F-F' CONVERSION BY FLASH-LIGHT IRRADIATION OF ADDITIVELY COLORED KCl NEAR ROOM TEMPERATURE

M. Georgiev, T. Todorov

► To cite this version:

M. Georgiev, T. Todorov. F-F' CONVERSION BY FLASH-LIGHT IRRADIATION OF ADDITIVELY COLORED KCl NEAR ROOM TEMPERATURE. Journal de Physique Colloques, 1976, 37 (C7), pp.C7-89-C7-94. 10.1051/jphyscol:1976713 . jpa-00216853

HAL Id: jpa-00216853

<https://hal.science/jpa-00216853>

Submitted on 1 Jan 1976

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

F-F' CONVERSION BY FLASH-LIGHT IRRADIATION OF ADDITIVELY COLORED KCl NEAR ROOM TEMPERATURE

M. GEORGIEV

Institute of Solid State Physics, Bulgarian Academy of Sciences,
Sofia 1113, Bulgaria

and

T. TODOROV

Central Laboratory of Optical Information Storage and Processing,
Bulgarian Academy of Sciences, Sofia 1113, Bulgaria

Résumé. — La cinétique de la formation et de la décomposition des centres F' produits par un éclair lumineux intense dans du KCl coloré additivement a été étudiée pour des intensités et des durées d'excitation lumineuse différentes dans l'intervalle de température 290-350 K. Nous avons trouvé des preuves de l'existence d'un processus de désexcitation à activation thermique qui tend à faire baisser l'efficacité d'ionisation du centre F excité et à élargir la section efficace de piégeage de la lacune. Nous supposons que les probabilités de transition du centre F excité et les sections efficaces de piégeage d'électrons dépendent de l'intensité, de sorte que l'on puisse rendre compte de la dépendance observée du taux de production à niveaux d'excitation élevés par rapport à la température et à l'intensité. Des résultats analogues ont été obtenus pour des centres $F_A(\text{Na})$.

Abstract. — The yield and the decay kinetics of F' centers produced by an intense light flash in additively colored KCl are investigated at different excitation-light intensities and durations within the temperature range between 290-350 K. Evidence is found for the occurrence of a thermally-activated de-excitation process tending to decrease the ionization efficiency of the excited F center and to increase the trapping cross-section of the vacancy. Both the transition probabilities of the excited F center and the electron trapping cross-sections are assumed to be intensity-dependent to account for the observed temperature and intensity dependences of the yield at high excitation levels. Analogical results are obtained for the $F_A(\text{Na})$ centers.

The primary objective of this work was an experimental investigation of the transient changes in the absorption spectra of colored alkali halide crystals which occur on illumination in the F band near room temperature (RT). Under the experimental conditions employed the main changes resulted from the F - F' optical conversion. The present paper is aimed at summarizing all the collected data [1-7] and reconsidering their physical significance.

Experimental. — Inasmuch as the anticipated F' lifetime was rather short — the order of 10^{-3} s [8], the most promising way to initiate and study the F - F' conversion at RT was by excitation spectroscopy, e. g. using a flash-light excitation.

The experimental technique has already been described in detail [2]. The flash-lamp, energized at about 40 W.s, was operated in two modes to produce light flashes of about 1 ms and 40 μ s effective durations respectively; for the sake of brevity these shall be referred to correspondingly as « Long Flash (LF) » and « Short Flash (SF) ».

The samples were cleaved from large single crystals of KCl doped with about 0.1 mole % NaCl and colored additively to the order of 10^{17} F centers/cm³. The F - F' conversion was investigated in samples freshly quenched to RT following a 1-2 min thermal anneal at 400 °C to destroy aggregates and randomize the F centers. Parallel studies were performed of the F_A - F'_A conversion after a preliminary F_A center formation by optical bleach of the F band at RT.

