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*Physics Department, University of Utah, Salt Lake City***The  $F_2^+$  Center in KCl Crystals<sup>1)</sup>****Part I: Formation and Bleaching Kinetics**

By

M. A. AEGERTER<sup>2)</sup> and F. LÜTY

A quantitative analysis of the higher transitions of the M center in the UV up to 5.0 eV in KCl crystals with high  $[M] : [F]$  ratio and unaligned and aligned M centers shows several new excitations ("L<sub>M</sub> bands"). Assuming that the L<sub>M</sub> excitation leads to conductive states, a simple electron kinetic model shows that UV irradiation of the F + M center system produces ionized F and M centers ( $\alpha$  and  $F_2^+$ ) while competing capture processes partially destroyed them or form F' and M' centers. The  $F_2^+$  center production spectrum should closely follow the absorption ratio of L<sub>M</sub>:L<sub>F</sub> while the bleaching spectrum should follow the F' and M' spectrum. Experimental confirmation of this model is presented. By X-raying the crystal (containing F + M centers) at LHeT, extra electron traps are introduced into the crystal and shift the equilibrium of the reaction to higher amount of  $F_2^+$  center, which are not stabilized by F' and M' centers. These extra  $F_2^+$  centers anneal out near 40 °K in parallelity with the third stage annealing of X-ray produced  $\alpha$ -centers—interstitials anions.

L'analyse quantitative des transitions optiques du centre M dans l'ultraviolet jusqu' à 5 eV dans des cristaux de KCl ayant un rapport de concentration  $[M]:[F]$  élevé et des centres M non alignés ou alignés montre la présence de plusieurs nouvelles bandes d'absorption (bandes L<sub>M</sub>). En supposant que l'excitation optique de ces dernières conduisent à des états photoconducteurs, un modèle de cinétique électronique simple montre que l'irradiation UV des centres F et M produit des centres F et M ionisés (centres  $\alpha$  et  $F_2^+$ ), tandis que des processus compétitifs de capture les détruisent partiellement ou créent des centres F' et M'. Le spectre de production des centres  $F_2^+$  devrait alors suivre celui du rapport des constantes d'absorption  $K(L_M):K(L_F)$  tandis que le spectre de blanchiment optique s'identifierait aux spectres F' et M'. Une confirmation expérimentale de ce modèle est présentée. L'irradiation X d'un cristal (ayant préalablement des centres F et M) à la température de l'hélium liquide introduit des trappes électroniques supplémentaires. L'équilibre de la réaction est alors déplacé vers de plus grandes concentrations de centres  $F_2^+$  qui ne sont plus stabilisés par des centres F' et M'. Les centres  $F_2^+$  supplémentaires s'annihilent au voisinage de 40 °K en parallélisme avec le 3ème stade d'annihilation des paires de Frenkel créées par rayons X (centre  $\alpha$ -anions interstitiels).

**1. Introduction**

In recent years several works have been reported on two ionized F-aggregate centers,  $F_2^+$  and  $F_3^+$ , which are the singly ionized M (=  $F_2$ ) and R (=  $F_3$ ) centers respectively [1 to 6]. These ionized centers were produced by various irradiation treatments of alkali halide crystals. In a first group of experiments the ionized

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centers were observed in LiF [2, 3] and in NaF [4, 5], and KCl [6] either directly after a heavy X-ray or electron irradiation near 300 °K, or after annealing near room temperature of samples previously irradiated in the same way at lower temperature. In this latter process the ionized center appears likely as an intermediate step toward the formation of the neutral aggregate centers via a mechanism proposed by Delbecq [7] involving the thermal diffusion of anionic vacancies. A more controlled approach was carried out by Schneider and Rabin [1]. Starting from a crystal containing the aggregate centers (M and R) they produced the respective ionized centers in KCl and KBr (and with some uncertainty in KI and NaCl) at liquid helium temperature by exposing such a crystal to X-rays and subsequently to near UV light. In this case two principal mechanisms for producing ionized centers can be visualized:

- a) Direct photoionization of the neutral aggregate centers.
- b) Capture of a hole by the neutral aggregate centers.

Schneider and Rabin interpret their measurements in terms of the second process assuming that the UV irradiation of the X-rayed crystal transfers a hole from a V-type center to the aggregate center. It can be expected, however, that M or R centers (similar to F [8] and  $F_A$  centers [9, 10]) possess higher excited states which give rise to absorption bands in the UV region. As light excitation in these bands corresponds to transitions into conductive states, the UV irradiation in the above experiments could be suspected to have produced the  $F_2^+$  centers by direct photoionization of M or R centers as well. To distinguish between these two mechanisms (a and b), a quantitative knowledge about the higher F aggregate center transitions is therefore needed.

In this present work (part I), we shall restrict ourselves to study the formation and destruction of  $F_2^+$  centers in KCl. A careful examination of the UV absorption of both unaligned and aligned M centers (Section 3) will provide the basis for our analysis. By measurement of the spectral distribution of the UV light production of  $F_2^+$  centers we will subsequently show (Section 5) that  $F_2^+$  centers are indeed produced by direct photoionization of M centre via excitation in the  $L_M$  bands. A simple model kinetic will be presented, which accounts for the production and destruction spectra of  $F_2^+$  centers and for the role of additional electron traps (introduced e.g. by low temperature X-irradiation).<sup>3)</sup>

The next paper (part II) [11] will present a detailed analysis of the optical properties of several new absorption and emission bands related to the  $F_2^+$  center in KCl, with a particular emphasis to the close analogy of this center and the  $H_2^+$  molecular ion.

## 2. Experimental Procedures

The KCl single crystals used throughout these experiments were grown in our laboratory by the Kyropoulos technique from ultrapure material or prepared by the zone refining technique.<sup>4)</sup> Blocks of  $15 \times 15 \times 25 \text{ mm}^3$  in size were additively colored with distilled potassium in an evacuated Supremax or Vycor tube, to a concentration of  $3 \times 10^{16}$  to  $3.2 \times 10^{17}$  F centers/cm<sup>3</sup>, depending on the experimental requirements. Cleaved crystals, taken from the middle of the block

<sup>3)</sup> A preliminary report of this work was presented at the Berkeley meeting of the APS (1968) [23].

<sup>4)</sup> We are indebted to the Crystal Laboratory of the II. Physikalisches Institut der Universität, Stuttgart, for a zone-refined KCl crystal rod.

were heated and quenched on a copper block under a dry nitrogen atmosphere and immediately transferred into a Janis stainless steel dewar equipped with a detachable variable temperature tail.

