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EPR Optical Detection of F Centre Pairs in Alkali Halides[1] [2]

II. Spin-Lattice Relaxation of the F Centre in Its Relaxed Excited State

By

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Like the EPR line of the fundamental state of the F centre in most of the alkali halide crystals, the line attributed to the relaxed excited state, detected optically for F centre pairs is also Gaussian in shape. That is explained by an inhomogeneous broadening due to hyperfine interactions with the surrounding nuclei. The measurements of these resonances as a function of the microwave power allow to determine the saturation parameter and the broadening of the elementary line (homogeneous). On the other hand the measurement of the resonance signal as a function of temperature, the other parameters remaining constant, shows that it stays constant for $T < 10$ °K and decreases for increasing temperature. This is attributed to the spin-lattice relaxation time T_1 of the defect in its relaxed excited state. The relaxation mechanism is characterized by an Orbach process.

A l'instar de la raie de résonance paramagnétique de l'état fondamental du centre F dans les halogénures alcalins, celle de l'état excité relaxé, détecté optiquement pour des paires de centres F est également de forme Gaussienne. Cela s'explique par un élargissement inhomogène dû à l'interaction hyperfine avec les noyaux voisins. Les mesures de ces résonances en fonction de la puissance hyperfréquence permettent de déterminer le paramètre de saturation et l'élargissement de la raie élémentaire (homogène). D'autre part, la mesure du signal de résonance en fonction de la température, tout autre paramètre étant maintenu constant, montre que celui-ci est constant pour $T < 10$ °K et décroit lorsque la température augmente. Le phénomène est attribué au temps de relaxation spin-réseau T_1 du défaut dans l'état excité relaxé. L'analyse de T_1 montre que le processus de relaxation est du type Orbach.

1. Introduction

The process responsible for the decrease of the luminescence when electronic transitions are induced between the spin levels of an F centre pair is described in the preceding paper [1]. The accuracy of the model has been verified by studying the phenomena as a function of the luminescence wavelength, the F centre concentration, and the optical irradiation intensity. Moreover we have obtained an estimate of the non-radiative de-excitation rate of the return process:

$$F' + \alpha \rightarrow F_0 + F_0 \,.$$

All this has to deal essentially with the kinetics of the pumping cycle but nothing has been said about the kinetics of the transitions between the spin levels of the F centre pair. As mentioned in [1] the antisymmetric pair popula-

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tion is smaller than the symmetric one because of its faster radiationless decay. Thus the net effect of transitions between Zeeman levels is to transform pairs with parallel spins into pairs with antiparallel spins; however this transition rate is effective only if it is at least of the order of the radiative probability.

In this paper we present two types of measurements:

1. The analysis of the microwave induced luminescence decrease as a function of the incident r.f. power at constant optical excitation and temperature. This gives the value of the saturation parameter $s^2 = \gamma^2 h_1^2 T_1^* T_2$ and provides a means of calculation for the time T_2 characterizing the width of the elementary resonance line (homogeneous broadening).

2. The analysis of the resonance signals as a function of temperature at constant microwave transition and optical pumping rates. The signal is found constant for $T \lesssim 10$ °K but decreases strongly above this temperature. This provides us with a way of determining the spin–lattice relaxation time $T_1(T)$ of the $\tilde{\mathrm{F}}^*$ state.

Finally our results for KCl and KF are compared with the Stark effect measurements in the relaxed excited state performed by Bogan and Fitchen [2].

2. Inhomogeneously Broadened Resonance Line

Paramagnetic resonance manifests itself by a dip of the luminescence intensity while varying the static magnetic field. According to our previous paper [1], this would be expressed by the following equation (at constant field but varying r.f. frequency):

$$\Delta I_\mathrm{L}(\omega) = -\frac{1}{2} I_\mathrm{L}\, n\, V_\mathrm{t} \; \frac{M(\omega)}{(1+R)\bigl(1+R+M(\omega)\bigr)},$$

where I_L is the luminescence intensity (maintained experimentally at a constant level), n is the instant F centre concentration, and V_t the effective volume for pair coupling (independent of temperature). The function $M(\omega)$ is the r.f. transition rate multiplied by the radiative lifetime τ_r and R is this lifetime divided by twice the spin–lattice relaxation time T_1.

However, this expression is valid only if all the centres have the same resonance frequency ω_0, i.e. if the line broadening is homogeneous. It is well known that this is not the case for the ground state of the F centre [3]. The $\tilde{\mathrm{F}}^*$ relaxed excited state resonance appears also to be inhomogeneously broadened because of its Gaussian shape.