Results. — That the transient absorption which occurred on flash-light excitation was due to $F'(F'_A)$ centers was verified in an investigation of the spectral distribution of ΔD . A typical result obtained by a rapid-scanning equipment is shown in figure 1 representing both the bleach in the F band range and the increase in absorption in the F' band range. The time-kinetics of the transient absorption were investigated at various flash-light intensities and temperatures, both for SF and LF excitation. Inasmuch as the time-resolution of the photodetecting unit was inadequate for a proper study of the rise in absorption during the

FIG. 1. — Spectrum of the optical density change induced by a light flash in a freshly-quenched sample, correspondingly at 5 ms and 25 ms after the excitation. The scan time was less than 60 μ s.

light pulse, the only information about the processes under light was obtained from the yield ΔD_m — the net change in optical density produced by the flash. At the same time the resolution was more than sufficient to secure a thorough analysis of the F'(F'_A) decay in the dark.

Within reasonable limits of reliability the decay of ΔD in the dark was found to follow the equation [3, 4]

$$t = A(\Delta D)^{-1} + B \ln \Delta D + C \quad (1)$$

where A , B and C are constants. This equation was exactly what was expected on the basis of the F-F' conversion model giving

$$A \propto (\sigma_F/\sigma_a)\tau_{F'}, \quad B \propto (1 - 2\sigma_F/\sigma_a)\tau_{F'};$$

here $\tau_{F'}$ is the thermal lifetime of the F' center, while σ_F and σ_a are the cross-sections for electron trapping at the F center and at the empty vacancy respectively.

The dependence of the yield ΔD_m on the excitation-light intensity at RT was investigated for both SF and LF (Fig. 2) [2, 7]. The yield first increased with

FIG. 2. — Dependence of the yield of the primed bands on the excitation-light intensity at room temperature for two flash-light durations: SF (10 μ s) and LF (1 ms).

the intensity I following the $I^{1/2}$ dependence but further gradually saturated. The corresponding dependences for the F'_A band exhibited the same general character. A more intriguing situation occurred with the temperature dependences shown in figures 3 and 4 where correspondingly the SF and LF yields both follow the Arrhenius functions but with different activation energies (0.41 eV, 0.21 eV), which are 2 : 1 in ratio. Apparently the same situation appeared in the F'_A case but the activation energies were generally lower (0.30 eV, 0.15 eV).

FIG. 3. — Temperature dependence of the SF yield for the F' band.

FIG. 4. — Same as figure 3 for the LF yield.

Perhaps not less intriguing are the temperature dependences of the decay kinetics. Figures 5 and 6 show the temperature behaviour of the *bimolecular decay parameter A* which is Arrhenius for both F'

FIG. 5. — Temperature dependence of the bimolecular decay parameter A for the F' band. F_0 — the initial F center density, $C_{F'}$ — the F' absorption cross-section, d — the sample thickness.

FIG. 6. — Same as figure 5 for the F_A band.

and F'_A but with activation energies too high (0.89 eV, 1.10 eV) to be ascribed to the corresponding thermal lifetimes alone. This suggests that σ_F/σ_α might also be temperature dependent. Though the second parameter B showed considerable scatter, an attempt was made to extract the values of σ_F/σ_α and τ_F from the data on A and B . Obtained in this way both the thermal lifetime and the cross-sections' ratio were found to drop steadily as the temperature was raised.

Discussion. — The observed thermal ionization energy of the F' center (0.42 ± 0.21 eV), obtained from the τ_F vs. reciprocal temperature plot, is, within the dispersion limits, not far from the values found by other authors [8-12] (0.50 eV (F' half-life) [8], 0.44 eV (from an analysis of photoconductivity data) [9], 0.50 eV (from the decay kinetics based on the assumption $\sigma_F/\sigma_\alpha = 0.5$ between 200-250 K) [10], 0.53 eV (from an analysis of the decay kinetics based on the assumption of a variable F' lifetime) [11], 0.42 eV (from an early analysis of photoconductivity data) [12].

The increased F'_A ionization energy (0.75 ± 0.05 eV) found presently seems consistent with the larger optical depth of the F'_A level below the conduction band. As mentioned above, the considerable dispersion in the present ionization energy data reflects mainly the scatter in the temperature data on B . A possible source of this scatter will be discussed later.

