

**Zeitschrift:** Helvetica Physica Acta

**Band:** 51 (1978)

**Heft:** 3

**Artikel:** F-center pairs in KCl-effects of light excitation, static magnetic field and magnetic resonances on F and F<sup>-</sup> absorption bands

**Autor:** Ecabert, M. / Jaccard, C.

**DOI:** <https://doi.org/10.5169/seals-114953>

### **Nutzungsbedingungen**

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. [Siehe Rechtliche Hinweise.](#)

### **Conditions d'utilisation**

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. [Voir Informations légales.](#)

### **Terms of use**

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. [See Legal notice.](#)

**Download PDF:** 16.03.2025

**ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>**

# F-center pairs in KCl—effects of light excitation, static magnetic field and magnetic resonances on F and F<sup>-</sup> absorption bands<sup>1)</sup>

by M. Ecabert<sup>2)</sup> and C. Jaccard

Institut de Physique de l'Université, Rue A.-L. Breguet 1, CH-2000 Neuchâtel, Switzerland.

(16.II.1978)

*Abstract.* The optical densities of the F and F<sup>-</sup> absorption bands are measured at 10–15 K in a static magnetic field (0–0.5 T) and a resonant microwave or rf field in additively doped crystals ( $C_F = 10^{17}$  to  $10^{18}$  cm<sup>-3</sup>), under F band excitation. For distant pairs, the effects on the F optical density follow those on the luminescence but are opposite for the F<sup>-</sup> optical density. The transient behaviour under pulsed excitation is also measured and shows a field dependent relaxation time of about 1 s. The results are compatible with a non radiative disexcitation mechanism of F center pairs involving the fast formation of F<sup>-</sup>-vacancy pairs which transform back slowly into F pairs, either in their ground or in their excited state. No effects on the optical densities have been found for close pairs.

## 1. Introduction

In alkali halide crystals at low temperature, the emission quantum yield of the optically excited F centers depends on the concentration of these defects [1]. It also varies on application of static magnetic field [2, 3], and when the EPR conditions are satisfied for the F center electron. The emission quantum yield is also influenced by nuclear magnetic resonance of the neighbouring ions. Optical detection of these resonances has been performed on the F center luminescence in two cases: (1) In well quenched crystals the EPR [4] and the NMR [5] correspond to a decrease of the luminescence intensity; (2) when crystals have been submitted to a short irradiation in the F band at room temperature, resonances appear as an increase of the luminescence intensity [6]. These phenomena are generally attributed to the presence of F center pairs among which two classes have been considered. They correspond to the cases mentioned above: distant pairs (separation of 5 to 8 nm) and close pairs (separation of 2 to 5 nm) respectively. The origin of the discrimination lies in the relative magnitude of the electronic exchange energy with respect to the hyperfine energy. The models are based on the competition between the well known radiative disexcitation of the isolated centers from their relaxed excited state  $\tilde{F}^*$ , and a non-radiative disexcitation of pairs F- $\tilde{F}^*$ , with a probability depending on the spin symmetry as it is revealed by the effects due to the magnetic field. According to Markham [7], the non radiative disexcitation can be explained by an electron

<sup>1)</sup> To Prof. Jean Rossel for his 60th birthday.

<sup>2)</sup> Present address: Contraves AG, Zürich (Switzerland).

transfer from the  $\tilde{F}^*$  center to its F neighbour, yielding a  $F^-$  center and an anionic vacancy  $F^+$ .

The effects of the static magnetic field and of the electron and nuclear resonances have been measured exclusively on the F luminescence in previous experiments. In this paper, we present corresponding effects examined on the F and  $F^-$  populations in order to verify the assumed non-radiative mechanism. The experimental conditions are briefly presented in the next section. The experimental results, given in Section 3, are interpreted in the last section by a simple model of the distant pairs in terms of the transition rates for the different disexcitation channels.

## 2. Experimental

All measurements are performed at a temperature of 10 to 15 K on KCl single crystals (K. Korth, 'Ultrapur') doped with F centers by additive coloration to concentrations between  $10^{17} \text{ cm}^{-3}$  and  $10^{18} \text{ cm}^{-3}$ . The samples, cleaved to the approximate dimensions  $5 \times 5 \times 0.3 \text{ mm}^3$ , are quenched just before the measurements in order to obtain a homogeneous distribution of the F centers. The equipment for the static magnetic field (0 to 0.5 T), the EPR (X-band spectrometer with cylindrical cavity and optical accesses), the NMR and the luminescence measurements are described elsewhere [4, 6, 8, 9].

