ and M₃ bands each decrease only 5% on warming the crystal from 77° K to 0° C and that the M₁ transition does not become less anisotropic. Because of the overlapping of the F, M₂ and M₃ bands, it is difficult to detect a small change in the anisotropic nature of these M transitions;

however, since the M_1 and $(M_2 + M_3)$ bands show the same 5% decrease in area (oscillator strength) upon warming to 0°C and since the M_1 transition remains very anisotropic, it is believed that the M_2 , M_3 and M'_2 transitions also remain very anisotropic. Thus, it appears that the experimental results cannot be explained by a change in the anisotropic nature of the M transitions.

Another observation which is pertinent to this subject is that a short excitation of a crystal containing M centers, which had been well oriented with $[0\bar{1}1]$ 5461 \AA light at 200°K , with this same light at 0°C causes a) at relatively low conversion of F to M centers, a disorientation of M centers and the formation of more M centers, and b) at higher conversion of F to M centers, primarily only a disorientation of M centers. It is perhaps possible that all these results concerning the orientation distribution of M centers as a result of $543\text{ m}\mu$ excitation at 0°C may be understood as follows: Trapping of an electron from the conduction band by an M center to form a short-lived M' center occurs with a high frequency. The thermal spike associated with either the formation or the destruction (by absorption of $543\text{ m}\mu$ light in an assumed isotropic M' transition) of the center is sufficient at 0°C , but not at 200°K (similar to excitation of the M_1 transition), to cause a disorientation of the M center.

3.5. Conversion of F Centers to F' Centers

In addition to the marked decrease in the fluorescence efficiency during the delay period, there is also a marked reduction in the ability to convert F centers to F' centers. This conversion of F to F' centers was carried out by excitation of the crystal with $550\text{ m}\mu$ light at 173°K until a steady state was reached. Fig. 10 shows a plot of the per cent conversion of F to F' centers (100 minus the per cent of F band remaining) as a function of time of excitation with $543\text{ m}\mu$ light* at 0°C . In a freshly quenched crystal containing about $1.2 \times 10^{17}\text{ F/cm}^3$ about 75% of the F centers can be converted into F' centers; ** however, it is apparent from the figure that exposure of the crystal to a small amount of F-light, sufficient to produce only a very small M band, causes a reduction of a factor of 3 to 4 in the ability to convert F to F' centers. The production of more M centers causes the F to F' conversion to approach about 15%. It seems clear from these experiments that as a result of excitation of F

* Photon intensity and time scale are the same as used in Fig. 1.

** From the relative areas of the initial F band and final F and F' bands, the relative oscillator strength of the F' band was calculated assuming that (a) the F' center is a F center which has captured an electron and (b) F centers are converted to F' centers only. Calculated on the basis of the number of centers it is found that $f_{\text{F}}/f_{\text{F}'} = 1.87$. On the assumption that the two electrons in a F' center are equivalent, the relative oscillator strength per electron is given by $f_{\text{F}'}'/f_{\text{F}} = 0.93$.

centers at 0° C, and consequent migration of the F centers, there is an interaction between the F centers and some type of defect, present in comparable or higher concentration, which causes both a quenching of the F center luminescence and a decrease in the conversion of F to F' centers. It also seems clear that this defect cannot be the M center (or R, N, etc. centers) since at such a low concentration it seems quite improbable that their presence could affect such a large fraction of the F centers.

Fig. 11 shows how the conversion of F to F' centers, under the conditions described above, in freshly quenched crystals varies as a function

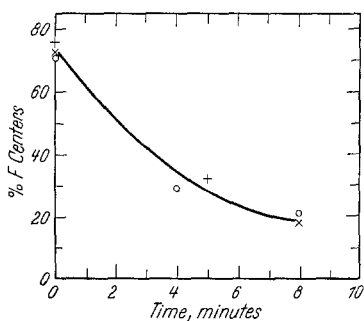


Fig. 10

Fig. 10. The per cent conversion of F centers to F' centers for a crystal containing 1.2×10^{17} F/cm³ plotted as a function of the time of excitation with 543 m μ light at 0° C