There are all reasons to believe that the observed temperature dependence of σ_F/σ_α arises from σ_α . Assuming excited-state pre-trapping (σ_α^*) in addition to direct ground-state trapping (σ_α^0) the cross-section σ_α for electron capture by the vacancy is given by

$$\sigma_\alpha = \sigma_\alpha^0 + \sigma_\alpha^* \tau_F / \tau_{rF} \quad (2)$$

where τ_F is the total lifetime, while τ_{rF} is the total de-excitation time of the excited F center (F^*). The theory derives for the trapping coefficient (proportional to σ_α^*) of a Coulomb center [13] $\gamma_\alpha^* = 4\pi e\mu/\epsilon$ where μ is the electron mobility and ϵ is the dielectric constant. The latter expression applies to both σ_α^0 and σ_α^* indicating that these quantities are in effect nearly temperature-independent; consequently the observed temperature dependence should arise from τ_F/τ_{rF} . Although the theory does not distinguish between σ_α^* and σ_α^0 (provided both refer to a Coulomb center), it is intuitively clear that σ_α^* should exceed σ_α^0 , for the excited state in the field of the vacancy is much less compact and extends to a larger volume than the ground state. Moreover, the electronic potential in the ground state is not coulombic in character. Consequently, the trapping volume of the excited state may reasonably be expected to be much larger. For this reason we shall confine most of our discussion to trapping in the excited state neglecting the first term in the right-hand side of equation (2).

The total F^* lifetime τ_F is given by

$$\tau_F^{-1} = \tau_{rF}^{-1} + \tau_{iF}^{-1}$$

where τ_{iF} is the F^* ionization time. Under normal conditions near RT thermal ionization can reasonably be expected to prevail over all other processes with the F^* electron; consequently $\tau_{iF} \ll \tau_{rF}$, $\tau_F = \tau_{iF}$ and

$$\sigma_\alpha = \sigma_\alpha^* \tau_{iF} / \tau_{rF} \quad (3)$$

Now, since the thermal ionization energy in τ_{iF} is about 0.15 eV for both F and F_A it follows that an activation energy of the order of 0.5 eV should be ascribed to τ_{rF} . Thus the present data from the F' decay kinetics indicate that a thermally-activated de-excitation process occurs in both F^* and F'_A near RT. It has been suggested earlier that at high vibrational quantum numbers the breathing mode oscillator in the F excited state can pass non-radiatively into the F ground state with a probability proportional to $\exp(-E_{wF}/kT)$ where E_{wF} is the height of the intersection point of the potential energy curves of the

ground and excited states relative to the minimum of the excited state curve [14]. This process can be identified with the de-excitation observed presently. The obtained activation energy of about 0.5 eV, ascribed to τ_{rF} , is consistent with the height of the *intersection-point barrier* as calculated in the literature for the KCl F-center on the basis of absorption and emission data [15].

Under certain assumptions the F-F' conversion model leads to the following equation for the development of the F' density with the time t during a rectangular light pulse (cf. [9])

$$F'(t) = F'_s \tanh(t/\theta), \quad t \leq t_{\text{flash}} \quad (4)$$

where

$$F'_s = F_0 \sqrt{(\eta_F \sigma_F q_F / \sigma_\alpha q_{F'})} \quad (5)$$

is the F' density at photoequilibrium, while

$$\theta = \sqrt{(\sigma_F / \sigma_\alpha \eta_F q_F q_{F'})} \quad (6)$$

is a time-constant which determines the time of attaining the photoequilibrium. Here q_F , $q_{F'}$ are the optical excitation rates (per center) in the F, F' bands respectively. In accordance with the data on $\tau_{F'}$ [4], the F' optical bleaching rate was assumed to exceed largely the F' thermal bleaching rate during the light flash ($q_{F'} \gg \tau_{F'}^{-1}$). Since the exact shape of the growth kinetics is not known experimentally, we shall confine our discussion to the F' yield assuming that it is given by equation (4) at $t = t_{\text{flash}}$. This is justified at not too high excitation-light intensities when the yield is far from saturating with the intensity (the linear parts in Fig. 2). Assuming further that $t_{LF} \gg \theta \gg t_{SF}$ it follows