Two optical beams reach the sample. One of them, used to excite the F centers, is produced in a conventional optical system by a halogen lamp (250 W) followed by anticaloric filters (Schott KG3, thickness: 3 mm), a filter limiting the excitation to the F band (Wratten 74 or interferential Oriel with  $\lambda_{\text{max}} = 546 \text{ nm}$  and  $\Delta\lambda = 10 \text{ nm}$ ) and possibly grey filters (Schott NG9). The incident flux  $I_F$  in the F band, previously measured by a calibrated thermopile (Kipp E 20) reaches up to  $2 \times 10^{17} \text{ photons s}^{-1} \text{ cm}^{-2}$ . The second beam, called here photometer beam, measures the light which is transmitted through the sample at any point of the F band and in part of the  $F^-$  band. Particular care has been taken to limit its intensity  $I$  to a small value. The incident light is filtered by a monochromator. The transmitted light is detected through a second monochromator by a photomultiplier (Philips XP 1002 or XP 1005). The optical density can be calculated by comparing with measurements without sample.

NMR and EPR spectra are detected selectively by chopping at 13 Hz the rf or microwave power and sending the photomultiplier signal into a lock-in amplifier (PAR 124). In order to study the effects of a slowly varying magnetic field at one point of the F or  $F^-$  absorption band, the incident light of the photometer beam is chopped at 22 Hz and the signal is detected as mentioned above. Besides, a large continuous background is eliminated electrically and the interesting part of the signal is averaged in a signal analyser (HP 5480 A). The transient response of the F and  $F^-$  absorption bands when turning on or off the F excitation is obtained with a mechanical chopper (0 to 5 Hz, rise time 1 ms) placed in the excitation beam. In this case the photometer incident light has a constant intensity and the signal is averaged after subtraction of the continuous level.

In order to extend the results appearing at a particular point of the F and  $F^-$  bands, the variation of the transmitted light due to EPR has been detected continuously versus the wave length. The optical excitation is then limited to a very small part of the absorption band and one monochromator alone is used in the photometer beam.

The signal is detected selectively according to the frequency and phase of the microwave pulses. It can be normalized by means of the response of the optical system.

### 3. Results

It has been verified first that the optical density of the F band is independent of the magnetic field without excitation of the F centers. When the excitation is switched on the optical density of the F band decreases. It increases then when the magnetic field grows from 0 to 0.4 T. This behaviour of the optical density is exactly the same as for the luminescence intensity studied by Jaccard et al. [3]. The optical density of the  $F^-$  band shows an opposite behaviour. It is zero without optical excitation in the F band. It grows when this excitation is switched on and decreases when the magnetic field increases. The variations of the F luminescence and the optical densities of the F and  $F^-$  bands, measured under identical conditions, are shown in Figure 1 as a function of the magnetic field.

The decrease of the luminescence which appears at 0.346 T (for a microwave frequency of 9,58 GHz) corresponds to the EPR of the F center, studied by Ruedin [4]. The same lines occur on the optical density curves. They correspond to a decrease

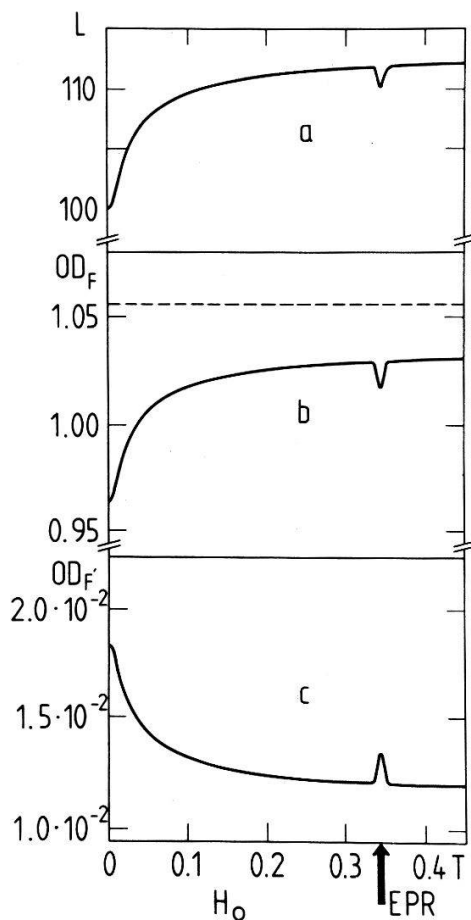


Figure 1

Dependence of the luminescence of the F centers (a), the optical density of the F band (measured at 530 nm) (b), and the optical density of the  $F^-$  band (measured at 629 nm) (c) on the magnetic field  $H$ , and under EPR conditions with an optical excitation of the F centers. Dotted line: level of F-optical density without excitation.