The calculation of the inhomogeneous line can be performed in our case in the same way as Portis [3] has done. We obtain for the maximum height of the Gaussian peaks $S(\omega_0)$

$$S(\omega_0) = -\left(\frac{\pi}{2}\right)^{1/2} I_\mathrm{L}\, n\, V_\mathrm{t} \frac{T_1^*}{\tau_\mathrm{r}} \frac{T_2^*}{T_2} \frac{s^2}{t}.$$

Here T_1^*, the effective relaxation time, is defined by

$$(T_1^*)^{-1} = (T_1)^{-1} + \left(\frac{\tau_\mathrm{r}}{2}\right)^{-1}.$$

T_2^* corresponds to the width of the Gaussian peak measured at the inflexion points and T_2 to the width at half maximum of the elementary Lorentzian peaks. The parameters s and t are functions of the incident r.f. power P

$$s^2 = t^2 - 1 = \gamma^2 T_1^* T_2 A P$$

(A geometrical factor) .

In order to obtain informations about T_1 and T_2, it is then necessary to measure the signal dependence of the microwave power and of the temperature, while keeping in mind that the radiative lifetime is practically constant in the temperature range considered here.

The homogeneous broadening is related to the mean lifetime of the electrons in their different states. For the antiparallel configuration we admit that this time is given by the inverse of the tunnelling rate [4]. Let us note that a spin-spin relaxation time smaller than W_t^{-1} would quench the signal completely.

Moreover Stiles et al. [5] showed that the F centre luminescence quantum yield η for KCl ($n_F = 3 \times 10^{16}$ F centres/cm^3) is constant below 77 °K ($\pm 2\%$). Taking into account Miehlich's results [6] and the fact that η depends exponentially upon V_t [4] it can be shown that the relative change in T_2 as a function of temperature has an upper limit of about 20%. Therefore it is reasonable to assume that all the temperature dependence is contained in the spin-lattice relaxation time T_1.

3. Temperature and Microwave Power Dependence

At low temperature the spin-lattice relaxation time T_1 is larger than the radiative lifetime τ_r (almost temperature independent) and the signal $S(\omega_0)$ is constant. If T_1 becomes smaller, the signal decreases and this gives information about $T_1(T)$. To determine the saturation parameter s^2, we transform the expression for $S(\omega_0)$ into

$$\frac{P}{[S(\omega_0)]^2} = \frac{2}{\pi I_L^2 n^2 V_t^2 \gamma^2 A} \frac{T_2}{(T_2^*)^2} \frac{\tau_r^2}{(T_1^*)^3} \left(1 + \frac{1}{\gamma^2 A P T_1^* T_2}\right).$$

In this representation the ratio of the ordinate at the origin to the slope gives the value $A \gamma^2 T_1^* T_2$.

At low temperature ($T \approx 0$) T_1^* is equal to $\tau_r/2$ and this defines the parameter s_0

$$\frac{s_0^2}{P} = \frac{1}{2} A \gamma^2 T_2 \tau_r .$$

In order to analyze the temperature dependence of $S(\omega_0)$ the heights of the resonance peaks are normalized to unity at low temperature by defining

$$S_{\text{norm}}(T) = \frac{S(\omega_0, T)}{S(\omega_0, T \approx 0)}.$$

We obtain

$$S_{\text{norm}}(T) = \left\{\frac{\tau_{r0}}{\tau_r}\left[1 + \frac{\tau_r}{2 T_1(T)}\right]^{3/2} \left[1 + t_0^{-2} \frac{\tau_r}{2 T_1(T)}\right]^{1/2}\right\}^{-1}.$$

τ_{r0} and t_0 being the values of τ_r and t at low temperature and assuming that

$$\frac{2 W_r + \gamma^2 T_2 A P}{2 W_r + \gamma^2 T_2 \frac{\tau_{r0}}{\tau_r} A P} \approx 1 .$$

We can therefore determine T_2 and $T_1(T)$ by two sets of measurements without knowing the value of the multiplicative parameters in $S(\omega_0)$.

4. Experimental Procedure

The details of the experimental technique and of the F centre production by X-rays are described in the preceding report. Let us here examine the error affecting the variables P, T, and T_2.

As previously mentioned [1] P is measured by means of a thermistor and a wattmeter which is a somewhat crude method. The wattmeter accuracy of 5% (fullscale) can induce errors up to 15%. Since the saturation parameter s^2 depends only upon the relative value of P, the error on s^2 is estimated to be of the order of 20% by taking into account especially the signal errors due to low signal-to-noise ratio at low microwave power.

Moreover the value of T_2 requires the knowledge of the geometrical factor A which is a function of the cavity dimensions, of the Q-factor, and of the sample location in the cavity.

The Q-factor is determined by measuring the power reflected by the cavity with an oscilloscope, the sweep being synchronized with the sweep of the klystron frequency. This method is not very precise and we estimate the error of Q to be about $\pm 30\%$. This leads to an error of about $\pm 50\%$ for the T_2 value.