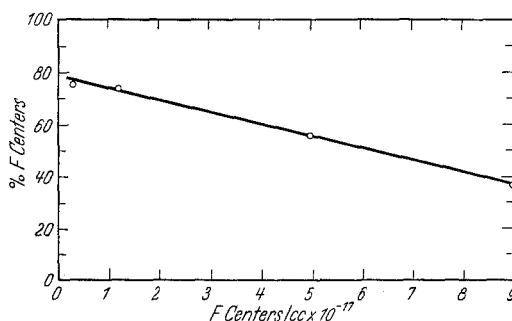


Fig. 11

Fig. 11. Variation of conversion of F to F' centers in freshly quenched crystals as a function of F center concentration

of concentration. The decrease in the per cent conversion with increasing F center concentration is in agreement with observations by LÜTY²². These results suggest that as the average separation between F centers decreases there is an increasing interaction which inhibits the formation of stable F' centers.

§ 4. Discussion

4.1. Condensation of F centers by F Band Excitation

From the results presented in the previous section it seems probable that a) the delay period in M center formation, b) the strong quenching of the F center fluorescence which occurs during the delay period, and c) the large decrease in the ability to convert F centers to F' centers which occurs during the delay period are all interconnected and arise because of the characteristics of the mechanism by which F centers are converted to M centers. In view of the increasing support for the van

²² LÜTY, F.: Halbleiterprobleme, Bd. VI, S. 238. 1961.

Doorn-Haven model of the M center, it is concluded that the excitation of F centers near room temperature with light absorbed in the F band causes a migration of F centers through the crystal and the association of some of them to form M centers. During the delay period the number of F centers remains essentially constant and the formation of M centers, or other centers, is minimal; however it is believed that the migration of F centers, as a result of the photoexcitation, is occurring. Therefore it is suggested that observations b) and c) arise because of the migration of the F centers into regions where a large fraction of the F centers are near to, and interact with, some lattice defect; arguments will be given shortly which indicate that the perturbing defect is a nearby F center. When a crystal containing F centers is heated to 500 to 600° C the F centers become mobile due to thermal agitation and move about at random; upon rapid cooling in the dark it is believed that the F center distribution remains random. It is found that the $F \rightarrow F'$ conversion and the efficiency of F-luminescence are relatively high; this suggests that the migration of F centers caused by F-excitation near room temperature and resulting in the coagulation of F centers (M center formation) is not a random diffusion but a migration which is influenced by attractive forces caused by the presence of short-lived species.

The efficiency of F center luminescence in freshly quenched crystals decreases with increasing concentration, as shown in Fig. 7. This behavior seems to be independent of the particular KCl crystal used and therefore independent of impurity concentration, dislocation concentration, etc. Therefore it seems probable that the behavior shown in Fig. 7 is caused by an interaction between neighboring F centers; as the F center concentration increases the average separation between nearest neighbor F centers decreases and it is suggested that the probability of a radiationless transition from the excited to the ground state of an F center increases, and that the lifetime of the F center in its excited state (F^*) decreases, as the separation between the F center and its nearest neighbor F center decreases. This concentration quenching may be caused by a perturbation of the local vibrational modes of the lattice, or by an interaction between the spread out excited state F^* and a nearby F center which favors a radiationless transition to the ground state. The probable existence of concentration quenching in this case suggests that the strong decrease in the efficiency of F luminescence during the delay period is also caused by concentration quenching. This implies that as a result of a short excitation* of the F band at 0° C, during which essentially none of the F centers have coagulated to form M centers, the

* In a period of excitation of 10 min. each F center is excited an average of 60 times.

average distance between an F center and its nearest neighbor* has decreased appreciably.

The degree to which F centers in freshly quenched crystals can be converted to F' centers decreases with increasing F center concentration as shown in Fig. 10A**. This behavior could be caused by

1. A decrease in the ionization efficiency of the F center at -100°C , perhaps brought about by the decreasing lifetime*** of an F center in the excited state, F*, with increasing F center concentration. Since the F' transition is generally believed to be a transition into the conduction band, the ionization efficiency of the F' center would be expected to remain constant. The F and F' bands overlap; therefore exposure to 550 m μ light causes simultaneous excitation of F and F' centers and could lead to this behavior.