The absorption measurements were carried out in a Cary Model 14R spectrophotometer, in which the polarized light was obtained by inserting in the sample and the reference beam different sheets of Polaroid plastic laminated polarizers (type HNP'B for the UV, HN38 for the visible and HR for the IR). This restricted the polarized measurements to the wavelength range from 270 nm to 2  $\mu\text{m}$ .

For the measurement involving the kinetic of formation and bleaching of  $F_2^+$  center and the excitation of its luminescence the monochromatic excitation light was provided by a high intensity Bausch and Lomb grating monochromator. The light was focused on the crystal by an achromatic condenser lens and its intensity kept at a constant level by a rotatable venetian blind light attenuator and controlled by a Kodak Ektron detector. The visible luminescence at 600 nm was analyzed at right angles to the excitation beam either by a broad band interference filter centered at 605 nm or by another Bausch and Lomb monochromator with a visible grating (350 to 800 nm). In the last case a Schott (OG1) filter was also used in order to cut the possible overlapping second order of the scattered excitation light. The detector was an EMI 9558QA photomultiplier cooled at dry ice temperature.

Optimum signal to noise ratio was achieved by using a lock-in signal processing technique. The UV excitation light was chopped at 37 Hz by an adequate (OG1 Schott) filter, which is transparent in the range of the visible emission, mounted on a vibrator. This technique practically eliminates the chopping of all the stray light having a wavelength longer than 550 nm.

### 3. The Optical Absorption of M Centers

The model of the M center, a pair of F centers in the next nearest neighbouring (110) position (" $F_2^+$  model") is secured beyond any doubt by a large number of investigations. (See for instance the review articles by Compton and Rabin [12] and Fowler [13].) As there are six possible M center orientations (parallel to the six equivalent  $\langle 110 \rangle$  directions, Fig. 1a), any optical experiment on macroscopic M center systems depend on the distribution of centers among these directions. Experimental geometry and anisotropy of macroscopic optical experiments will

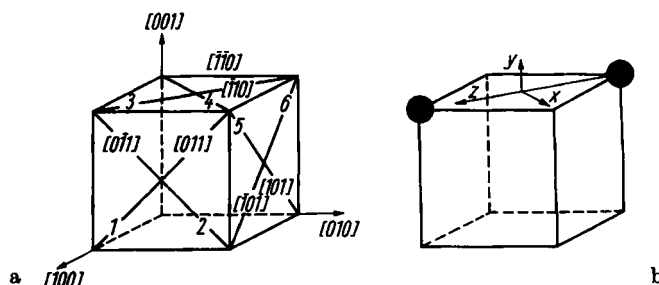


Fig. 1. a) The six equivalent  $\langle 110 \rangle$  orientations of the M center shown in a crystal coordinate system. b) The center coordinate system with perpendicular axes  $x$ ,  $y$ , and  $z$ . The main optical transition moments should lie parallel to these three axes

therefore be described best by a "crystal coordinate system" with the usual notation for crystal directions. With the knowledge about the specific M center distribution used, one can try to derive from these macroscopic results the microscopic anisotropic optical properties of a single M center, which are then best described in a "center coordinate system" with perpendicular axes  $x$ ,  $y$ , and  $z$  (Fig. 1 b). The analysis of the dichroic absorption spectrum of a partially aligned M center system by Okamoto [14] and later by Haarer and Pick [15] showed that the main optical transitions of the M center in KCl consist of three excitations at 801, 546, and 538 nm, polarized parallel to the  $z$ -,  $x$ -, and  $y$ -directions of the center respectively. These transitions correspond to the threefold degenerate  $1s \rightarrow 2p$  transition of the F center split by the lowered  $D_{2h}$  symmetry of the M center. The measurements of these authors as well as those by Hirai and Hashizume [16] also indicate the presence of absorption structure associated to transitions from the ground state to higher excited states of the M center.

The purpose of this section is to present a more detailed study of these transitions lying on the high energy side of the F band and extended in an energy range not previously covered by the earlier works. In order to overcome the difficulty to measure accurately very high and very low optical density, a "sandwich technique" was used throughout the measurement. A crystal containing  $3.2 \times 10^{17}$  F center  $\text{cm}^{-3}$  was cut in three pieces of  $10 \times 5 \times 0.5$  mm<sup>3</sup> in size, and then each part prepared in the same manner. They were separately measured in order to get the high optical density (OD) and afterwards clamped together in order to measure the low optical density absorptions.

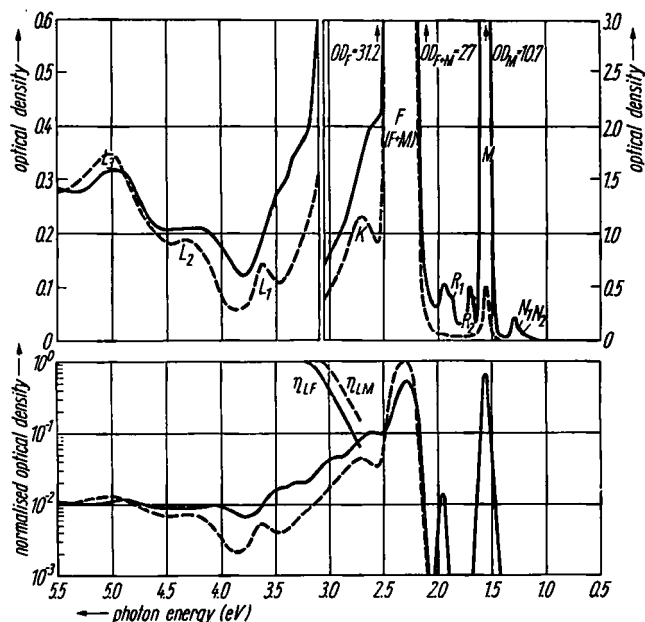


Fig. 2. The upper part of the figure shows the measured absorption spectra at 7 °K of a block of three KCl crystals ( $N_F = 3.2 \times 10^{17} \text{ cm}^{-3}$ ,  $d = 1.78$  mm) additively colored and quenched (broken line) and after subsequent F  $\rightarrow$  M conversion (solid line). The lower part of the figure is the logarithmic plot of the absorption spectrum of a pure F center system (broken line) and a pure undichroic M-center system (solid line) in a KCl crystal at 7 °K and both normalized to the same number of electrons. The energy dependence of the quantum efficiency  $\eta_F$  and  $\eta_M$  for photoelectron production of the F center is also shown (see Section 5.1 and Fig. 5)

### 3.1 Absorption spectrum of unaligned M centers

The broken line on the upper part of Fig. 2 shows the experimental absorption at 7 °K of a carefully quenched block of three crystals. The F, K,  $L_1$ ,  $L_2$ , and  $L_3$  bands are clearly observed. On the low energy side a small M band appears but practically no R or N centers are observed. As Lüty [8] established that the ratio of the absorption constant of the K and F band was a constant independent of the concentration and equal to 0.046 for KCl at LNT, the height of the F band at LHeT was determined as follows:

$$OD_F(\text{LHeT}) = \frac{OD_K(\text{LNT})}{0.046} \frac{W_F(\text{LNT})}{W_F(\text{LHeT})} = 31.2,$$

where the  $W_F$  are the half width of the F band at LNT or LHeT. In order to obtain a uniform M-center system and also the lowest admixture of other aggregate F centers, the F → M conversion was performed at -10 °C by shining on both sides of each crystal monochromatic light into the low energy side of the F band in a region where the OD was always as low as 0.4.

