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UNIVERSITE DE NEUCHATEL INSTITUT DE PHYSIQUE

PAIRES DE CENTRES F DANS LES HALOGENURES ALCALINS : ETUDE DE TRANSFERTS ELECTRONIQUES, PROPRIETES OPTIQUES ET MAGNETO-OPTIQUES

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par

A.C. MEZGER

Ingénieur-physicien diplômé EPFL

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Paires de centres F dans les halogénures alcalins: Etude de transferts électroniques, propriétés optiques et magnéto-optiques

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MM. les professeurs C. Jaccard, J. Rossel, H. Beck et J.M. Spaeth (Paderborn)

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Institut de Physique, Université de Neuchâtel[1])

Electron Transfer within F Center Pairs in KCl from Optical Emission and Absorption

By

A. C. MEZGER and C. JACCARD[2])

Transient F luminescence and F′ population after F band excitation and the effect of a static magnetic field (0.5 T) are measured in KCl at 10 K for F center concentrations between 5×10^{16} and 1×10^{18} cm^{-3}. The results are explained by an F center pair model involving a radiative decay (time τ_r), direct and inverse non-radiative electron transfers within the pair depending exponentially on the separation: $\tau = \tau_0 \exp(r/\lambda)$, and a Poisson spatial distribution of the individual centers, with the following parameters: $\tau_r = (890 \pm 5)$ ns; $\tau_0 = (0.4 \pm 0.2)$ ns, $\lambda = (0.8 \pm 0.1)$ nm (direct); $\tau_{0i} = (2 \pm 1)$ ms, $\lambda' = (0.8 \pm 0.1)$ nm (inverse).

Le déclin de la luminescence F et de la population F′ après une excitation dans la bande F ainsi que l'effet d'un champ magnétique de 0,5 T ont été mesurés dans KCl à 10 K pour des concentrations allant de 5×10^{16} à 1×10^{18} cm^{-3}. Les résultats sont expliqués par un modèle de paires de centres F comportant: un déclin radiatif (temps τ_r), des transferts électroniques non-radiatifs (direct et inverse) entre les membres des paires dépendant d'une manière exponentielle de leur séparation $\tau = \tau_0 \exp(r/\lambda)$, une distribution spatiale de Poisson des centres individuels. Pour les paramètres les valeurs suivantes sont obtenues: $\tau_r = (890 \pm 5)$ ns; $\tau_0 = (0{,}4 \pm 0{,}2)$ ns, $\lambda = (0{,}8 \pm 0{,}1)$ nm (direct); $\tau_{0i} = (2 \pm 1)$ ms, $\lambda' = (0{,}8 \pm 0{,}1)$ nm (inverse).

1. Introduction

The optical properties of F center pairs in alkali halides are influenced in several ways at low temperature by electromagnetic fields. Beside the effect of high static magnetic fields on the spin level populations [1], lower fields change markedly the average luminescent quantum yield [2], which can display zero frequency NMR of the neighbouring ions [3].

The optical detection of EPR [4 to 6] and of NMR of the environment [7, 8] is also possible by monitoring the F luminescence as well as the F or F′ absorption. All these phenomena are due to a fast non-radiative electron transfer from the excited pair member into the other one ($\tilde{F}^* + F_0 \rightarrow F' + \alpha$), followed by a slow back transfer restoring the pair ground state ($F' + \alpha \rightarrow F_0 + F_0$). Since this process requires F center pairs, the effects mentioned above are concentration dependent, and since the pair separation is distributed more or less at random, time dependences consist generally in a superposition of many exponentials. This is the case for the luminescence decay, which has been measured firstly by Swank and Brown [9]. A later study by Bosi and Bussolati [10] revealed its non-exponential behaviour, which has been attributed to contributions from M and R centers; however, these can be avoided by means of a monochromatic laser excitation (as described below), and secondly by preparing the crystals in such a way that M-center absorption is not observed, so that the observations can be completely accounted for by pair effects.

The purpose of the investigations reported in this paper is to determine near 10 K the electron transfer rate in KCl as a function of the pair separation. To this end the

[1]) Rue A.-L. Breguet 1, CH-2000 Neuchâtel, Switzerland.

[2]) Present address: EISLF, Weisfluhjoch, CH-7260 Davos-Dorf, Switzerland.

direct transfer has been studied by careful measurements and analysis of the transient luminescence after short excitation pulses in the F band, with a low repetition rate to prevent a disturbance of the spin level populations. The parameters for the back transfer are obtained from the transient behaviour of the F and F′ absorption after turning off a steady excitation.

The results are interpreted by assuming an exponential pair separation dependence for the rates and a quasi-Poisson distribution of the individual centers, which are all considered to form a pair with their nearest neighbour. After a description of the experimental conditions, we develop in Sections 3 and 4 models for both types of transfer. In Section 5 the experimental results are analysed in view of the models and the characteristic parameters are determined.

2. Experimental

Thin KCl monocrystals ("Ultrapure", Korth, Kiel, FRG) coloured by the van Doorn method are cleaved to about $5 \times 5 \times 1$ mm^3 and well quenched in total darkness just before measurement in order to obtain a homogeneous distribution of F centers; thereafter they are placed in a liquid helium cryostat (Andonian) and cooled down to 10 K. The F concentrations ranging from 5×10^{16} to 5×10^{17} cm^{-3} are determined directly inside the cryostat by measuring the optical density; for higher concentrations up to 1×10^{18} cm^{-3} thinner crystals from the same origin are measured with a spectrophotometer (Varian, Superscan) outside the cryostat.

The experiment consists in two distinct parts: a) measurement of the transient luminescence after a short exciting pulse in the F band (lifetime about 1 μs); b) measurement of the transient response of the F′ population when the F excitation is turned on and off (lifetime about 1 s).