$$\Delta D_m \propto F'_s = F_0 (\eta_F \sigma_F q_F / \sigma_\alpha q_{F'})^{1/2}, \quad t_{fl} = t_{LF}$$

$$\Delta D_m \propto F_0 \eta_F q_F t_{SF}, \quad t_{fl} = t_{SF}. \quad (7)$$

The observed temperature dependences of the LF and SF yields whose activation energies are 1 : 2 in ratio suggest therefore that these originate from η_F . However, as the decay kinetics indicate, σ_α , which enters into F'_s , is also temperature-dependent. Moreover in the approximation leading to equation (3) $\eta_F = 1$. In order to cope with this situation it will be assumed that non-linearities occur at high flash-light excitations leading to intensity-dependent τ 's, of the form

$$\tau_F = \begin{cases} \tau_{iF} (\tau_{iF} \ll \tau_{rF}) & \text{at low } I \\ \tau_{rF} (\tau_{iF} \gg \tau_{rF}) & \text{at high } I \end{cases} \quad (8)$$

The presumed non-linearity will obviously have a profound effect on the trapping cross-section σ_α , given by equation (2), as well as on the ionization quantum yield

$$\eta_F = \tau_F / \tau_{iF} \quad (9)$$

At normal excitation-light intensities thermal ionization is predominant among all transitions of the F* electron ($\tau_{iF} \ll \tau_{rF}$); consequently, σ_α and η_F are

given by equation (3) and $\eta_F = 1$. At high excitation-light intensities the above situation is reversed: now the de-excitation process becomes predominant and as a result $\sigma_\alpha = \sigma_\alpha^*$, while

$$\eta_F = \tau_{rF} / \tau_{iF}. \quad (10)$$

As already revealed by the decay kinetics measurements, the thermally-activated transition is the main de-excitation process in the temperature range investigated. From these data and equation (10) it follows $\eta_F \propto \exp(0.4 \text{ eV}/kT)$ for F and $\eta_F \propto \exp(0.3 \text{ eV}/kT)$ for F_A . Having in mind that σ_α^* is practically temperature independent, this explains the observed temperature dependences of the SF and LF yields, proportional to η_F and $\eta_F^{1/2}$ respectively for both F and F_A .

In any event, introducing the above non-linearity seems to be the most reasonable way to cope with the problem arising from the temperature behavior of the SF and LF yields [5]. Assuming a non-linearity would more or less mean a revision of the « conventional » F-F' conversion model with lifetime and trapping parameters constant in I . That this conventional model cannot explain the observed intensity dependence of the F-F' equilibrium at high excitation levels has been appreciated for some time [16]. Low temperature measurements have indicated that the F' photoequilibrium density (F'_s) increases as I is increased rather than remaining independent of the intensity as the model predicts. These deviations from the model have been interpreted in terms of an intensity dependence of σ_F due to the presence of large amounts of ionized species. However, as the present measurements seem to show, non-linearities are likely to occur in the ionization efficiency as well.

The observed intensity dependences of the SF and LF yields are instructive in the pursuit of the origin of the non-linearities. Both yields have been found to be proportional to $I^{1/2}$ far from saturation which implies $\eta_F \propto I^{-1/2}$ and $\sigma_F / \sigma_\alpha^* \propto I^{3/2}$. Inasmuch as both yields have nearly the same intensity behavior and

$$\Delta D_{mSF} \propto \Delta D_{mLF} / \theta,$$

θ is independent of I . An estimate of θ can be made based on $\sigma_F / \sigma_\alpha^* \sim 0.05$, $\eta_F \sim 1$, $q_F = q_{F'} \sim 10^3$ leading to $\theta \sim 10^{-4}$ at RT which is quite reasonable.