The final experimental result of this optical conversion is shown at LHeT by the solid curve on the same figure (Fig. 2). It is worthwhile to point out that with this technique a very good F → M conversion was achieved and that the height of the R and N band was kept at a minimum with the ratio  $K_{M_1}/K_{R_2} \approx 20$ . By assuming that the Smakula relation is valid for F and M centers and that all the F centers used for the aggregation have only formed M centers, we can subtract from the experimental solid curve the amount of the absorption due to the remaining F centers left in the crystal. If

$$\left. \begin{aligned} A &= \frac{[F]_{\text{initial}}}{[M]_{\text{final}}} = \frac{f_{M_1}}{f_F} \frac{OD_{F(\text{initial})} W_F}{OD_{M_1(\text{final})} W_M}, \\ [F]_{\text{final}} &= [F]_{\text{initial}} \left(1 - \frac{1}{A}\right). \end{aligned} \right\} \quad (1)$$

The relative oscillator strength per electron of the  $M_1$  transition for randomly oriented M center used [7] is  $f_{M_1} = 0.21 f_F$ . From the spectrum thus obtained the very small amount of the R and N bands was subsequently subtracted by using the data of Okamoto [14].

The final result is shown on the lower part of Fig. 2 in a logarithmic plot. The broken line represents the measured absorption spectrum of a pure F-center system, while the solid line is the absorption spectrum of a pure M center system calculated with the described method from the measured curves. Both spectra are normalized to the same number of electrons.

We see very clearly that an extended absorption structure appears in the energy range above 2.5 eV. As this absorption is produced by M centers of six different  $\langle 110 \rangle$  orientations, each of them having optical transition moments in three perpendicular directions ( $x, y, z$ ) relative to its center axis, only the study of the dichroic properties of this absorption can lead to identification of absorption bands and their assignment to specific M center transitions.

### 3.2 Absorption spectrum of aligned M Centers

The study of the dichroic difference spectrum of a partially aligned M center system, as it was used in recent investigations [14, 15] eliminates with security all absorption contributions from other isotropically absorbing or unaligned

centers. It does however not always allow the separation into the three absorption spectra of the center for its three basic polarization directions  $x$ ,  $y$ , and  $z$ . Using a nearly fully aligned M center system and combining three experimental absorption measurements we can achieve such a separation. By referring to Fig. 1 a the almost perfect alignment was achieved by shining [011] monochromatic polarized light at 495 nm along the [100] direction at  $-150^\circ\text{C}$  (or some times LNT) during several hours. The centers were found to be aligned with their axes in the [011] crystallographic direction. From the symmetry of the irradiation procedure it follows that the relative concentration  $n_i$  in each of the six possible orientations is given by

$$n_1 \neq n_2 \neq n_3 = n_4 = n_5 = n_6 \quad \text{with} \quad \sum_{i=1}^6 n_i = 100\% . \quad (2)$$

The absorption coefficient at the peak of the  $M_1$  band measured with [011] or [011] polarized light traveling in the [100] direction is given by

$$\left. \begin{aligned} K_{M_1}[011] &\propto n_1 + \frac{1}{4}(n_3 + n_4 + n_5 + n_6) , \\ K_{M_1}[0\bar{1}1] &\propto n_2 + \frac{1}{4}(n_3 + n_4 + n_5 + n_6) . \end{aligned} \right\} \quad (3)$$

However since our experimental ratio  $K_{M_1}[011]/K_{M_1}[0\bar{1}1]$  was greater than 20 we have simplified the following discussion by the well-justified approximation that our distribution is given by

$$n_1 \neq n_2 = n_3 = n_4 = n_5 = n_6 . \quad (4)$$

With this approximation the relation (3) allows us to determine the relative concentration  $n_i$  of our system, which we find in our case to be

$$n_1 = 89\% , \quad n_2 = n_3 = n_4 = n_5 = n_6 = 2.2\% .$$

With the knowledge about the distribution of M center orientation  $n_i$ , the three basic absorption spectra  $K_x(E)$ ,  $K_y(E)$ , and  $K_z(E)$  can be determined by the measurement of the three following experimental spectra. (For each of them the contribution of the F center and the very small amount of R and N center absorption was subtracted):

1. For [011] polarized light traveling along the [100] direction:

$$K[011](E) = \alpha K_z(E) + \beta K_x(E) + \gamma K_y(E); \quad (5)$$

2. For [011] polarized light traveling along the [100] direction:

$$K[0\bar{1}1](E) = \beta K_z(E) + \alpha K_x(E) + \gamma K_y(E); \quad (6)$$

3. For [100] polarized light traveling along the [010] direction:

$$K[100](E) = B[\gamma K_z(E) + \gamma K_x(E) + \alpha K_y(E)]; \quad (7)$$

with

$$\begin{aligned} \alpha &\propto n_1 + \frac{1}{4}(n_3 + n_4 + n_5 + n_6) = 91.2\% , \\ \beta &\propto n_2 + \frac{1}{4}(n_3 + n_4 + n_5 + n_6) = 4.4\% , \\ \gamma &\propto \frac{1}{2}(n_3 + n_4 + n_5 + n_6) = 4.4\% , \end{aligned}$$