Transient luminescence is measured by a fast detector coupled with a signal averager. A block diagram of this spectrometer is shown in Fig. 1: the F centers are excited

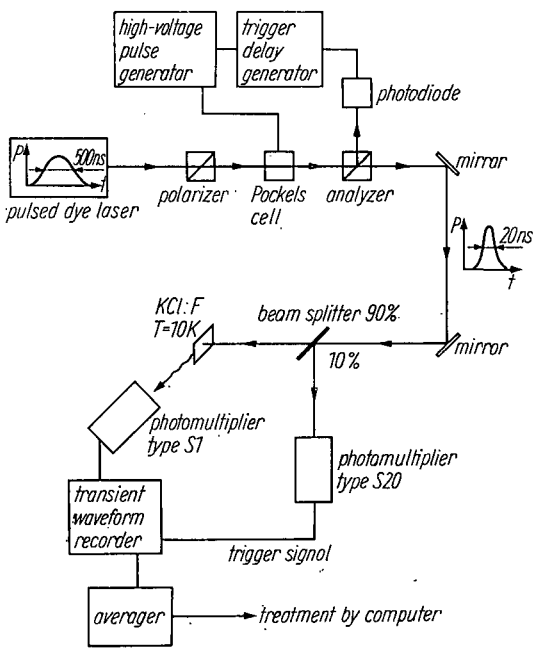

Fig. 1. Block diagram of the spectrometer for the detection of transient F luminescence

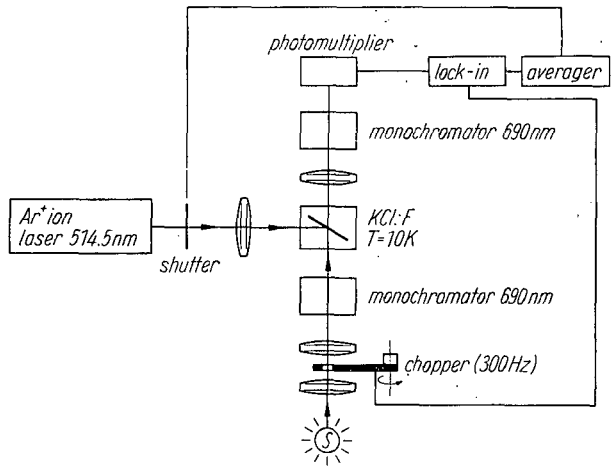

Fig. 2. Block diagram of the spectrometer for the detection of transient transmission of the F′ band

by a pulsed dye laser (Electrophotonics model 23) with a low repetition rate of 1 to 2 Hz (in order to avoid a disturbance of the F and F′ populations) tuned to the maximum of the F band (540 nm for KCl) and from which a pulse of 10 to 20 ns half-width is selected by means of a Pockels cell arrangement (electro-optic developments PC 12 KD KD*P) as shown in the figure. By means of a beam splitter a signal is derived to trigger the electronic part of the experiment. The luminescence pulse passing through an appropriate filter (Wratten 87, Kodak) is detected by a near infrared photomultiplier (EMI 9808 B, S1 type) and sampled with a resolution of 10 ns by a transient wave-form recorder (Biomation 8100); thereafter the signal is averaged (HP 5480 A) over 2^7 pulses. The output signal is then analysed with a computer.

For the measurement of the transient behaviour of the F′ population, an excitation beam and a probe beam measuring the light transmitted by the F′ band are directed on the sample (Fig. 2). In this case the excitation is achieved by an Ar^+ ion laser (50 mW at 514.5 nm) chopped by a mechanical shutter (0 to 5 Hz; 1 ms risetime).

The transient response of the F′ population is then monitored by the probe beam which is filtered on both sides of the cryostat by monochromators. In order to improve the signal-to-noise ratio the probe beam is chopped at about 300 Hz and a phase detection method is used with a time constant of 10 ms; the signal is then averaged synchronously with the F excitation.

These experiments have been performed also with a static magnetic field up to 0.5 T.

3. Model of the Direct Transfer Process

3.1 Pair model and transient luminescence

In a previous paper [2] we diagonalized the Hamiltonian for an F center pair in a static magnetic field and we obtained four eigenstates and the corresponding energies; from this result we calculated for the direct tunnelling process ($\tilde{F}^* + F_0 \rightarrow F' + \alpha$) the transition frequencies which depend on the total spin state of the pair

$$\left.\begin{aligned} \omega_{t1} &= \omega_{t4} = \omega_{t0}(r)\,\frac{1}{\sqrt{2}}\,\sin\left(\frac{\psi}{2}\right), \\ \omega_{t2} &= \omega_{t3} = \omega_{t0}(r)\,\frac{1}{\sqrt{2}}\,\cos\left(\frac{\psi}{2}\right), \end{aligned}\right\} \tag{1}$$

where ψ is the angle between the fields resulting from the applied static field ($\boldsymbol{H}_0$), and from the local hyperfine fields (H_N^*, H_N), acting on the two pair members.

The frequency $\omega_{t0}(r)$ decreases strongly with the distance r between the two centers [11] and it can be expected to have an exponential behaviour of the form

$$\omega_{t0}(r) = \omega_0 \, e^{-r/\lambda} , \tag{2}$$

ω_0 and λ being constants characterizing the non-radiative process.

The distribution of the distances between the two pair members $N(r)$ can be evaluated from the F center concentration n_F if one assumes a random spatial distribution of the centers; this is an idealized case, since interaction between centers at short distances modifies this distribution. With this hypothesis and by using Poisson's law we obtain the following distribution for the pair separation r:

$$N(r)\, dr = 4\pi r^2 n_F \, e^{-(4/3)\pi r^3 n_F} \, dr .$$

From this and from equation (2) one calculates the distribution $N(\tau)$ of the tunnelling times defined by $\tau_0 = 1/\omega_0$ and $\tau(r) = 1/\omega_{t0}(r)$,

$$N(\tau)\, d\tau = 4\pi\lambda^3 n_F \ln^2\left(\frac{\tau_0}{\tau}\right) e^{(4/3)\pi\lambda^3 \ln^3(\tau_0/\tau)} \frac{d\tau}{\tau} . \tag{3}$$

The distribution of the angles ψ can be calculated easily only in two cases. At zero field the angle lies directly between the local hyperfine fields and assuming for them an isotropic space distribution we have

$$P(\psi, H_0 = 0) = \tfrac{1}{2} \sin\psi . \tag{4a}$$

At very high fields near 0.5 T, the angle ψ tends toward zero and we have

$$P(\psi, H_0 \gg H_N^*, H_N) \approx \frac{1}{2}\, \delta\left(\psi - \frac{\langle H' \rangle}{\sqrt{3} H_0}\right) \approx \frac{1}{2}\, \delta(\psi) , \tag{4b}$$

$\langle H' \rangle$ being the average field difference between the two members of the pairs (6.9 mT in KCl). Now with these equations (3, 4a, 4b) the transient luminescence of the F center pair is proportional to the sum of the two following expressions accounting for radiative and non-radiative disexcitation with decay times τ_r and τ respectively:

$$L_1(t, H_0) = \int_{\tau_0}^{\infty} \int_0^{\pi} N(\tau)\, P(\psi, H_0)\, e^{-t\left(\frac{1}{\tau_r} + \frac{\sin\psi/2}{\tau}\right)} d\tau\, d\psi$$

and

$$L_2(t, H_0) = \int_{\tau_0}^{\infty} \int_0^{\pi} N(\tau)\, P(\psi, H_0)\, e^{-t\left(\frac{1}{\tau_r} + \frac{\cos\psi/2}{\tau}\right)} d\tau\, d\psi .$$

Under our experimental conditions ($T = 10$ K, $H_0 \leqq 0.5$ T) all levels have the same population. The angular integration of these formulae can be performed analytically in the limiting cases and yields

$$\left.\begin{aligned} L(t, H_0 \approx 0) &= C\, e^{-t/\tau_r} \int_0^{\infty} e^{-z} e^{-\frac{t}{\sqrt{2}\tau_0} e^{-(z/\Lambda)^{1/3}}} dz , \\ L(t, H_0 \approx 0.5\,\mathrm{T}) &= \tfrac{1}{2} C\, e^{-t/\tau_r} \left[1 + \int_0^{\infty} e^{-z} e^{-\frac{t}{\tau_0} e^{-(z/\Lambda)^{1/3}}} dz\right], \end{aligned}\right\} \tag{5}$$

where $\Lambda = \frac{4}{3}\pi\lambda^3 n_F$ and C includes geometrical factors and the number of excited centers.