2. A decrease of the capture cross section of an F center relative to that of a negative ion vacancy.

3. An increased probability of tunneling of an electron from an F' center to a nearby negative ion vacancy²². In a crystal in which $\frac{1}{4}$ of the original F centers remain and the rest have been converted to F' and α centers, it is clear that among the near neighbors of each α center will be several F' centers. As the average separation between α and F' centers decreases, the importance of this tunneling process increases.

It seems that either (1) or (3) are more probable explanations of this effect than is (2), and both (1) and (3) are associated with the decreasing separation between neighboring F centers with increasing F center concentration. Thus it is suggested that both the decrease in efficiency of F fluorescence and the decrease in conversion of F \rightarrow F' centers during the delay period are brought about by the decrease in the average separation between nearest neighbor F centers.

4.2. Possible Mechanisms for M Center Formation

A decrease in the average nearest neighbor F center separation would imply that the nearest neighbor pair distribution shifts to smaller separations and that the concentration of F centers at a given r_F is increased for r_F appreciably smaller than the most probable value. If such a condensation of F centers into local "clouds", containing relatively high "non-associated F center" concentrations, takes place; then it seems clear

* It is assumed that the quenching of the luminescence is determined chiefly by the distance to the F center which is closest.

** For reasons similar to those presented in the previous paragraph the decrease in F \rightarrow F' conversion is believed to be caused by an interaction between F centers, or F' and α centers, instead of between F centers and some other kind of defect.

*** This decreasing lifetime of F* is associated with the concentration quenching of the F fluorescence.

that during the first part of the irradiation, as the local concentration increases, the rate of formation of M centers should also increase and give rise to what has been called the "delay period" in M center formation*. There are a number of factors which help determine whether or not such a condensation will occur. Two of the most important are (1) the initial nearest neighbor pair distribution of the F centers in the crystal and (2) the dependence of the attractive force between the reacting species on r_F . It is intuitively clear that, for a given initial pair distribution (for example, a random distribution), a sufficiently short range attractive force will cause a decrease in the concentration of F centers in a region of small r_F because the rate of influx of F centers into this region is smaller than the rate of reaction to form F_2 , and on the other hand a sufficiently long range attractive force will cause an increase in the concentration of F centers in a region of small r_F .

It seems reasonable to assume that the distribution of F centers in a freshly quenched crystal is dominated by the random thermal motion at high temperature and is a statistically random one; consequently, it is concluded that the migration of the species which is mobile, during irradiation near room temperature, is not a random migration. The F_2 model of the M center is generally accepted since it is believed that the same processes are occurring during the delay period as later, one must consider possible forces which could cause this coagulation of F centers.

Any interactions which could cause condensation of F centers will be determined by the species which are present in the crystal during excitation in the F band at 0° C. The F' center can be readily formed at -100° C and is thermally stable at that temperature; it is estimated that the lifetime of an F' center or an α center at 0° C is about 10^{-2} sec^{23**}, a time which is long compared to the lifetime of an electron in the conduction band. Therefore most of the electrons which have been liberated from F centers at a given time will be trapped as F' centers; but as a result of the continual ionization of the F centers and the thermal instability of the F' centers there is a continual flux in the crystal such that a given F center is at one time ionized and at another time acquires another

* PETROFF² has attributed this delay period in M center formation to the formation of the B band, assuming essentially that B center formation competes with, or is a prerequisite to, the formation of M centers. In the present work no appreciable formation of A or B bands has been observed so that this explanation does not appear to be valid.

** The average time that an electron is trapped at a given F center before being thermally released is much shorter than 10^{-2} sec; however, because of the large excess of F centers, an electron is retrapped at many F centers before being trapped at an α center so that the apparent lifetime of an F' center is about 10^{-2} sec.