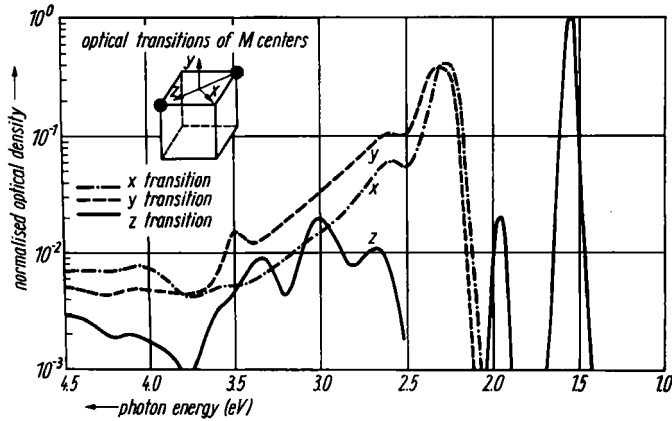


Fig. 3. Logarithmic plot of the corrected absorption spectra of a completely aligned M-center system in KCl at 7°K measured in the  $x$ -,  $y$ -, and  $z$ -directions of the center coordinate systems. The height of the  $M_1$  transition at 1.55 eV is normalized to 1

and  $B$  the appropriate ratio of the crystal thickness in  $[010]$  and  $[100]$  directions. We get finally a graphic representation for a set of three equations with three unknown quantities  $K_x(E)$ ,  $K_y(E)$ ,  $K_z(E)$  which is easily solved.

The final result of this graphical analysis is shown in Fig. 3. The spectral dependence of the three  $x$ ,  $y$ , and  $z$  absorption spectra of the M center in KCl crystals is plotted using a logarithmic scale with the height of the  $M_1$  band at 1.55 eV normalized to 1.

#### 4. Model for the Formation and Bleaching Kinetics of $F_2^+$ Center in KCl

The analysis in Section 3 clearly shows that M centers, similar to F and  $F_A$  centers, possess an extended absorption structure throughout the UV range, corresponding to electronic transitions from the M center ground state to higher excited M states. As the M center ground state will lie in the band gap at an

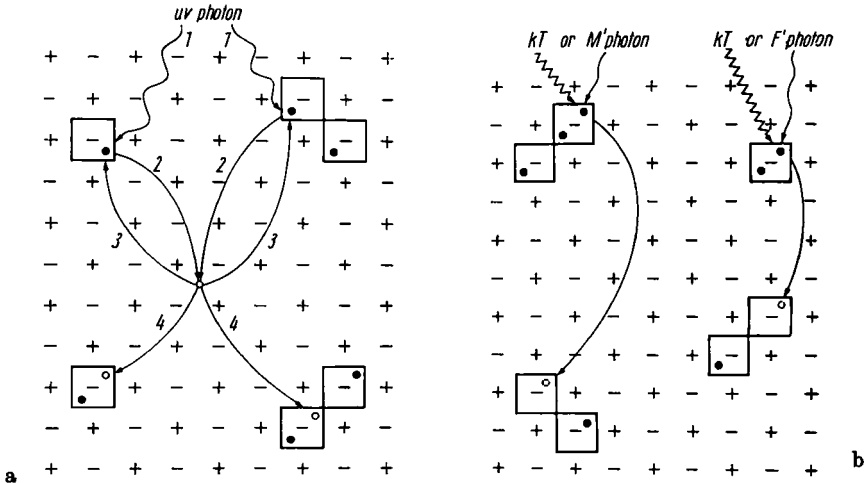
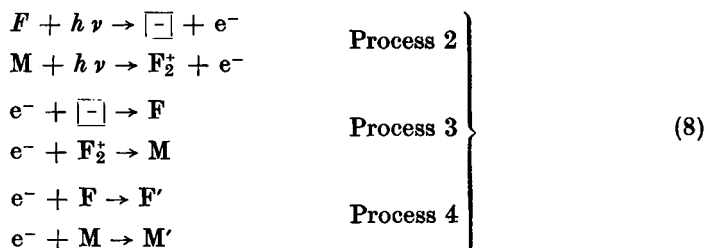


Fig. 4. Schematic description of the basic kinetics leading to the formation and destruction of  $F_2^+$  centers in pure additively colored KCl crystals. a) Formation process. b) Optical or thermal destruction

energy similar to that of the F center one can expect from parallelity to the L bands of the F center that excitation into the "L<sub>M</sub>" bands will lead into conductive states. The threshold energy for the onset of this ionizing transition will thus be expected to be close to that of the F center ( $\approx 3$  eV).

With the quantitative knowledge about these higher "conductive" M center transitions, a mechanism for the production of F<sub>2</sub><sup>+</sup> centers by direct photoionization can be readily predicted including its expected production and destruction spectrum. The most simple and clear case, using an ideal crystal containing only F̄ and M centers is schematically illustrated in Fig. 4a. By shining at low temperature monochromatic UV light on the crystal (process 1), we remove electrons from the F and the M centers (process 2). These free electrons can obviously recombine either with the ionized centers (process 3) or with existing F or M centers (process 4) leading to the formation of F' and M' center. In other terms:



We can easily derive the kinetic equations governing the formation of F<sub>2</sub><sup>+</sup> centers. (The following relations are valid for small absorption constants  $K$ , which where in fact present in the L band region):

$$[\dot{F}_2^+] = I K_M \eta_M - \alpha_{F_2^+} [F_2^+] [e^-], \quad (9a)$$

$$\begin{aligned}
 [\dot{e}^-] = I (K_F \eta_F + K_M \eta_M + K_{F'} + K_{M'}) - \\
 - [e^-] (\alpha_{\square} [\square] + \alpha_F [F] + \alpha_{F_2^+} [F_2^+] + \alpha_M [M]), \quad (9b)
 \end{aligned}$$

where  $I$  is the intensity of the light,  $K_F$  or  $K_M$  the absorption constant of the F or M bands respectively,  $\eta_F$  or  $\eta_M$  the quantum efficiency for the photoelectron production in the F or M bands respectively,  $\alpha_i$  the electron capture cross section for  $i = \square, F, F_2^+$  or M center, respectively.

By using the steady state condition given by

$$[\dot{F}_2^+] = [\dot{e}^-] = 0 \quad (10)$$

we find finally that the number of F<sub>2</sub><sup>+</sup> centers created with this mechanism by light irradiation of various wavelengths is expected to be

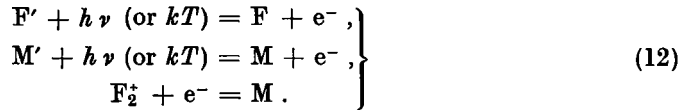
$$[F_2^+] = \frac{K_M \eta_M}{K_F \eta_F + K_{F'} + K_{M'}} \frac{\alpha_{\square} [\square] + \alpha_F [F] + \alpha_M [M]}{\alpha_{F_2^+}}, \quad (11)$$

where all the quantities  $[\square]$ ,  $[F]$ ,  $[M]$ ,  $[F']$ , and  $[M']$  are the steady state values obtained in dynamic equilibrium under UV irradiation.