The transient luminescence shows an exponential decay corrected by a function depending on time and on the F center concentration; λ, τ_0, τ_r are intrinsic constants. This function can be calculated numerically (we used the Gauss-Legendre method). The effect of an external magnetic field is also predicted to influence the decay time of the luminescence.

3.2 Average transfer rate and quantum yield

In this model the average transfer rate, the quantum yield and its behaviour in a magnetic field are also calculated as a function of the F center concentration.

The average transfer rate can be defined by

$$\langle \omega_t \rangle = \int_0^\infty N(r)\, \omega_0\, e^{-r/\lambda}\, dr\,. \tag{6}$$

Numerical integration of this formula gives $\langle \omega_t \rangle = 5.7\, \Lambda/\tau_0$. This quantity depends on the intrinsic constants τ_0 and λ, but also on the concentration through Λ.

The quantum yield (η) can be calculated by integrating formulae (5) over time,

$$\eta(H_0 = 0) = \int_0^\infty e^{-z} \frac{dz}{1 + \frac{\tau_r}{\sqrt{2}\,\tau_0} e^{-(z/\Lambda)^{1/3}}},$$

$$\eta(H_0 \approx 0.5\ \mathrm{T}) = \frac{1}{2}\left[1 + \int_0^\infty e^{-z} \frac{dz}{1 + \frac{\tau_r}{\tau_0} e^{-(z/\Lambda)^{1/3}}}\right].$$

Numerical integration yields a concentration dependence which is closely approximated by

$$\left.\begin{aligned} \eta(H_0 = 0) &= e^{-nV_c}, \\ \eta(H_0 \approx 0.5\ \mathrm{T}) &= e^{-(1/2)nV_c} \end{aligned}\right\} \tag{7}$$

for concentrations up to about 5×10^{17} cm^{-3}. V_c is defined as the critical volume in which the tunnelling probability is larger than the radiative transition probability and corresponds to the critical radius $R_c = \lambda \ln(\tau_r/\tau_0)$.

The quantum yield is therefore an exponential function of the concentration and of the critical transfer volume in agreement with our first paper [2] and Miehlich's observations [12].

The increase of the quantum yield in a magnetic field is then also given by (7)

$$\frac{\Delta\eta}{\eta} = e^{nV_c/2} - 1$$

and has been verified experimentally in our laboratory.

4. Model of the Inverse Transfer

In order to study the inverse transfer ($F' + \alpha \rightarrow F_0 + F_0$; rate ω_{ti}) we have to consider the optical cycle shown in Fig. 3. We take into account only two different populations of pairs $F_0 - F_0$ and $F_0 - \tilde{F}^*$ for which the direct process is given by equations (1) and assume that we do not have any spin memory loss (this is justified by the fact that this quantity is very small in KCl [3, 13]).

We introduce also a mechanism examined by Lüty [14] and reported in a previous publication [15]: the ionisation rate ω_i of the F′ center followed by a transfer of the electron into the vacancy to produce an F center in its excited state. This is due to the probe and excitation light, since the F′ absorption band extends to the F center band and the excited state of the F′ center lies in the conduction band. We also assume that this process produces a complete spin memory loss, i.e. the electron has equal probabilities to fall in each one of the excited states. According to this model the F′ band decays with the rate

$$\gamma = -\omega_{t1} - \alpha\omega_i ,$$

where α is given by

$$\alpha = \left[1 + \frac{1}{2}\,\frac{\omega_{t1} + \omega_{t2}}{\omega_r}\right]^{-1}.$$

The inverse transfer process can then be calculated in the same way as the direct one, and the F′ band transmission is given by

$$T(t, H_0) = C' \, e^{-t\alpha\omega_i} \int_0^\infty e^{-z} \, e^{-\omega_{0i} t e^{-(z/\Lambda')^{1/3}}} \, dz$$

with $\Lambda' = 4/3\pi\lambda^3 n'$ (n' being an equivalent concentration of pairs F′ — α corresponding to a mean separation).

The effect of a static magnetic field on the relaxation of the F′ center can also be predicted, α being dependent through ω_{t1} and ω_{t2} on the field and ω_{ti} being independent

$$\frac{\alpha\omega_i(H_0 = 0\ \mathrm{T})}{\alpha\omega_i(H_0 = 0.5\ \mathrm{T})} \approx \frac{\sqrt{2}}{2} \qquad \text{if} \qquad \frac{\langle\omega_t\rangle}{\omega_r} \gg 1 .$$

The apparent lifetime (observable at the end of the decay when it reduces to a simple exponential) is about 30% shorter in a field of 0.5 T than in zero field. This is the case for concentrations of the order of 3×10^{17} cm^{-3}.

5. Comparison with Experiments

5.1 Direct tunnelling

The model of the transient luminescence yields a decay composed of the radiative ($1/\tau_r$) and the non-radiative ($1/\tau$) frequencies. This behaviour is verified as can be seen in Fig. 4, where the luminescence decay has been measured in zero field for KCl at 10 K as a function of the F center concentration. This figure shows also the theoretical curves predicted by the model with the fitted parameters τ_0, λ, and τ_r, which are

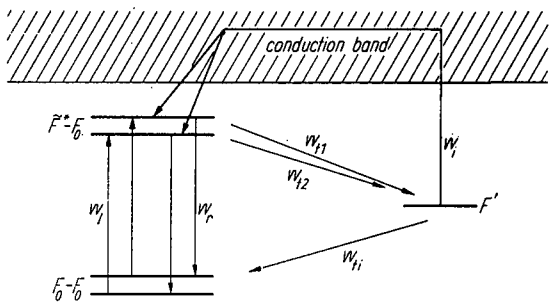

Fig. 3. Schematic diagram of transitions for F center pairs in a statie magnetie field; see text for explanation (ω_I is the pumping rate) (read ω instead of w)