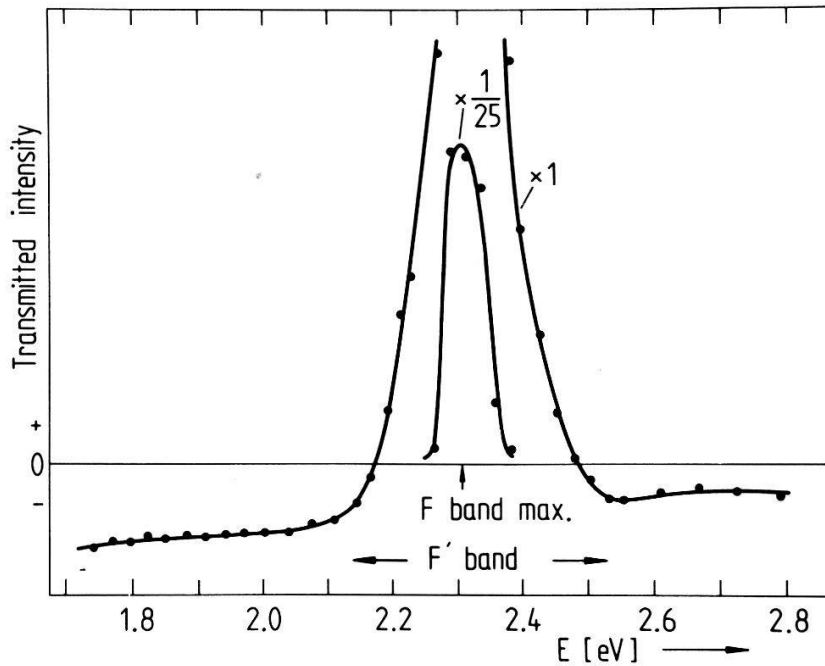


Figure 2

Variation of the transmitted light intensity in several points of the F and F<sup>-</sup> absorption bands, due to a resonant microwave field during F band irradiation.

of the F band and an increase of the F<sup>-</sup> band. This phenomenon is illustrated in Figure 2 where the intensity of the EPR line is given by phase sensitive detection of the transmitted light, while the wavelength sweeps the F and F<sup>-</sup> bands. NMR spectra, discovered on the F luminescence [5] and due to the ions surrounding the distant F center pairs, are also observed on the optical densities of the F and F<sup>-</sup> absorption bands, with the same sign as in the EPR case.