For the determination of T_1 (T), we proceed at constant microwave power and vary the temperature. The error in determining T_1, (due to the $\pm 20\%$ in s_0^2) is a systematic error smaller than 5%. The error affecting the temperature is always less than 2%. The essential error in the T_1 determination is thus the dispersion of the S_{norm} values.

5. Results and Discussion

5.1 *Saturation factor s^2 and homogeneous line broadening T_2*

The signal is studied as a function of microwave power for KF, KCl, KBr, KI, RbBr, and RbI crystals. Since in the first two cases the two resonance peaks are superimposed, we take into account the resulting peak heights only. However in KBr, KI, RbBr, and RbI, the excited and ground states resonances are fairly well separated and we can therefore determine s^2 and T_2 for each one.

In Fig. 1 are plotted the values of $P/[S(\omega_0)]^2$ for three concentrations of F centres in a KBr crystal, i.e. for $n = 1.5 \times 10^{16}$, 6×10^{16}, and 2×10^{17} cm^{-3}. Within the error limit, the values of T_2 obtained in each case are the same for the ground and for the excited states. Moreover they differ by less than 20% for the three concentrations and are also almost independent of the intensity of the light excitation (Table 1).

In Fig. 2 we illustrate the same measurement with KI. The mean T_2 values obtained for the different crystals are reported in Table 2.

It is somewhat surprising to discover different T_2 values for the excited and for the ground states in the same crystal. This is the case especially for KI, RbBr,

Table 1

T_2 values (ns) calculated for KBr for three different concentrations from the ground and relaxed excited state data $T = 7.6$ °K

n_F (cm^{-3})	1.6×10^{16}	6×10^{16}	2×10^{17}
ground state	106	109	125
relaxed excited state	104	123	107

Table 2

Mean values of T_2 (ns) determined from the ground and relaxed excited state resonance data

	KF	KCl	KBr	KI	RbBr	RbI
ground state	90	100	110	50	100	77
relaxed excited state			110	20	53	8
temperature (°K)	8.6	7.2	7.6	8.1	8.4	8.6

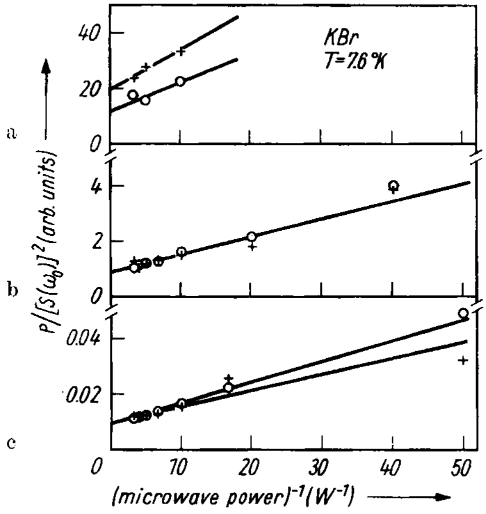

Fig. 1

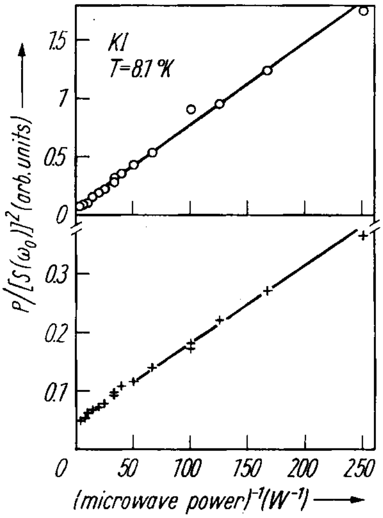

Fig. 2

Fig. 1. Determination of the saturation parameters s_0^2 in KBr for three different F centre concentrations at $T = 7.6$ °K. a) 1.5×10^{16} cm^{-3}, b) 6×10^{16} cm^{-3}, c) 2×10^{17} cm^{-3}. ○ and + correspond to resonances in the relaxed excited state $\tilde{F}^*$ and in the fundamental state F_0, respectively

Fig. 2. Determination of the saturation parameter s_0^2 in KI at $T = 8.1$ °K. ○ and + correspond to resonances in the relaxed excited state $\tilde{F}^*$ and in the fundamental state F_0, respectively

and KI for which the resonance lines are well separated and are associated to high values of the mean nuclear field $\langle H_N \rangle$ and $\langle H_N^* \rangle$. Therefore the values of the applied magnetic field required to fulfil the hypothesis of our model are not always attained. It can be shown at least qualitatively [7] that the number of centres which may contribute to the resonance signals becomes smaller for lower applied field. This phenomenon affects the s_0^2 parameter and consequently the values of the time T_2. The same effect explains also why the area of the relaxed excited state resonance is greater than that of the fundamental state. A quantitative calculation of both phenomena would require however a complete knowledge of the variation of the tunnelling transition probability in function of the pair distance.