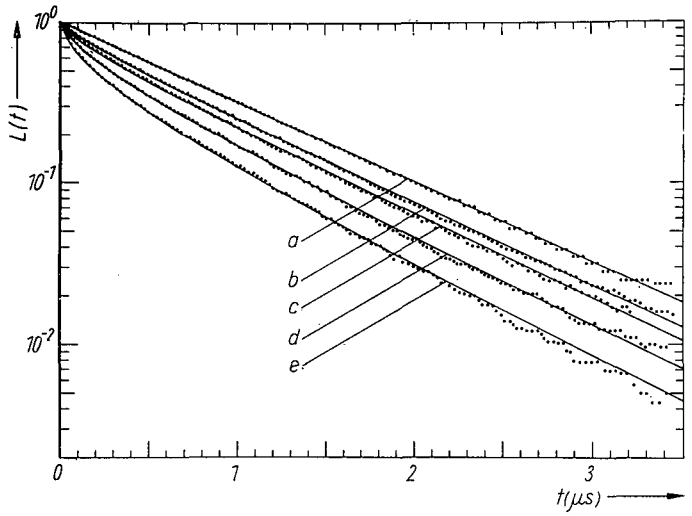

Fig. 4. Normalized luminescence decay, L, in KCl at 10 K for different concentrations: (a) 4×10^{16}, (b) 2.6×10^{17}, (c) 3.7×10^{17}, (d) 6.5×10^{17}, (e) 1×10^{18} cm^{-3}. ● measurements, ——— model best fits

found to have the values.

$$\tau_0 = 0.4 \pm 0.2 \text{ ns},$$
$$\lambda = 0.8 \pm 0.1 \text{ nm},$$
$$\tau_r = 890 \pm 5 \text{ ns}.$$

The behaviour of the luminescence decay in a magnetic field has also been measured: Fig. 5 shows the decay with and without a magnetic field of 0.5 T and the theoretical curves with the same parameters τ_0, λ_0, and τ_r.

From these results we obtain then for the critical transfer distance (6.2 ± 1.0) nm which is near the theoretical estimate by Lüty and Ferreira.

The average transfer rate is calculated from equation (6), for a concentration of 3×10^{17} cm^{-3}; we find $\langle \omega_t \rangle = 8.0 \omega_r$ as we already estimated by another method in a previous paper [2]. The same measurement performed with KBr at 10 K in zero field gives similar results for τ_0 and λ, but a radiative lifetime of (1925 ± 10) ns.

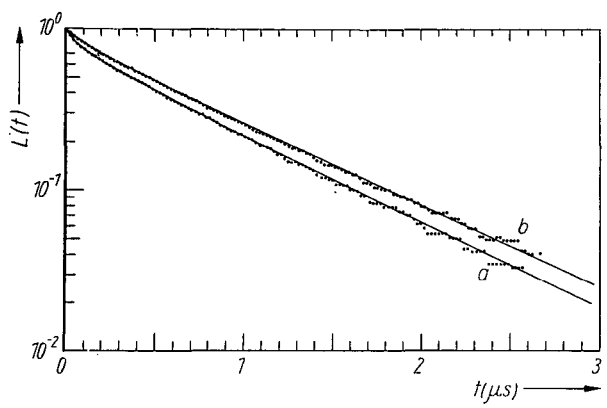

Fig. 5. Normalized luminescence decay, L, for KCl with a concentration of 3.5×10^{17} cm^{-3} at 10 K. (a) Without magnetic field, (b) with magnetic field of 0.5 T. ● measurements, ——— model best fits

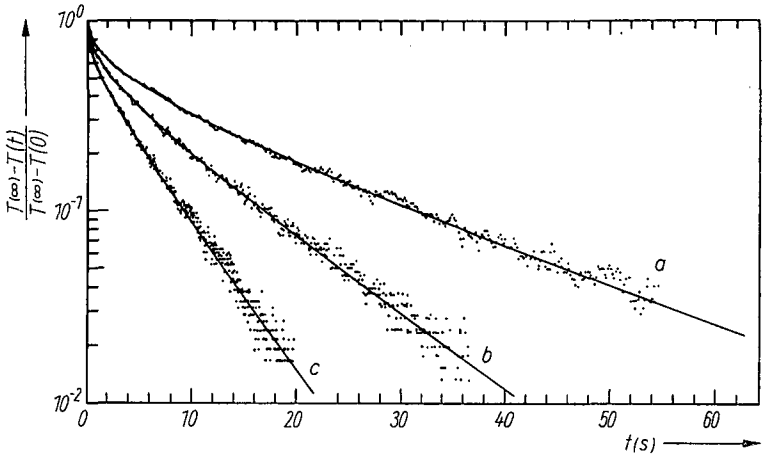

Fig. 6. Normalized transmitted intensity, $(T(\infty) - T(t))/(T(\infty) - T(0))$, in F′ band when switching off excitation in the F band for different intensities (I) of the monitor beam for KCl at 10 K. (a) $I = I_0$: $(\alpha\omega_i)^{-1} = 31.6$ s; (b) $I = 2I_0$: $(\alpha\omega_i)^{-1} = 15.3$ s; (c) $I = 4I_0$: $(\alpha\omega_i)^{-1} = 7.8$ s. ● measurements, ——— model best fits

5.2 Inverse tunnelling

The transient F′ population after excitation in the F band has been measured for different intensities of the probe light. The result is shown in Fig. 6. As predicted by the back transfer model the apparent lifetime $((\alpha\omega_i)^{-1})$ of the F′ center is proportional to the intensity of the monitor beam and therefore to the light absorbed by the F′ center; further analysis of these curves gives for the inverse transfer parameters (Λ' being the same for the three curves, because of the same excitation and consequently the same populations)

$$\tau_{0i} = 2 \pm 1 \text{ ms},$$

$$\Lambda' = 1 \pm 0.5 \times 10^{-3}.$$

A consistent interpretation of Λ' is to assume an F′ — α pair spatial distribution nearly the same as the original F pair distribution yielding a critical distance λ' equal to λ. The effect of the magnetic field on the F′ band decay can be seen in Fig. 7; as predicted by the model in Section 4, the apparent lifetime $((\alpha\omega_i)^{-1})$ is reduced by 30% without any change in the tunnelling parameters τ_{0i} and λ'.