The first factor in the product determines the relative spectral dependence of the F<sub>2</sub><sup>+</sup> center production, while the second part determines its magnitude. If we assume, as discussed before, a full photoelectron production  $\eta_M = \eta_F = 1$  for energies above  $\approx 3$  eV and neglect the small amount of F' and M' absorption



in this energy range, we expect the spectral dependence of the  $F_2^+$  center production to vary roughly with the absorption ratio  $K_M:K_F$ . Similarly one can easily derive from the kinetic equations (8) and (9) that the spectral dependence of the initial slope of the  $F_2^+$  center production is expected to be proportional to  $I K_M \eta_M$ . As the electron excess centers ( $F'$  and  $M'$ ) are the stabilizing anti-centers of the electron deficiency centers ( $\alpha$  and  $F_2^+$ ), we expect the optical destruction spectrum for  $F_2^+$  centers to follow the  $F'$  and  $M'$  bands. On the other hand, if the ionized centers themselves are stable to high enough temperatures, their effective thermal stability in this system should be limited by that of the  $F'$  and  $M'$  centers. Thus the thermal and optical destruction could be described by the following processes (Fig. 4 b):



The introduction of extra electron traps T (with electron capture cross section  $\alpha_T$ ) leads obviously to an increase of the amount of  $F_2^+$  centers, without changing the spectral dependence of the production process. The relations (9b) and (11) must be simply modified by the addition of a supplementary term  $\alpha_T[T]$ . In such a case however the optical and thermal stability of these extra  $F_2^+$  centers should be different and limited by that of their corresponding stabilizing anti-centers.

The outlined mechanism is based on direct photoionization of M centers and stabilization of the formed  $F_2^+$  centers by proper electron traps. In contrast to this the formation mechanism proposed by Schneider and Rabin [1] would give the following predictions:

1. The  $F_2^+$  center formation should not be possible in a merely additively colored crystal, which contains M centers but does not contain hole centers.
2. The formation spectrum for  $F_2^+$  centers should follow the spectral shape of the H or  $V_K$  band.

It is clear from the above discussion that an analysis of the formation and destruction spectrum for  $F_2^+$  centers and the determination of their effective thermal stability can clearly identify and distinguish the two mechanisms.

### 5. Experimental Investigation of the Formation and Bleaching Kinetic of $F_2^+$ Centers

$F_2^+$  centers in KCl can be identified by a characteristic absorption band at  $1.38 \mu\text{m}$ , which (together with its Stokes shifted emission band at  $1.67 \mu\text{m}$ ) was so far the only known optical transition of this center. We shall show however in part II of this work [11] that the  $F_2^+$  center has several other absorption transitions in the visible and near UV, which, when excited, produce at low temperature a red luminescence near 600 nm. For obvious experimental convenience only, we used this red emission as the identification of the amount of the  $F_2^+$  centers created or present in the sample. We must point out that the same results could be obtained by measuring the already known near IR absorption band at  $1.38 \mu\text{m}$ . The use of the 600 nm emission however allowed the detection of at least two orders of magnitudes lower concentrations of  $F_2^+$  centers as compared to the detection limit of the  $1.38 \mu\text{m}$  absorption.

### 5.1 Investigation in pure additively colored crystals

The first measurements involved pure additively colored KCl crystals with various  $[M]:[F]$  center ratios. UV irradiation of these crystals at temperatures below 150 °K indeed produces directly  $F_2^+$  centers, in accordance with the mechanism described previously. The production spectrum was determined by irradiating monochromatic light of constant quantum flux between 2.0 and 5.0 eV and measuring for each wavelength the final saturation value of the 600 nm emission. The relative spectral variation of this quantity at 7 °K is given by the full line in Fig. 5. As discussed in Section 4, we expect this  $F_2^+$  center saturation value to vary in its spectral dependence like the ratio of the M and F center absorption  $K_M:K_F$  in the range of full photoionization  $\eta_M = \eta_F = 1$  (see equation (11)). The broken line in Fig. 5 is a plot of this (arbitrarily scaled)  $K_M:K_F$  ratio, calculated from the experimental curves of Fig. 2. As can be seen, the  $F_2^+$  production spectrum follows the  $K_M:K_F$  spectrum very closely, the discrepancy between the relative ordinate values of both curves being smaller than a factor of two over the whole spectral range. This agreement can be improved further in the low energy range where the photoionization probability  $\eta_{LM}$  should no longer remain equal to one. Using the unknown  $\eta_{LM}(E)$  as an adjustable spectral function in the relation

$$[F_2^+] \propto \frac{K_M \eta_{LM}}{K_F \eta_{LF}}$$

a better fit (dash-broken line in Fig. 5) can be obtained to the measured behavior with an assumed spectral dependence of  $\eta_{LM}$  as shown in the lower part of Fig. 2. The shape of this  $\eta_{LM}$  curve looks identical to the known spectral dependence of  $\eta_{LF}$ , shifted by about 0.15 eV to higher energies. This result looks quite reasonable in view of the fact that the absorption transitions for the two centers in this spectral range, the  $K_M$  and  $K_F$  bands, are relatively displaced by the same energy amount.

On the right side of the figure the solid line is the experimental spectral dependence of the bleaching spectrum of the  $F_2^+$  center in KCl, obtained by taking the slopes of the bleaching curves of the 600 nm luminescence at 7 °K. This bleaching spectrum follows almost perfectly the  $F'$  absorption spectrum

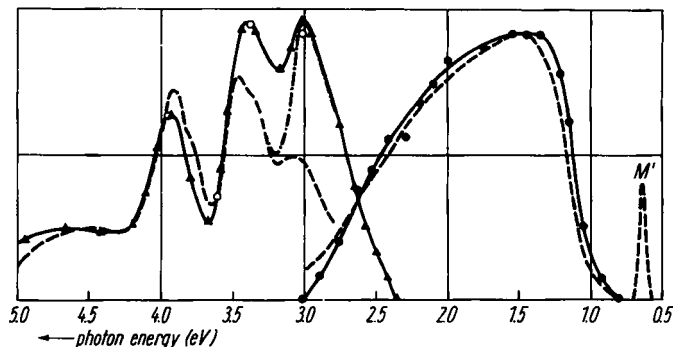


Fig. 5. Spectral dependence of the optical  $F_2^+$  center production and bleaching process. Left side: Measured production spectrum (full line) for a purely additively colored crystal ( $\blacktriangle$ ) and a similar crystal, X-rayed for 2 h at LHeT ( $\circ$ ). For comparison is plotted the  $K_{LM}/K_{LF}$  spectrum (dashed line), and the same corrected with the  $\eta_{LM}/\eta_{LF}$  ratio, (dash-broken line), using  $\eta_{LM}$  and  $\eta_{LF}$  as given in Fig. 2. Right side: Measured  $F_2^+$  bleaching spectrum (full line) as compared to the  $F'$  absorption spectrum (dashed line);  $T = 7$  °K