The drop in ionization efficiency at high I can be due to either a drop of τ_{rF} or an increase of τ_{iF} . From the detailed balance principle it follows

$$\tau_{iF} \propto \sigma_\alpha^{*-1} \exp(E_{iF}/kT)$$

so that an increase of τ_{iF} can be induced by a decrease of σ_α^* as I is increased. That the cross-section of an anion vacancy can drop as a result of screening due to a near-by center has already been suggested [17]. An intensity dependence of σ_α^* would imply that the screening particle is either an excited or ionized neighbor. The alternative is to assume that while τ_{iF} is constant τ_{rF} is reversely proportional to $I^{1/2}$. This implies that the transition through the intersection-

point barrier may be intensity-dependent through the effect of ionized and/or excited neighbors on the potential energy of the localized mode. The problem of an intensity-dependent σ_F seems more complex, though as before [16] the present experimental data require that σ_F should increase with I . The non-linearity in σ_F is likely to be related to some concentration effects on the F' lifetime below RT [11, 18]. Since the F' density is intensity-dependent, they would imply a non-linearity occurring in $\tau_{F'}$. This non-linearity can be understood in terms of the present result on σ_F , since from the detailed balance it follows

$$\tau_{F'} \propto \sigma_F^{-1} \exp(E_{F'}/kT).$$

Increasing the intensity would lead to increasing σ_F and, consequently, to decreasing $\tau_{F'}$ in accordance with the experimental observation that $\tau_{F'}$ is a declining function of the F' density [11].

The conclusion of an intensity-dependent σ_F can throw some light on the origin of the scatter in the data on B from the decay kinetics and on the greater stability of the bimolecular parameter A . As a matter of fact, while B is more sensitive to variations in the flash-light intensity, the product $\sigma_F \tau_{F'}/\sigma_\alpha$ is not since the main intensity-dependent quantity σ_F cancels.

The anticipated temperature dependences of σ_F/σ_α and η_F for the F center as given by equations (2) and (9) respectively are illustrated in figure 7. The solid lines represent experimental data, while extrapolations into regions where no such data are available are described by dashed lines. There are five temperature ranges determined by the relative magnitudes of the F* electron transition probabilities, as well as by the $\sigma_\alpha^*/\sigma_\alpha^0$ ratio. At the lowest temperatures (range A) radiative de-excitation (τ_{RF}^{-1}) predominates; consequently

$$\eta_F = \tau_{RF}/\tau_{iF}, \quad \tau_\alpha = \sigma_\alpha^* + \sigma_\alpha^0 \approx \sigma_\alpha^*.$$

The data on σ_F/σ_α^* are an average of several measurements cited in the literature [16, 19]. Within range B the thermal ionization becomes more and more efficient so that now $\eta_F \sim 1$ and $\sigma_\alpha = \sigma_\alpha^0 + \sigma_\alpha^* \tau_{iF}/\tau_{RF}$. Data in this range are available from experiments by Lütty *et al.* [20]. However, σ_F/σ_α will gradually saturate when as a result of the enhanced ionization probability trapping via the excited state becomes ineffective and is practically replaced by the direct trapping mechanism ($\sigma_\alpha \sim \sigma_\alpha^*$, range C). Further, the thermally-activated de-excitation is switched-on (range D); now, σ_F/σ_α drops steeply as a result of the new rise in trapping efficiency via the excited state due to the increased de-excitation probability. When the latter becomes predominant in range E the ionization quantum yield η_F will also drop steeply. The non-linearities occurring at high excitation levels lead in effect to a shift of the temperature curves to lower temperatures. The conclusion that even at normal excitations the ionization quantum yield can be lower than 1, provided

the temperature is sufficiently high, is supported by more direct measurements of η_F at RT [21]. However this behaviour seems to be structure or impurity sensitive for the quantum yield has been found to vary considerably from sample to sample. This can be interpreted as a corresponding sensitivity of the trapping cross-section σ_α^* through the influence of other defects or impurities which disturb the otherwise purely coulombic character of the excited state pre-trapping. It is also likely that in samples of lower σ_α^* the transition temperature between ranges D and E would be lower. This possibly explains why the trapping coefficient γ_α of the anion vacancy has been found to be fairly temperature-independent virtually following the equation of a Coulomb center between 290-350 K [9], while our data point to a temperature-dependent σ_α within the same temperature range: The former results can well refer to range E in figure 7.