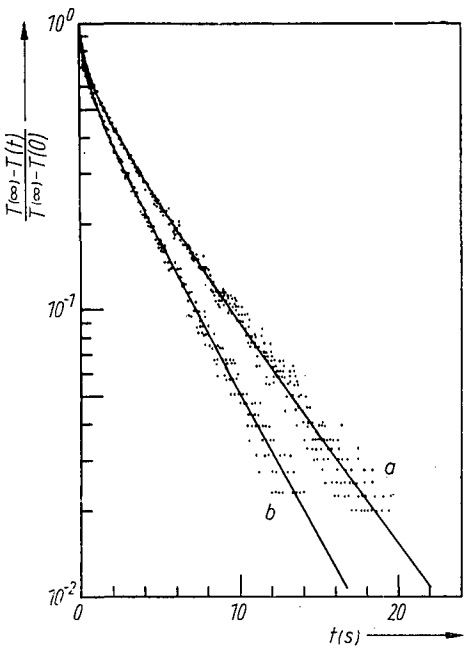

Fig. 7. Normalized transmitted intensity in the F′ band when switching off excitation in F band with fixed intensity of the monitor beam for KCl at 10 K. (a) Without magnetic field, $(\alpha\omega_i)^{-1} = 7.85$ s; (b) with magnetic field of 0.5 T, $(\alpha\omega_i)^{-1} = 5.95$ s. ● measurements, ——— model best fits

6. Conclusion

The agreement obtained between the experimental and the calculated data by fitting a small number of parameters (three intrinsic ones for the direct process, two intrinsic ones and one extrinsic one for the inverse transfer process) supports the validity of the models. The origin of the non-exponential luminescence decay lies therefore rather in the non-radiative electron transfer within the F center pairs than in contributions from M and R centres. Furthermore, the assumption of a Poisson distribution of the individual centers in well quenched samples is verified, at least for the separations involved here; a deviation at shorter distances due to the attractive potential does not appear, because of the very small relative number of such pairs and of the limited experimental time resolution.

The transfer rate within the pairs is well described by a exponential dependence of the separation. The fact that the characteristic distance in the direct transfer is nearly the same as in the reverse process, is certainly related with the similar extension of the wave functions in $\tilde{F}^* - F_0$ and $F' - \alpha$ pairs. On the other hand, the very large factor of 5×10^6 between the absolute transfer rate values is not surprising, since these processes involve a tunnelling through a potential barrier, with an exponential dependence of the latter. Lattice relaxation has certainly a strong influence, but an estimation of this effect is outside the scope of this paper.

This paper is concerned exclusively with so called distant pairs in which the spin exchange energy in the relaxed excited state is smaller than the Zeeman energy [2]. Considering our time resolution of 10 ns, this corresponds to separations larger than 2.5 nm. Close pairs, detectable by NMR after bleaching in the F band near room temperature [7], would require a resolution of 0.1 ns in order to be detected in the luminescence decay. Although their analysis is easier in the reverse transfer, their largely reduced number excludes easy measurements of the F′ absorption because of the low signal to noise ratio.

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EXCHANGE EFFECTS IN ODESR OF F CENTER PAIRS IN ALKALI HALIDES

A.C.Mezger and C.Jaccard*

Inatitut de Physique, Univeraité de Neuchâtel, CH-2000
Neuchâtel, Switzerland

(received 10 October 1981)

The electron psramsgnetic resonance of F center psirs has been measured by meana of an optical detection in the following alkali halide crystals at a microwave frequency of 35 GHz: KCl, NaCl, RbCl, KBr, KI snd CsBr. Besides the ESR of the ground and excited states, a third resonance line is obaerved and is attributed to a pair effect due to an exchange interaction between neareat neighbour F centers. A model based on this assumption is developed.

As reported in a previous publication [1] the F center ESR can be observed optically by measuring the variation of the luminescence when a resonant microwave field is applied; this process is based on a spin dependent electron transfer by a tunnel effect from the relaxed excited center $\tilde{F}^*$ to a neighbouring center in its ground state F_0 [2]. As a result an F' center and an anion vacancy are created which return to the ground state F_0-F_0 by an inverse electronic tranafer. The optical cycle produces through this non-radiative disexcitation a population difference between the pair spin states, which allows resonant microwaves to interact with the F center system and to modify its radiative yield.

In our first measurements we used a microwave frequency of 10 GHz (X-band) and we obtained unresolved resonances in several alkali halides except in KBr and KI, for which two clearly resolved resonances due to the ground and the excited state were obtained.

Later measurements by Murayama et al. [3] at a much higher frequency (35 GHz: Q-band) show that in KCl a third resonance is obtained with a g-value of $(g+g^*)/2$, where g and g^* are the Landé factors for the ground and the excited state, respectively. This result is explained by taking into account the exchange interaction between an F center in its excited state and another one in its ground state.

Recent measurements performed by another method of detection (MCD with a low F center concentration) [4] show also a third resonance in KCl, NaCl, KBr and CsBr, but in the last two crystals the third resonance is not related with the two other ones and it is therefore attributed to an unknown relaxed excited state of the F center. The results obtained by the different authors are shown in table I.

The origin of this third resonance is thus not clear and a more detailed study is necessary. In this paper we present new ESR spectra for several alkali halides obtained from the luminescence by the optical detection method at 35 GHz, and we propose a model based on the exchange interaction between F centers; by taking into account the distribution of these centers and the exchange energy as a function of distance, we explain the simultaneous observation of the three resonances and we obtain for KCl a rough estimation for the exchange energy between the F centers.

Figure 1 shows the ESR spectra obtained at 35 GHz. Excepting the case of CsBr, they all display a third more or less intense resonance, always situated in the middle between the resonances of the excited and of the ground state of the F center ($g'=(g+g^*)/2$). Numerical decomposition of these spectra gives the g-values and halfwidths of table 1. The data obtained from measurements at lower frequency (10 GHz) are erroneous in the case of KCl and NaCl, because the decomposition in two resonance lines is not justified as it can be seen from our new data.

The fact that in almost all the measured crystals a new resonance between the fundamental and the excited state resonances is obtained suggests an exchange effect for its origin. Moreover, the ESR spectrum shown in figure 2 and obtained with a bleached crystal containing short F center pairs shows that a pair effect ($\tilde{F}^*$-F_0) is responsible for the new resonance line. A model based on this assumption is developed below.

This model (first proposed by Murayama et al.)

*Present address: EISLF, Weissfluhjoch, CH-7260 Davos-Dorf

Table 1. ESR data (g-values and halfwidths) of the F center resonances. Also data from other authors are reported. The numbers 1,2 and 3 represent the ground state resonance, the excited state resonance and the new resonance respectively.