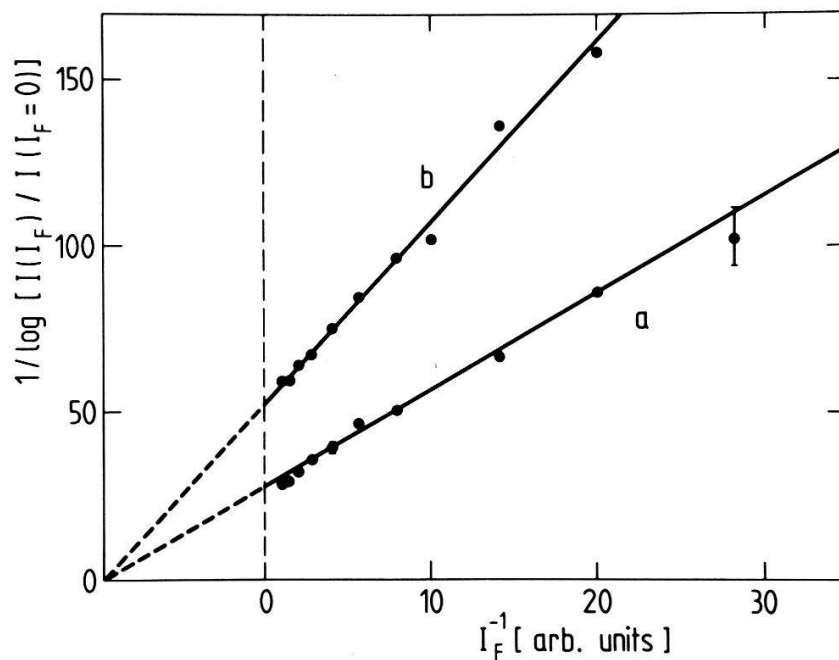


Figure 3

Linearized representation of the transmitted light intensity  $I$  in the F band as a function of the excitation light intensity  $I_F$ . (a)  $H_0 = 0$ ; (b)  $H_0 = 0.45$  T.

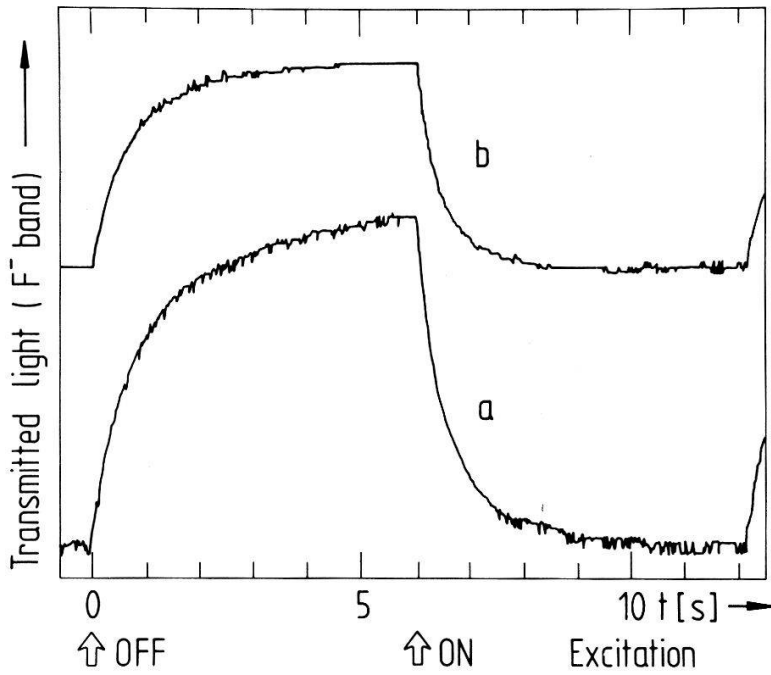


Figure 4 Evolution of the transmitted light intensity in the  $F^-$  band when switching on and off the excitation in the  $F^-$  band. (a)  $H_0 = 0$ ; (b)  $H_0 = 0.45$  T.

The optical density change of the  $F^-$  band depends in a simple way on the intensity  $I_F$  of the excitation light. This variation is best characterized by the logarithm of the ratio of the transmitted intensities  $I(I_F)/I(I_F = 0)$  which is proportional to the change of the optical density. Its representation in Figure 3 shows that  $(\Delta OD_F)^{-1}$  is a linear function of  $I_F^{-1}$ .

The relaxation of the  $F^-$  population can be observed by switching the exciting