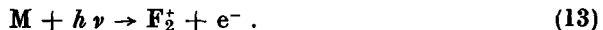
(broken line). Similarly, bleaching with monochromatic light of  $2 \mu\text{m}$  in the range of the  $M'$  band (see Fig. 5) bleaches the  $F_2^+$  center emission too (for reasons of too limited sensitivity no detailed bleaching spectrum was measured for this case). The observed effective thermal stability of the  $F_2^+$  centers confirms the model further: As will be shown in more detail in part II, the  $F_2^+$  centers created by this method are destroyed thermally around  $200^\circ\text{K}$  in parallelism with thermal ionization of the  $F'$  centers.

In summary both the production and destruction behavior of the  $F_2^+$  centers are in excellent agreement with the model presented in Section 4, experimentally verifying beyond question the validity of the proposed mechanism.

### 5.2 Formation kinetics of $F_2^+$ centers X-irradiated at LHeT

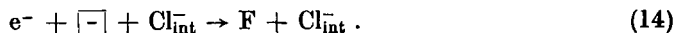
The second class of experiments involved the same additively colored crystals (as used in Section 5.1) containing M and F centers. The crystals, however, were in addition X-rayed for periods of 1 to 3 h at LHeT (50 kV, 20 mA) through two thin aluminum windows. After this treatment some  $F_2^+$  centers were already formed and detected by measuring the  $1.38 \mu\text{m}$  absorption. This was not an unexpected result since  $F_2^+$  centers could be expected to be produced either directly under X-rays by a statistical production or by X-ray ionization of the M centers present in the crystal. Monochromatic light from the region of the  $F_2^+$  center production spectrum near 3.0 eV was then irradiated on the crystal. The result of this UV irradiation is the formation of  $F_2^+$  centers in much higher amount than achieved in the non X-rayed crystals. For example an increase by a factor of 25 may easily be obtained after one hour X irradiation in a medium colored crystal with a high M to F ratio.

A check of the production spectrum at four different wavelengths (open circles in Fig. 5) shows full coincidence with that of the additively colored crystal, discussed in Section 5.1, which means it follows again closely the  $K_M:K_F$  ratio. There is not any indication that an increase of the  $F_2^+$  center photo-production is connected with the position of the H or  $V_K$  band. This definitely rules out the mechanism proposed by Schneider and Rabin [1], and shows that the primary part of the  $F_2^+$  production process is the same as in the non X-irradiated crystal, namely the direct photoionization of M centers:



Following (11), the strong increase of the observed  $F_2^+$  formation can therefore only be caused by the introduction of a large amount of extra electron traps by the X-ray process. What are these traps?

It is now well established (see e.g. the recent review article by Crawford [17]) that the main result of low temperature X irradiation is the formation of Frenkel defects. One part of these defects are charged Frenkel pairs, anion vacancies  $[-]$  and interstitial ions  $\text{Cl}_{\text{int}}^-$  (see process 1, Fig. 6a). When M centers are photoionized in such a crystal (process 2, Fig. 6a) the free electrons can efficiently be trapped by the vacancies of the X-ray produced Frenkel pairs (process 3):



However, following an idea introduced by Lütty [18] such a capture process should be possible only for "non-correlated" Frenkel pairs, as for a correlated Frenkel pair the Coulomb field from the close lying interstitial should prevent the capture process through the excited F state by electrical field ionization.

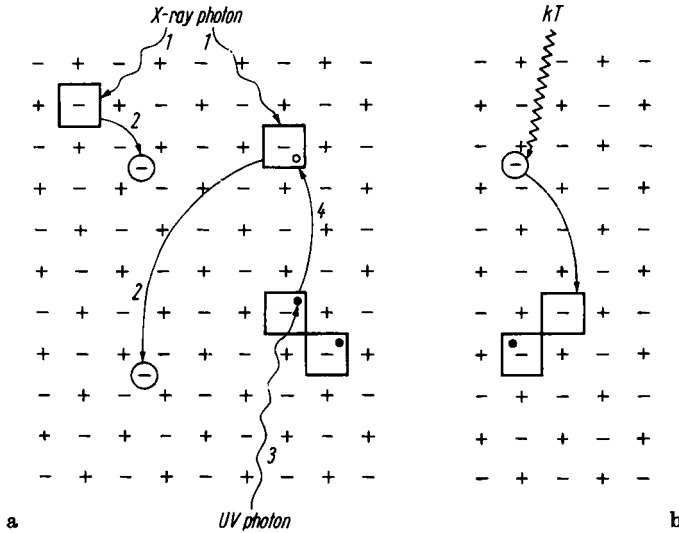
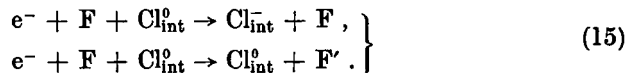


Fig. 6. Schematic description of the formation and destruction of  $F_2^+$  centers in an additively colored KCl crystal X-rayed at LHeT. a) Formation process, involving electron capture at anion vacancies. b) Thermal destruction of the  $F_2^+$  centers by mobile interstitial anions

Besides vacancies and interstitial ions, neutral Frenkel pairs (F and H centers) are created by the X-irradiation; (the latter are, chemically speaking, interstitial chlorine atoms  $Cl_{int}^0$ ). They give rise to additional possibilities for electron capture:



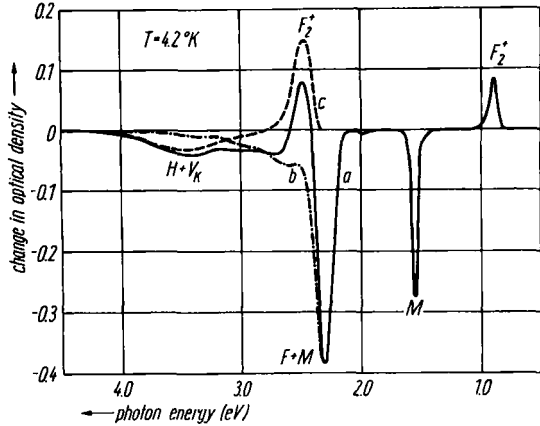
The first process leads to the same products as the reaction of the electron with the charged Frenkel pairs (equation (14)), namely  $Cl_{int}^-$  and F centers. The second process on the other hand leads to the same type of products as the reaction of the electron with the F and M centers from additive coloration, namely  $F'$  and  $M'$  centers.