Fig. 7. — Presumed temperature dependences of the ionization quantum yield η_F and the cross-sections' ratio σ_F/σ_α . The available experimental data are plotted by circles, extrapolations are presented by dashed lines. The authors' data on σ_F/σ_α are also included as a solid line with no circles. The whole temperature range is divided into five subranges, A through E, according to the relative magnitudes of the transition probabilities of the excited F electron as indicated on the top

Conclusion. — In the opinion of the authors an essential result of the present investigation is the revival of the problem of the non-linearities in the transition and trapping probabilities of color centers. While this problem is still far from being solved, the present study seems to have even added to its complexity by introducing new non-linearities. Clearly, a lot of experimental and theoretical work has to be done before these very intriguing properties are understood in detail.

Acknowledgment. — Thanks are due to Professor St. Petroff and the Physics Department at VIM-MESS, Rousse for supplying the KCl crystals, as well as for numerous stimulating discussions. One of us (M. G.) is also indebted to the German Academic Exchange Service for a grant which made his participation at the Conference possible.

References

- [1] DECHEV, G., GEORGIEV, G., KORALOV, N., TODOROV, T., GOCHEV, A., GEORGIEV, M., Proc. 5th IMEKO, *Symp. Photon Detectors*, Budapest 1971.
- [2] TODOROV, T., DECHEV, G., GEORGIEV, M., *Solid State Commun.* **11** (1972) 1731.
- [3] TODOROV, T., DECHEV, G., TOMOVA, N., GEORGIEV, M., *Phys. Status Solidi (a)* **15** (1973) K123.
- [4] TODOROV, T., TOMOVA, N., GEORGIEV, M., *Solid State Commun.* **15** (1974) 1501.
- [5] GEORGIEV, M., TODOROV, T., *Phys. Status Solidi (a)* **27** (1975) K85.
- [6] TODOROV, T., KORALOV, N., GEORGIEV, M., *Opt. Commun.* **13** (1975) 439.
- [7] TODOROV, T., BALTOVA, M., GEORGIEV, M., *C. R. Acad. Bulg. Sci.* **28** (1975) 747.
- [8] PICK, H., *Ann. Phys. (5)* **37** (1940) 421.
- [9] HOFFMANN, H. J., STÖCKMANN, F., TÖDHEIDE-HAUPT, U., *Phys. Status Solidi (b)* **56** (1973) 549 ;
HOFFMANN, H. J., *Phys. Status Solidi* **57** (1973) 123.
- [10] IKEZAWA, M., HIRAI, M., UETA, M., *J. Phys. Soc. Japan* **17** (1962) 1474.
- [11] GOLDBERGER, G. H., Thesis, Univ. of Connecticut, 1971.
- [12] SEITZ, F., *Rev. Mod. Phys.* **26** (1954) 7.
- [13] PEKAR, S. I., *Issledovaniya po elektronnoj teorii kristallov*, Moscow 1951, p. 221.
- [14] PICK, H., *Nuovo Cimento* **7** (1958) 498.
- [15] RUSSELL, G. A., KLINK, C. C., *Phys. Rev.* **101** (1956) 1473.
- [16] COSTICAS, A., GROSSWEINER, L. I., *Phys. Rev.* **126** (1962) 1410.
- [17] MIEHLICH, A., *Z. Phys.* **176** (1963) 168.
- [18] SCHMID, D., WOLF, H. C., *Z. Phys.* **170** (1962) 455.
- [19] MARKHAM, J. J., *F. Centers in Alkali Halides* (Academic Press, New York) 1966.
- [20] LÜTY, F., *Halbleiterprobleme* **6** (1961) 238.
- [21] GUDAT, A. E., SCOTT, A. B., WAGNER, M., *J. Chem. Phys.* **60** (1974) 4396.