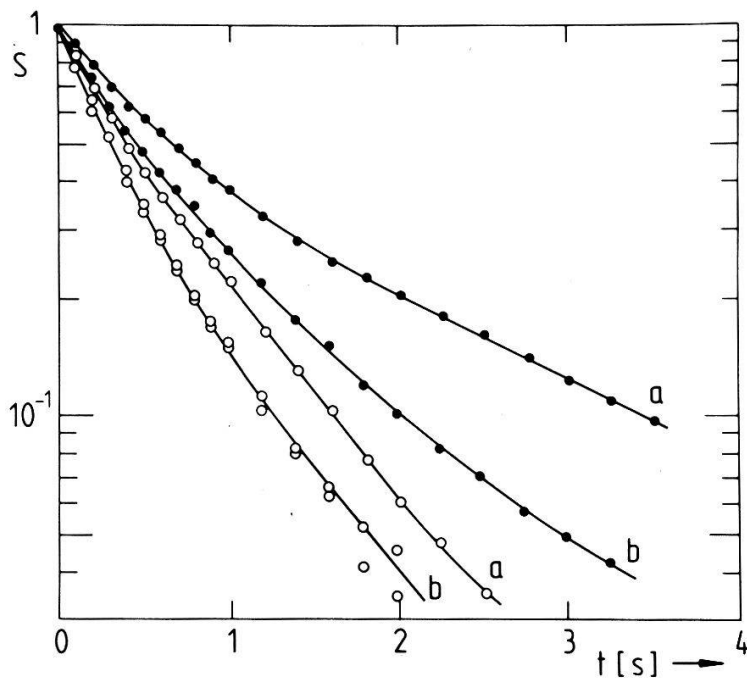


Figure 5 Normalized representation of the variation of the  $F^-$  optical density when  $F^-$  excitation is switched on (○) and off (●). (a)  $H_0 = 0$ ; (b)  $H_0 = 0.45$  T.

light on and off. The transmitted intensity follows rather slowly, as it can be seen in Figure 4, and moreover it shows a magnetic field dependence. The changes of the optical density, suitably normalized, have been represented in a semilog plot in Figure 5. The significant curvature of the lines can be interpreted by a distributed relaxation frequency  $\gamma$ . In this case, the signal is expressed by  $S(t) = \int_0^\infty \exp(-\gamma t) f(\gamma) d\gamma$  and the average relaxation frequency just by  $-(dS/dt)_{t=0}$ . The values obtained this way are given in Table I for the different cases.

Table I  
Measured relaxation frequencies of the  $F^-$  optical densities when the excitation of the F centers is switched on or off, for two values of the static magnetic field.

$\langle\gamma\rangle [S^{-1}]$	$H_0 = 0$	$H_0 = 0.45 \text{ T}$
$I_F$ switched on	$1.7 \pm 0.1$	$2.3 \pm 0.1$
$I_F$ switched off	$1.1 \pm 0.1$	$1.7 \pm 0.1$

In order to transform distant pairs into close pairs, the sample has been submitted to short F excitations at room temperature. The shape of the luminescence curve versus the magnetic field then changes, in particular the variation due to the EPR or NMR changes its sign as reported elsewhere [9]. Parallel investigations on the optical densities show that the signals described in this section decrease and finally vanish without otherwise changing their behaviour: no variation of the F and  $F^-$  absorption bands have been found in the case of close pairs though a signal subsists on the luminescence.

#### 4. Discussion

The complementarity of the F and  $F^-$  optical densities (Fig. 1) support strongly the hypothesis of a population transfer between these species due to the optical pumping. A quantitative comparison can be performed if the contribution of the isolated F centers is eliminated. This can be done by considering the height of the EPR peak with respect to the change due to the magnetic field between 0 and 0.45 T since single centers do not respond to these parameters. The ratios are nearly the same ones (typically 15–18%) for the luminescence, the F and the  $F^-$  optical densities.

A simple model for the population transfer is given in Figure 6 (full lines). It takes only the pairs into account, with populations  $n_0$  (both centers in the ground state),  $n$  (one center in the relaxed excited state) and  $n'$  ( $F^-$  + vacancy). The total population  $N = n_0 + n + n'$  remains constant. Optical excitation occurs with a frequency  $w_I$  proportional to the intensity  $I_F$  of the light irradiation. Excited pairs return radiatively to the ground state at a rate  $w_r$  of  $0.8 \mu\text{s}$  [10] or transform into a  $F^-$ -vacancy pair (rate  $w_t$ ) which then returns to the ground state at a rate  $w'_t$ . These last processes are non radiative.