Crystal	Ruedin et al.[1] X-band		Murayama et al.[3] Q-band	Hahn et al.[4] Q-band		present results Q-band	
	g	$\Delta H_{1/2}$ (G)	g	g	$\Delta H_{1/2}$ (G)	g	$\Delta H_{1/2}$ (G)
1:	1.985	65.	1.995	1.995	55.	1.995	69.
KCl 2:	1.981	79.	1.968	1.968	83.	1.969	66.
3:			1.982	1.982	43.	1.984	56.
1:	1.999	143.		1.997	170.	1.997	206.
NaCl 2:	1.973	71.		1.966	76.	1.966	88.
3:				1.982	90.	1.983	111.
1:				1.980	522.	1.976	521.
RbCl 2:				1.940	188.	1.940	181.
3:						1.960	264.
1:	1.983	157.		1.984	147.	1.987	165.
KBr 2:	1.873	256.		1.873	234.	1.873	245.
3:				1.995	138.	1.93	~200.
1:	1.969	258.		1.964	256.	1.964	266.
KI 2:	1.63	570.		1.686	541.	1.632	569.
3:						1.80	~300.
1:				1.958	722.	1.955	760.
CsBr 2:				1.638	480.	1.638	490.
3:				2.184	488.		

consists in two F centers (one in its excited state and one in its ground state) coupled by an exchange interaction of the type:

$$J(r)\vec{S}_1.\vec{S}_2$$

where J(r) is a function of the distance between the two centers.

The resolution of the spin Hamiltonian taking into account this interaction yields for the possible ESR transitions the g-values shown in figure 3 as functions of the exchange energy.

In a well quenched crystal of KCl the F centers are uniformly distributed and the distribution of the nearest neighbour pair separation and of the exchange interaction is continuous. However, this is not the case for the g-values. This can be explained by the fact that the exchange interaction varies rapidly with distance; the distribution of the g-values is then concentrated on three delta functions: g and g* for the long pairs ($J/\beta_e H < 0.01$) and $(g+g^*)/2$ for the short pairs ($J/\beta_e H > 0.1$). The diverging branches ($g'>g$ or $g'<g^*$) do not contribute to the spectra, because the lines are smeared and their intensity vanishes with increasing J.

From the relative intensity of the new line and the matrix elements for the transitions, one quarter of the F center pairs can be estimated to contribute to this resonance; from this and by using the pair distribution [5] the exchange energy in KCl can be estimated to be about 10% of the Zeeman energy for a separation of about 5 nm in a $\tilde{F}^*$-F_o pair. This result is in agreement with the exchange energy as a function of the distance estimated from the calculation by Schwoerer and Wolf [6] for F center pairs in their ground state and from the extension of the wave-function in the excited state:

$$J=J_o\exp(-r/\lambda)$$

with $J_o \simeq 25$ eV and $\lambda \simeq 0.25$ nm.

In other crystals than KCl no information is obtained about the exchange energy, because the distribution and the concentration of the F centers is not well known.

These reaults show that in most of the alkali

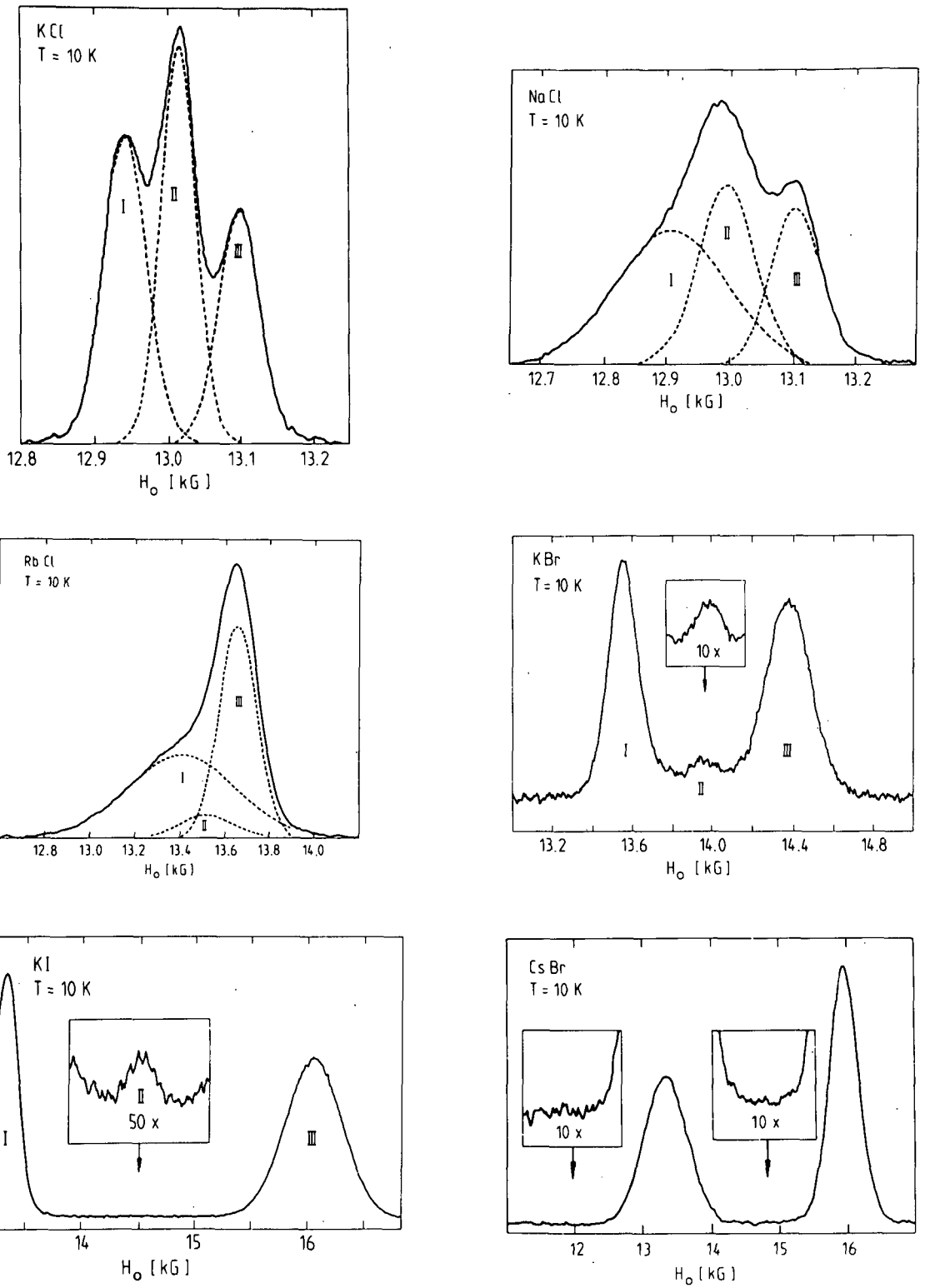

Fig.1. Optically detected ESR signal in several alkali halides at 35 GHz and 10 K; full line: signal as recorded, dotted line: numerical decomposition

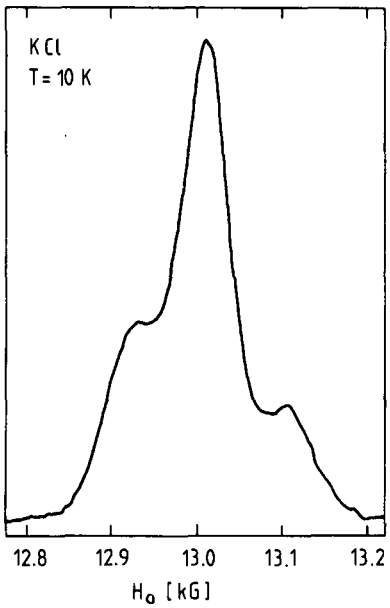

Fig.2. g-values of an F center pair $\tilde{F}^*$-F_0 in KCl as functiona of the exchange energy normalized by the Zeeman energy; the thicknesa of the line gives an indication of the ESR tranaitions intenaity.