As IR irradiation can destroy the  $F'$  and  $M'$  centers, it will bleach (like in the case of the additively colored crystal in Section 5.1) all  $F_2^+$  centers, stabilized by these anticenters. Experimentally it is found in the X- and UV-irradiated crystal that only a very small fraction of the  $F_2^+$  centers (typically 4% after one hour of X irradiation) can be bleached by  $F'$  and  $M'$  light. In all experiments discussed below, this small fraction of  $F_2^+$  centers stabilized by  $F'$  and  $M'$  centers, was removed optically.

The main part ( $\approx 96\%$ ) of the  $F_2^+$  centers however is found stable against any light irradiation with wavelengths longer than 610 nm. This clearly demonstrates that different types of anticenters are involved in their stabilization, which do not absorb light in this spectral range.

Fig. 7 shows the measured change in the absorption spectrum caused by 410 nm irradiation in a KCl crystal previously X-rayed at LHeT for two and one-half hours (curve a). It shows clearly the formation of the  $F_2^+$  center absorption at  $1.38 \mu m$  at the expense of the M band. Since we know quantitatively

Fig. 7. Change in the absorption spectrum of an additively colored KCl crystal X-rayed at LHeT, produced by 410 nm light irradiation (curve a). After subtracting the F and M contribution (curve b), the remaining spectrum c = a - b contains the increase of the  $F_2^+$  center spectrum (bands at 0.9 and 2.5 eV) and the decrease of the H +  $V_K$  centers spectrum



vely the absorption spectrum of both F and M centers in the visible and UV range (see Fig. 2 and 3), a graphical decomposition of the observed difference spectrum in this range is also shown. The curve b refers to the change due to the F and M centers contribution while the dashed curve c is the difference between the curves a and b. The increase observed around 500 nm, as will be discussed in more detail in part II of this work [11], is due to a higher  $F_2^+$  center absorption transition.

**5.3 Bleaching kinetics of  $F_2^+$  centers in crystals X-rayed at LHeT**

A study of the thermal annealing of the  $F_2^+$  centers created by the above method confirms our model further. We expect that the  $F_2^+$  centers should become irreversibly destroyed in the temperature range where thermal migration of the free anion interstitial takes place (Fig. 6b). Thus mobile interstitials should anneal out all anion vacancies irrespective if they are isolated ( $\alpha$  centers) or associated with an F center ( $F_2^+$  centers):

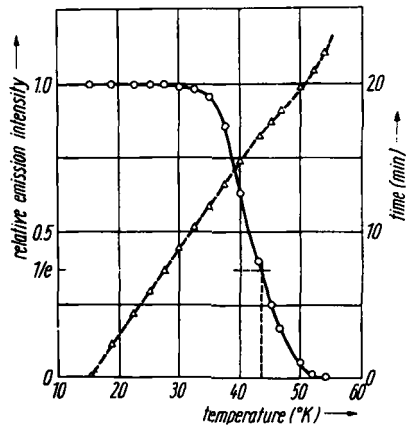
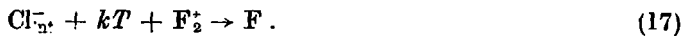
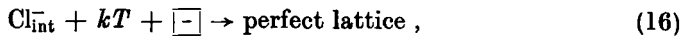


Fig. 8. Temperature dependence of the relative concentration of  $F_2^+$  centers, created after X-rays and 410 nm irradiation in an additively colored KCl crystal, as measured by the intensity of their 600 nm emission (with a heating rate of 1.7 deg/min)

Fig. 8 shows the annealing behavior of the  $F_2^+$  centers created by X-ray and UV irradiation. The observed temperature of maximum annealing rate (43 °K), for a heating rate of about 1.7 °K/min) coincides well with the last annealing stage of anion vacancy interstitial pairs in KCl, corresponding to the recombination of non-associated Frenkel pairs [19, 20].

An explicit check can be made which excludes any contribution of the associated Frenkel pairs (annealing below 32 °K) to the electron capture and  $F_2^+$  center stabilization process. If a crystal after X-irradiation is pulse-annealed to 32 °K (thus destroying all associated Frenkel pairs), the subsequent UV irradiation creates accurately as many  $F_2^+$  centers as in case without pulse annealing. In spite of the fact that the number of associated Frenkel pairs is much higher (about 14 times [19]) than that of the unassociated Frenkel pairs, no electron capture (i.e.  $F_2^+$  center stabilization) takes place at the close pairs; this gives a very direct experimental proof for the hypothesis [18] that electrons can only be captured in vacancies of the last annealing stage, corresponding to unassociated Frenkel pairs.

The optical  $F_2^+$  production thus allows to differentiate unassociated from associated Frenkel pairs and to observe them separately. The electron transfer process (by UV irradiation) from the M center to an anion vacancy of a last stage Frenkel pair exchanges the isolated anion vacancy ( $\alpha$  center) into an "anion vacancy with a next nearest neighbour F center" ( $F_2^+$  center). In principle this allows to study the annealing of the last stage Frenkel pairs by that of the  $F_2^+$  centers (with much higher accuracy than by measuring the small last stage  $\alpha$  band annealing). A quantitative analysis of this measured  $F_2^+$  center annealing from Fig. 8 shows that this process is best described by a second-order reaction (Fig. 9). This is the expected result for the recombination of the unassociated mobile interstitials with an equal number of vacancies ( $\alpha$  and  $F_2^+$  centers). The obtained activation energy of  $\Delta E = 0.049$  eV should characterize the free interstitial motion. Behr et al. [19] were not able to determine this value from the small third stage  $\alpha$  center annealing curve. Our obtained value is, as expected, slightly higher than those measured for the first two annealing stages involving correlated Frenkel pairs. (Calculated values for the motion of  $Cl_{int}^-$  in