In the stationary state, the ground state population is

$$n_0 = 2N \frac{1}{1 + \frac{w_I(w_t + w'_t)}{w'_t(w_r + w_t)}}$$

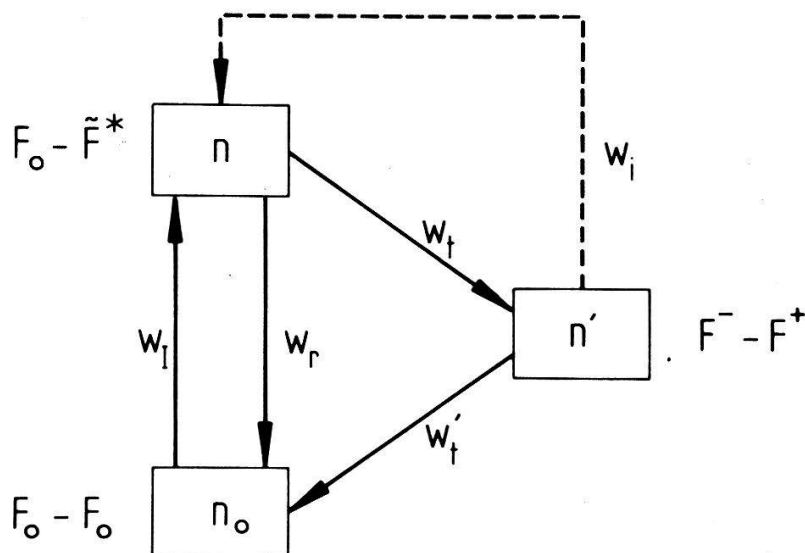


Figure 6

The optical cycle for distant F center pairs (see text).

Introducing the population difference  $\Delta n_0 = n_0(w_I = 0) - n_0(w_I)$ , it can be seen that  $(\Delta n_0)^{-1}$  is a linear function of  $(w_I)^{-1}$ , in agreement with Figure 3:

$$\frac{1}{\Delta n_0} = \frac{1}{2N} \left[ 1 + \frac{w'_t(w_r + w_t)}{w_t(w_t + w'_t)} \right]$$

In a previous paper [2], it has been shown that at zero magnetic field, all pairs have a spin symmetry such that  $w_t \gg w_r$ . The measured relaxation times suggest that  $w'_t \ll w_t, w_r$ . In this case:

$$\left( \frac{1}{\Delta n_0} \right)_0 \simeq \frac{1}{2N} \left[ 1 + \frac{w_t}{w_I} \right]$$

At high magnetic field ( $H_0 = 0.45$  T), about one half of the pairs are in a spin triplet state which prohibits the electron transfer ( $w_t = 0$ ) [2], so that:

$$\Delta n_0 \simeq \frac{1}{2} \cdot 2N \left[ \frac{1}{1 + \frac{w'_t}{w_t}} + \frac{1}{1 + \frac{w_r}{w_I}} \right]$$

The last term of this expression can be neglected because  $w_r \gg w_I$  and

$$\left( \frac{1}{\Delta n_0} \right)_{\text{hf}} \simeq \frac{1}{N} \left( 1 + \frac{w'_t}{w_t} \right)$$

The model predicts then in the linearized representation a doubling of the slope and of the ordinate at the origin, when the high magnetic field is applied. This agrees with the results of Figure 3 where the ratio is  $1.8 \pm 0.2$ .

In the model used thus far, the  $F^-$  population possesses two relaxation frequencies when the F excitation is switched off. One of them is bound to the decrease of the excited pairs. This component is fast ( $w_r, w_t \simeq 10^{-6}$  s) and of small amplitude in our experimental conditions ( $w_I \ll w_r, w_t$ ), and it has not been detected. The other one pertains to the emptying rate  $w'_t$  of the  $F^-$  population. Such a process which



involves an electron transfer from a  $F^-$  center into a vacancy does not depend *a priori* on the magnetic field. However the measured average frequencies are not the same at 0 or at 0.45 T as shown in Table I. This behaviour can be explained by introducing, for the destruction of  $F^-$  centers, a second mechanism examined by Lüty [11]: the center is ionized at a rate  $w_i$  and the electron is transferred into the vacancy to produce a F center in its excited state (dashed line in Figure 6). In this case, the  $F^-$  band relaxes with a frequency  $\gamma' \simeq w'_t + w_i w_r / (w_r + w_t)$ . At zero magnetic field,  $w_t \gg w_r$  for all pairs as mentioned previously, so that  $\gamma'_0 \simeq w'_t$ . At high field  $w_t \ll w_r$  for about one half of the pairs so that  $\gamma'_{hf} \simeq w'_t + \frac{1}{2}w_i$ . When the excitation of the F centers  $w_I$  is switched on, the  $F^-$  population increases with a relaxation frequency  $\gamma'' \simeq w'_t + w_i w_r / (w_r + w_t) + w_I w_t / (w_r + w_t)$ , reducing to  $\gamma''_0 \simeq w'_t + w_I$  and  $\gamma''_{hf} \simeq w'_t + \frac{1}{2}w_i + \frac{1}{2}w_I$  in the low and high field cases, respectively. The predicted trends correspond roughly to the values of Table I. However  $w_t$ ,  $w'_t$  and  $w_i$  are strongly dependent on the pair separation and therefore widely distributed. No quantitative analysis is possible thus far, but these experiments indicate a branching ratio  $w_i/w'_t$  of the order of unity. Moreover, the pumping light in the F band does also excite  $F^-$  centers, because of the overlap of the absorption bands, and the intensity dependence of the relaxation is certainly not accounted for completely by this model.