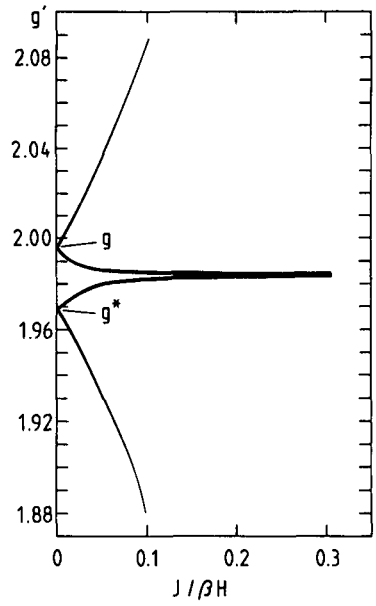

Fig.3 Optically detected ESR aignal in KCl for a bleached crystal containing "short" F center paira at 35 GHz and 10 K.

halides meaaured sofar, a third resonance ia obtained which can be attributed to F center paira $\tilde{F}^*$-F_0 separated ao that a exchange interaction can not be neglected. In KCl and NaCl the third resonance observed by Hahn et al. can then be explained by thia model ; however, in the case of CaBr and KBr the resonancea with the g-values reported by Hahn et al. are not obaerved by our optical detection method and their origin remaina unexplained.

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HYPERFINE PARAMETERS FROM NONRESONANT LUMINESCENCE EFFECTS AND SPIN MEMORY OF F CENTER PAIRS IN ALKALI HALIDES

A. MEZGER and C. JACCARD
Institut de Physique de l'Université, CH-2000 Neuchâtel, Switzerland

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In a static (100) magnetic field, the luminescence of F centers in KCl shows peaks at 1134, 1516, (790) G, attributed to 4th (3rd) nearest neighbouring nuclei with equal Zeeman and hyperfine energies. The electronic spin memory losses for KCl, NaCl and KBr are in the ratio 1: (4.5 ± 1): (11 ± 3).

When single F centers in alkali halides are irradiated in the F band at low temperature, their luminescent quantum yield is unity, but if the F concentration is higher than about 10^{17} cm^{-3}, the yield is reduced by a competing nonresonant de-excitation pathway [1]: the excited electron is transferred to a neighbouring center, giving a F^- (or F') center plus a halide vacancy, then it returns into its original ground state in the vacancy [2]. Since in the F^- center the electron spins are antiparallel, this process requires an appreciable singlet component in the pair spin state. This has been demonstrated by applying a strong static magnetic field such that the Zeeman energy becomes larger than kT; nearly all the electrons have then parallel spins, the pairs are mainly in the triplet state and the quantum yield increases to unity [3]. Interesting effects have also been discovered at rather low values of the field for which the temperature has no effect on the populations. In this case, the spin state is determined also by the hyperfine coupling with the neighbouring nuclei [4]. When the applied field varies from zero to a few kG, the luminescent yield increases significantly, e.g. by 50% for well doped KCl samples. The nonradiative process is also sensitive to a resonant microwave field, allowing optical detection of EPR (ODEPR) in the ground and in the relaxed excited state of the F centers [5]. Moreover the average pair separation can be reduced by irradiation in the F band near room temperature, transforming the "distant" pairs for which the ODEPR signal appears as a decrease of the luminescence into "close" pairs with a response of opposite sign [6]. If a radiofrequency field is applied, ENDOR spectra can be obtained from the luminescence. However the same effects show up even in the absence of microwaves, allowing the optical detection of the nuclear magnetic resonance alone (ODNMR) for the nuclei surrounding the F centers, with the corresponding change of sign between distant and close pairs [7,8]. The spectra obtained this way can be interpreted by means of the single center hamiltonian used for standard ENDOR [9], because the pair separation is larger than 5 interionic distances and therefore the close environment of each center is not perturbed by its neighbour [10]. The ODNMR has been explained by taking into account (1) the effect of the nuclear spins on the electronic spin states by means of the hyperfine coupling, and thereby on the nonradiative de-excitation probability; (2) the total spin conservation during the de-excitation for distant pairs [8]; and (3) the electronic exchange energy for the close pairs [7]. In this paper, we present experiments showing that in certain cases some of the hyperfine parameters occurring in the spin hamiltonian can be obtained from the luminescence of distant pairs as a function of the static magnetic field only, without any r.f. or microwave field.

In KCl crystals doped with F centers, either additively or by X irradiation, the luminescence as a function of the static magnetic field along (100) displays near 1 and 1.5 kG two well visible small peaks

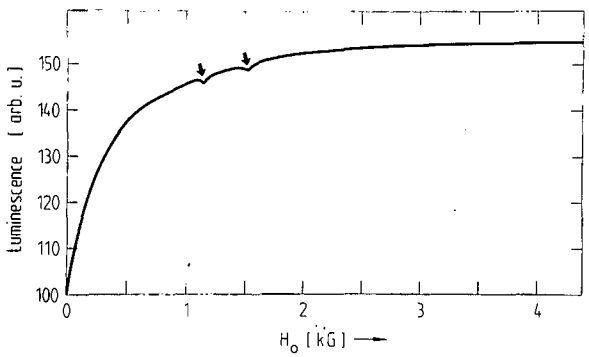

Fig. 1. Luminescence of F centers in KCl at 12 K as a function of a static magnetic field along (100) ($n_F = 5 \times 10^{17}$ cm^{-3}).

superimposed on the overall increase, as it can be seen in fig. 1. Their height can be as large as a few percent of the total luminescence. They are certainly due to pair effects, since they change their sign if the initially distant pairs are changed into close pairs. With a modulated field and phase detection of the luminescence they appear quite clearly (fig. 2, upper curve) with a low relaxation frequency near 50 Hz, and a temperature behaviour indicating that they are related with the nuclear resonance. Tentative experiments with impure crystals suggest that these peaks are not related with chemical impurities.