²³ PICK, H.: Ann. d. Physik **31**, 365 (1938).

electron*. Since M centers are formed only extremely slowly in the dark, it is believed that the mobility of the F center is very low and is not involved in the process we are considering. The reacting species are most probably the α center (negative ion vacancy), the F center and the F' center. The mobility of the α center in the perfect KCl lattice, although quite low, must be greater than the mobility of an F or F' center. The migration of the α center through the lattice will be influenced by two factors (1) the local energetic lattice vibrations, thermal spike, associated with the excitation and ionization of the F center, and (2) the attractive or repulsive interactions with other species in the crystal. The thermal spike will remain sufficiently localized only long enough to promote one or two lattice jumps, and the attractive and repulsive potentials will affect the height of the barrier to diffusion and give some direction to the migration of the α center.

The attractive forces considered here which may cause the coagulation of F centers are electrostatic in nature and arise from the charges on the F' and α centers and the large polarizability of the F center. These forces are

A. The Coulomb attraction between the F' and α centers. The degree to which this force, which has an r^{-2} dependence, is important will be determined by the separation of the α and F' centers. In the experiments which have been described here, approximately one F center in 10^3 is ionized at a given time.

a) If the distribution of F' and α centers among the F center sites is random then the average separation between F' and α centers will be about 10 times greater than the average separation between F centers. Of course, the average separation between an α center and the nearest F' center, which is the significant quantity, will be smaller and will result in a tendency of the α center to migrate toward this F' center.

b) Endor experiments^{24, 9} on F centers in the alkali halides show that, although the trapped electron in the F center ground state is largely confined to the vacancy, the probability density of the electron out to the 6th or 7th shell of neighbors is not negligible. In the case of the excited state, F*, the electron density would extend to much larger distances. Consequently, it seems probable that for not too large separations the overlap in electron wave functions between an excited F center and its nearest neighbor F center is sufficiently large to favor appreciably the trapping of the excited electron at the neighboring F center. In this case

* It will be assumed here that there is no source of α centers other than ionized F centers and that positive ion vacancies are not involved in any of the processes which occur.

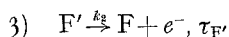
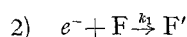
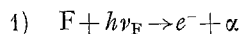
²⁴ SEIDEL, H.: Z. Physik **165**, 218 (1961).

the distribution will no longer be random and small separations between nearest neighbor F' and α centers will be favored, increasing the importance of the Coulomb attraction. Because the electron wave function of the F' center is also quite extended, one should expect that the lifetime of an F' center in the neighborhood of an α center is less than the lifetime of an isolated F' center because of tunneling of the electron to the α center.

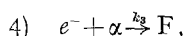
B. The monopole-dipole attraction between α and F centers. The large polarizability of the F center causes an electric dipole to be induced on the F center by a nearby charged species, such as an α center. The monopole-dipole attractive force is proportional to r^{-3} for a constant dipole moment; however, the induced dipole moment on an F center is proportional to r^{-2} so that the monopole-dipole attractive force considered here varies as r^{-5} .

In the case of randomly distributed F' centers a given α center will at one time be attracted to one F' center and at another time to another so that it is not clear that the nearest neighbor separation will decrease. On the other hand, if there is an appreciable probability that an electron from an excited F center is trapped at the nearest neighbor F center, or if the monopole-dipole attraction between F and α centers is appreciable, an α center will be predominately attracted to one F center, or one group of F centers, and the nearest neighbor separation might be expected to decrease. Calculations are now being carried out to determine if the attractive forces considered here, when superimposed on the random diffusion of the negative ion vacancy, will cause a decrease in the nearest neighbor F center separation if the initial distribution of F centers is statistically random.

The possible mechanisms of M center formation which have been discussed are complicated by the attractive forces which are assumed to operate; however, it is still worthwhile to consider briefly the kinetics of M center formation on the assumption that the processes which occur are of a random nature. The growth of M centers, at constant temperature as a result of F band excitation, will be considered after the delay period when the rate of growth becomes approximately constant. A given F center is excited many times before it reacts to become an M center, and the following reactions are considered to be the important ones in establishing the distribution of electrons among the various traps and the conduction band.



and



where

F = F center

$h\nu_F$ = a photon absorbed in the F band (the efficiency for ejection of an electron into the conduction band from F* is about one in the temperature range considered).

e^- = electron in the conduction band

α = negative ion vacancy

F' = F' center (an F center which has trapped an electron)

$\tau_{F'}$ = mean lifetime of an F' center.