The fact that for close pairs no signal has been observed on the absorption bands (i.e. that the  $F^-$  concentration is too low to be detected) can be attributed to two causes: a non radiative disexcitation involving no  $F^-$ -vacancy pair formation, or a very short  $F^-$  lifetime. The former, developed in a previous paper [12], involves the electronic exchange energy, and therefore is more likely to apply to close than to distant pairs. The latter requires a lifetime shorter than 1 ms, (time resolution of our detection system), which should be possible for an electron transfer within a close  $F^-$ -vacancy pair as shown by Schmid and Wolf [13] and Itoh and Suita [14].

## 5. Conclusion

For distant F center pairs, as they occur in a well quenched crystal, the non radiative disexcitation occurs by an electronic transfer from the excited to the other member of the pair, thus forming a  $F^-$ -vacancy pair, as can be inferred from the behaviour of the luminescence and of the F and  $F^-$  optical density on application of a static magnetic field and of a resonant microwave field. This fast transfer frequency is strongly field dependent, and its magnitude with respect to the direct radiative disexcitation frequency is determining. The electron is transferred back from the  $F^-$  center by a slow process, with a characteristic time of the order of 1 sec (between 10 K and 15 K), restoring the pair in its ground state. The effects observed on the optical densities depend then on the excitation rate and they saturate when it surpasses the backtransfer frequency. The field dependence of the transient relaxation process observed with a pulsed excitation implies the existence of a second type of backtransfer (probably through ionization of the  $F^-$  center) leading to a pair in its excited state. These measurements confirm the corresponding hypotheses put forward by Markham et al. [7] and by Lüty [11]. With close F center pairs the optical densities are not modified by the optical pumping and therefore do not display any field or magnetic resonance effect (which is not the case for the luminescence). The measurement of the optical densities can therefore be used to obtain unbiased information on distant pairs alone.

## Acknowledgments

The authors are indebted to the Swiss National Science Foundation for the support of this work.

## REFERENCES

- [1] A. MIEHLICH, *Z. Phys.* **176**, 168 (1963).
- [2] C. JACCARD, Y. RUEDIN, M. AEGERTER and P.-A. SCHNEGG, *Phys. Stat. Sol. (b)* **50**, 187 (1972).
- [3] F. PORRET and F. LÜTY, *Phys. Rev. Letters* **44A**, 391 (1973).
- [4] Y. RUEDIN, P.-A. SCHNEGG, C. JACCARD and M.-A. AEGERTER, *Phys. Stat. Sol. (b)* **54**, 565 (1972).
- [5] C. JACCARD and M. ECABERT in *Semiconductors and Insulators*, Gordon and Breach, London and *Phys. Stat. Sol. (l)* **87** (1978) (in press).
- [6] C. JACCARD, P.-A. SCHNEGG and M. AEGERTER, *Phys. Stat. Sol. (b)* **70**, 485 (1975).
- [7] J. J. MARKHAM, R. T. PLATT and I. L. MADOR, *Phys. Rev.* **92**, 597 (1953).
- [8] M. ECABERT, Thèse, Neuchâtel, juillet 1977.
- [9] P. A. SCHNEGG, C. JACCARD and M. AEGERTER, *Phys. Stat. Sol. (b)* **63**, 587 (1974).
- [10] R. K. SWANK and F. C. BROWN, *Phys. Rev.* **130**, 34 (1963).
- [11] F. LÜTY, *Halbleiterprobleme*, Vol. VI, 238 (1961), F. Vieweg, Braunschweig.
- [12] C. JACCARD and M. A. AEGERTER, *Phys. Letters* **44A**, 391 (1973).
- [13] D. SCHMID and H. C. WOLF, *Z. Phys.* **170**, 455 (1962).
- [14] N. ITOH and T. SUITA, *J. Phys. Soc. Japan* **24**, 524 (1968).