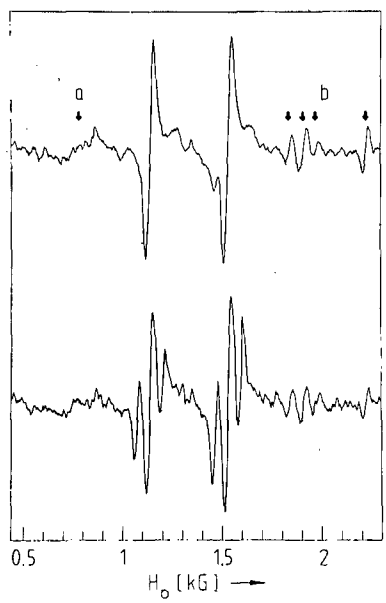

Fig. 2. First derivative of the luminescence of F center pairs in KCl at 12 K. Upper curve: without resonant r.f. field (arrows a, b: see text). Lower curve: with a nonsaturating r.f. field (25 kHz).

Careful examination of their position, together with a transverse AC field of low frequency giving ODNMR peaks (fig. 2, lower curve), shows that their position corresponds to the static field values for which the resonant frequency of the 4th nearest neighbour ions Cl_{IV} vanishes. The field values are given by $W_{hfs}/2g_n\beta_n$ (W_{hfs} = hyperfine coupling energy for the nucleus, $g_n\beta_n$ = nuclear magnetic moment), if the quadrupolar interaction is neglected (it is smaller than the peak width). The centers of the peaks lie at 1134 ± 1 and 1516 ± 1 G, in agreement with the ODNMR results and the ENDOR measurements [9]. Since the hyperfine energy is also proportional to the nuclear magnetic moment, the peak position is the same for the two isotopes ^{35}Cl and ^{37}Cl. A small peak at 790 G corresponds to the 3rd nearest neighbour ions K_{III} (fig. 2, arrow a). It is smaller because the peak height in the first derivative representation is inversely proportional to the second power of the width (the magnetic moment of ^{39}K is about two times smaller than that of ^{35}Cl).

These findings can be explained in the following way. In the nonradiative optical cycle $F_0F_0 \rightarrow \widetilde{F}^*F_0 \rightarrow F^+F^- \rightarrow F_0F_0$ the electron transfer probability for the second step is nearly proportional to the singlet component of the pair spin state. With an electronic Zeeman energy larger than the average total hyperfine energy ($g_e\beta_e H_0 \gg \Sigma W_{hfs}$) two states ($m_{s1} = \pm\frac{1}{2}$); $m_{s2} = \mp\frac{1}{2}$) are essentially in the singlet state and are therefore nonradiative. The two other states are nearly triplets ($m_{s1} = \pm\frac{1}{2}$; $m_{s2} = \pm\frac{1}{2}$) but with a small singlet admixture proportional (to the first order) to the ratio of the total average nondiagonal hyperfine term and of the Zeeman energy $\langle\mathcal{H}_{hfs}\rangle/g_e\beta_e H_0$. This ratio depends on the occupation of the nuclear spin states. As it has been shown in a previous paper [8] nuclei in the states $|m_I| = \frac{1}{2}$ favour the electronic transfer with respect to those with $|m_I| = \frac{3}{2}$. Acting as a pump from the $|m_I| = \frac{3}{2}$ to the $|m_I| = \frac{1}{2}$ states, the optical cycle produces a disequilibrium of the nuclear populations, which is reduced if a resonant r.f. field is applied, giving ODNMR. When the nuclear Zeeman energy $g_n\beta_n H_0$ is equal to the hyperfine coupling $\frac{1}{2}W_{hfs}$, half of the nuclei have degenerate spin states, so that the populations can be exchanged by dipolar coupling without the necessity of intervening phonons or photons to ensure energy conservation. The spin states can-

not be distinguished from each other, the populations are mixed together, and this produces the same effect as a saturating r.f. field in the case of ODNMR.

This process can be observed only under special conditions: The applied field H_0 has to be larger than the total average nuclear field "felt" by the electrons in order to separate the electronic states into triplets and singlets. On the other hand, it should not be too high, so that the triplet states still contain an appreciable nonradiative singlet component which can be modified by changing the nuclear spin populations. These conditions are well satisfied for Cl_{IV} in KCl. For K_{III}, at a lower field, the singlet component is larger and the optical pumping of the nuclear states is less efficient. The phenomenon described here can be interpreted as a zero frequency resonance and corresponds to the particular response of systems in which the levels of interacting states can cross each other for definite values of a parameter.

It is worth stressing here that these zero frequency peaks are conditioned by an efficient optical pumping of the nuclear states. This is obviously possible only if the *electronic spin memory* is preserved during an optical cycle. This is the case for KCl, in which the spin memory loss parameter ϵ is quite low [11]. Comparison of the intensities of ODNMR lines in different crystals can give a qualitative information on this parameter since according to our model [8] the peak height is proportional to ϵ^{-2} (the change in luminescence from zero to 5 kG can be used as a measure of the distant pair concentration). From the resonance of chlorine in KCl and NaCl, and of bromine in KBr we obtain $\epsilon(KCl) : \epsilon(NaCl) : \epsilon(KBr) = 1 : (4.5 \pm 1) : (11) \pm 3)$. In a study of the optical pumping cycle of single F centers in KBr, Mauser et al. [12] show that ϵ is dependent on the excitation wavelength. Their measurements, averaged over the F band, yield a spin memory loss of 0.13 ± 0.01, about three times larger than determined by Mollenauer and Pan [11]. Fitting our results to Mauser's, it gives $\epsilon(KCl) = (1.2 \pm 0.4) \times 10^{-2}$ and $\epsilon(NaCl) = (5.5 \pm 1.5) \times 10^{-2}$. The high value of 0.24 for KI found by Mollenauer and Pan would then explain our unsuccessful attempts to observe ODNMR in KI. The same could be said of CsI, in which the spin–orbit coupling, and hence the spin memory loss are large too.

We have not yet found an explanation for the smaller peaks (fig. 2, arrow b) which are found at near equidistant field values up to 5 kG. They do not satisfy the conditions mentioned above but they might be the result of interactions between the different nuclear species.

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2. Exchange Effects in ODESR of F Center Pairs in Alkali Halides. A.C. Mezger and C. Jaccard; Solid State Communications, Vol. 41, No. 4, 301 (1982)

3. Hyperfine Parameters from Non-resonant Luminescence Effects and Spin Memory of F Center Pairs in Alkali Halides. A.C. Mezger and C. Jaccard; Physics Letters, Vol. 79A, No. 1, 118 (1980)

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