Considering these reactions, the rates of disappearance of F' and α centers are

$$5) \quad -\frac{d[F']}{dt} = k_2 [F'] - k_1 [e^-] [F]$$

and

$$6) \quad -\frac{d[\alpha]}{dt} = k_3 [e^-] [\alpha] - [h\nu_F],$$

where the brackets indicate the concentrations and $[h\nu_F]$ indicates the number of photons absorbed per second in the crystal. It will be assumed that any other reactions which involve the conduction electrons, F centers, F' centers, or α centers have rates which are negligible compared to the rates of the above reactions. Consequently one may write

$$7) \quad [F'] + [e^-] = [\alpha]$$

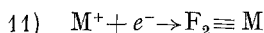
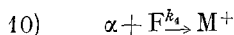
and since τ_{e^-} is much smaller than either τ_α or $\tau_{F'}$,

$$8) \quad [F'] = [\alpha].$$

In addition it follows that a steady state is established in which $\frac{d[F']}{dt} = \frac{d[\alpha]}{dt} = 0$. Therefore, using the steady state condition and 5), 6) and 8), it is found that

$$9) \quad [\alpha] = \left\{ \frac{k_1}{k_2 k_3} [h\nu_F] [F] \right\}^{\frac{1}{2}}.$$

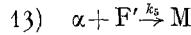
If it is now assumed that M centers are formed according to the following reactions



where (10) occurs by a random process and is the rate controlling step, then the rate of formation of M centers is given by

$$12) \quad \frac{d[M]}{dt} = k_4 [\alpha] [F] \propto [h\nu_F]^{\frac{1}{2}} [F]^{\frac{3}{2}}.$$

On the other hand if M centers are formed by a random encounter between α and F' centers



then the rate of formation of M centers is given by

$$14) \quad \frac{d[M]}{dt} = k_5 [\alpha] [F'] \propto [h\nu_F] [F].$$

It has been suggested that M center formation occurs by a random migration of α centers upon which is superimposed electrostatic interactions between the α center and the F and F' centers; therefore, k_3 and k_4 will be to a certain extent dependent on the separation between the interacting species and therefore on the local F center concentration. However, since it would be very difficult to evaluate the dependence of k_3 and k_4 on $[F]$, they will be assumed to be constants. Experimentally it is found that

$$15) \quad \frac{d[M]}{dt} \propto [h\nu_F]^{0.27} \times [F]^{1.3}.$$

This experimental dependence of the rate of growth of M centers on $[F]$ and $[h\nu_F]$ is in better agreement with 12) than with 14) and seems to suggest that M center formation takes place by reactions 10) and 11) in which the mobile α center encounters an F center to form a stable M^+ , which subsequently traps a conduction band electron to form an M center.

It is assumed that $\tau_{F'}$ depends only on the temperature. However from Eqs. (1 to 4) it can be shown that $\tau_\alpha = \tau_{F'}/P_{e^-+\alpha}$ where $P_{e^-+\alpha}$ is the probability that an electron in the conduction band is trapped at an α center and $1 \gg P_{e^-+\alpha} \propto \frac{[\alpha]}{[F]}$. Using (9) it is apparent that the lifetime of the mobile α center, and therefore the distance it moves during one lifetime, decreases for increasing light intensity; this is in qualitative agreement with the data of Fig. 5.

PETROFF², using additively colored KCl, and more recently ITOH and SUITA²⁵, using photochemically colored KCl, have followed the growth of M centers upon exposure to a pulsed source of F-light near room temperature. It seems possible that their results may be partially determined by the lifetime of the α center, τ_α ; however more experiments must be performed in order to gain some understanding of the effects of pulsed excitation.

Acknowledgement. It is a pleasure to acknowledge informative discussions with F. BASSANI, F. LÜTY and P.H. YUSTER. I would like to thank Professor H. PRICK for the opportunity to work in his laboratory and to thank the Richard-Merton-Fonds of the Stifterverband der deutschen Wissenschaft for financial support.

²⁵ ITOH, N., and T. SUITA: J. Phys. Soc. Japan **17**, 348 (1962).