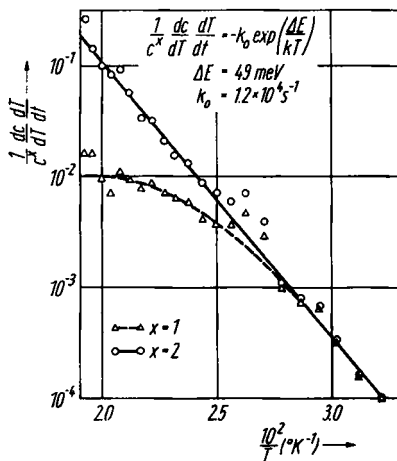
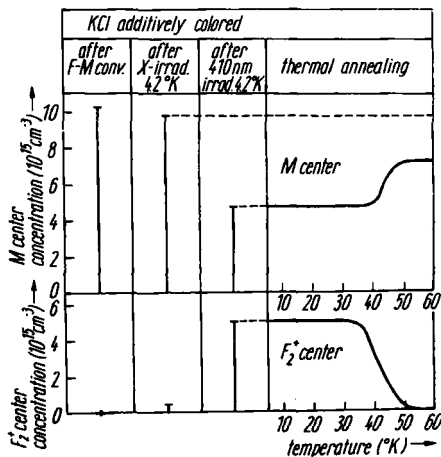


Fig. 9. Activation energy  $\Delta E$  and order of the reaction  $x$  for the thermal annealing of  $F_2^+$  centers created after X-rays and 410 nm irradiation in a pure additively colored KCl crystal

Fig. 10.  $F_2^+$  and M center concentration, as measured after the three processes leading to the  $F_2^+$  formation (F → M conversion, X irradiation and UV irradiation) and during subsequent thermal annealing

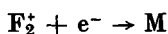
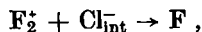


KCl are 0.17 and 0.44 eV using a Born-Mayer and Born-Mayer-Verwey potential, respectively [21]).

The described bleaching kinetics, based on the thermal motion of  $Cl_{int}^-$  and their recombination with empty vacancies ( $\alpha$  and  $F_2^+$  centers) only, turned out by further experiments to be oversimplified. A consequence of this simple kinetics would be the parallel annealing of  $Cl_{int}^-$  and  $F_2^+$  without any increase of the M band, and with an appropriate increase of the F band, as given by (17). An experimental check of the  $F_2^+$  and M absorption during this process (Fig. 10) showed, however, a partial recovery of the M band during  $F_2^+$  annealing. Furthermore the F band increase was found smaller than predicted by (17). The only possibilities to account in this temperature range for the observed increase of the M band are the reactions



The amount of  $F_3^+$  centers present in the crystal (formed not intentionally from the small amount of R centers by optical ionization parallel to the M center ionization process), is more than an order of magnitude too low to account for the observed M increase. Thus we are left with the electronic capture process (18). The measurement of Fig. 10 was repeated several times under somewhat varied conditions, and always gave an M center increase roughly one-half of the  $F_2^+$  center decrease. Thus apparently an equal amount of the two reactions (17) and (18)



can account for the observed behavior. The first reaction is the simple interstitial recombination mechanism, discussed above. We have to postulate now that during this process free electrons are available in the crystal too, accounting for the second process. As sources for this electron one can visualize two possibilities:

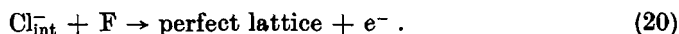
a) Some unknown extrinsic electron traps, which were filled during the prior optical M ionization process release electrons at about 40 °K.

b) Intrinsic defects (like F centers or  $\text{Cl}_{\text{int}}^-$ ).

The first possibility can be ruled out with high probability. Experiments of the type in Fig. 10 with crystals from reagent grade, ultrapure and highly zone-refined material gave practically identical results for the ratio of M band increase to  $\text{F}_2^+$  decrease. Moreover we will show elsewhere [22] that when using extrinsic ( $\text{H}^-$ ) interstitials for recombination with  $\text{F}_2^+$  centers, a similar (but in this case much weaker) admixture of electronic capture process takes place leading to an M band increase. It seems highly unlikely that in both cases extrinsic electron traps would release electrons in exact parallelity to the interstitial recombination process.

Thus we are left with the necessity to assume some electron release mechanisms from intrinsic defects parallel to the interstitial migration and recombination process. For a possible release mechanism one can first suspect photoionization of F centers by thermo-luminescence, because KCl crystals X-rayed at LHeT show indeed a thermo-luminescence in the 40 °K range. We observed, however, that by the UV irradiation of the X-rayed crystal (which makes the M center ionization and bleaches out the  $\text{V}_\text{K}$  and H centers) this thermo-luminescence becomes strongly suppressed and even completely quenched. Independent of this strength of the luminescence, we find the same amount of the electronic process (18).

The most likely and reasonable nonradiative induced electron release process from intrinsic defects would be the reaction of a mobile  $\text{Cl}_{\text{int}}^-$  with an F center:



This process seems particularly likely, because in the prior optical M center ionization the released electrons were captured to a good part by H centers ( $\text{Cl}_{\text{int}}^0$ ) forming  $\text{Cl}_{\text{int}}^-$  (see Fig. 10 and equation (15)). As most H centers can be supposed to be located close to the F center, from which they were produced, we would thus have produced in the crystal a considerable amount of close lying  $\text{Cl}_{\text{int}}^-/\text{F}$ -center pairs. When the  $\text{Cl}_{\text{int}}^-$  become thermally mobile, the above reaction (20) would occur in parallelity to the  $\text{Cl}_{\text{int}}^-$  recombination with  $\alpha$  and  $\text{F}_2^+$  centers, while the released electrons from (20) account for the electronic destruction of  $\text{F}_2^+$  centers (18). The before-mentioned fact that the F band increase during the thermal reaction was found to be smaller than predicted by the reaction (17) can be explained by the superimposed F decrease due to reaction (20).

As in this interpretation the  $\text{F}_2^+$  decay around 40 °K is a superposition of an electronic (first order) and interstitial (second order) recombination process, the observed simple behavior (Fig. 8) indicating a single second order process is somewhat surprising, and the analysis in Fig. 9 loses somewhat its significance. More accurate measurements are under way to resolve in the  $\text{F}_2^+$  center decay the twofold nature of the process.

In summary we find that  $\text{F}_2^+$  center production and destruction in an crystal, X-irradiated at LHeT, can be consistently described by the following mechanism:

1. Direct photoionization of M centers, creating free electrons.
2. Electron capture by anion vacancies of unassociated Frenkel pairs or by H centers forming  $\text{Cl}_{\text{int}}^-$ .



3. Thermal destruction of the  $F_2^+$  centers by mobile interstitials  $Cl_{int}^-$ , either by direct capture of  $Cl_{int}^-$  or by the capture of electrons, released from  $Cl_{int}^-$ -F center recombination.

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