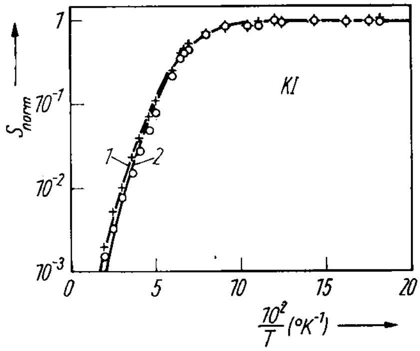

Fig. 3

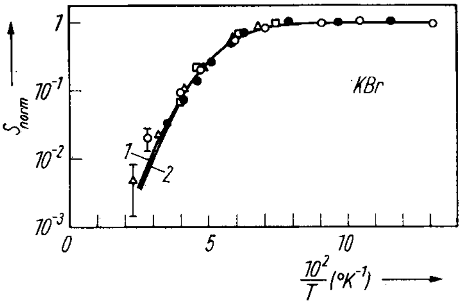

Fig. 4

Fig. 3. Normalized resonance peak height versus reciprocal temperature in KI. + measured values for the ground state resonance, ○ measured values for the relaxed excited state resonance. The solid curves 1 and 2 are calculated after the determination of the spin–lattice relaxation time $T_1(T)$ with a s_0^2 value of 8.4 (ground state) and 2.4 (relaxed excited state)

Fig. 4. Normalized resonance peak height versus reciprocal temperature in KBr for four different F centre concentrations. All the measured values are representative of both the ground state and the relaxed excited state resonances. ● concentration unknown. In this case the light excitation (quartz-iodine lamp at $T \approx 3000$ °K) is unfiltered. The solid curve 1 is calculated after the $T_1(T)$ determination with $s_0^2 = 2$. □ 1.5×10^{16} cm^{-3}, ○ 6×10^{16} cm^{-3}, △ 2×10^{17} cm^{-3}. An interference filter was placed in the optical excitation beam ($\lambda_0 = 6050$ Å, full width at half height: 400 Å). The solid curve 2 is calculated after the $T_1(T)$ determination with $s_0^2 = 4$

5.2 Temperature dependence and spin–lattice relaxation

Fig. 3 and 4 illustrate the temperature dependence of the resonance signals in KI and KBr crystals but similar variations are observed in all samples presently studied. The resolution of the $S_{\text{norm}}(T)$ expression for the different experimental values allows the determination of the spin–lattice relaxation time $T_1(T)$. The temperature variation of T_1 is shown for KBr and KI in Fig. 5 and 6 respectively in a semilog plot. These diagrams are a clear evidence for an Orbach type relaxation process such that

$$T_1 = T_0 \left(\exp \frac{\Delta E}{kT} - 1 \right).$$

The values of ΔE and T_0 are summarized in Table 3.

These results are in fair agreement with those obtained from Stark effect measurements performed by Bogan and Fitchen [2] and Stiles et al. [5] and confirm the level scheme proposed by these authors for the relaxed excited state and in which the lowest level has essentially an s character while the upper one is a p-like state. Odd mode vibrations of the lattice produce a mixing of both states (Fig. 7).

Indeed an Orbach process requires the presence of at least two levels separated in energy by a few meV. Moreover the isotropy of the g-factor, verified in this work for KBr [1] and by Mollenauer et al. [8] for KCl and KBr, suggest also for the lowest level essentially an s character.

Since the $|2\,s'\rangle$ state is the only one populated at low temperature it is responsible for the relaxed excited state resonance whereas the $|2\,p'\rangle$ level is the real level responsible for the Orbach process.

Table 3

Parameters characterizing the Orbach process

$T_1 = T_0\,(\exp(\Delta E/kT) - 1)$

(relative errors: T_0 ($\pm$ 30%), ΔE ($\pm$ 10%))

	ΔE (meV)	T_0 (ns)	ΔE ([2, 5] meV)
NaCl	9.4	40	–
KF	7.1	300	16
KCl	14.2	2.5	17
KBr	9.4	2	–
KI	6.5	15	–
RbBr	7.0	3.1	–
RbI	7.2	1.9	–

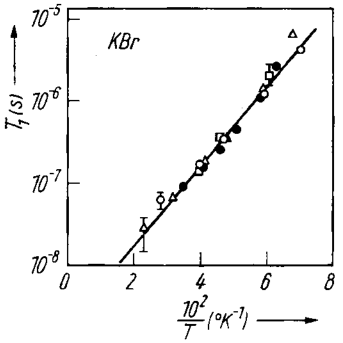

Fig. 5

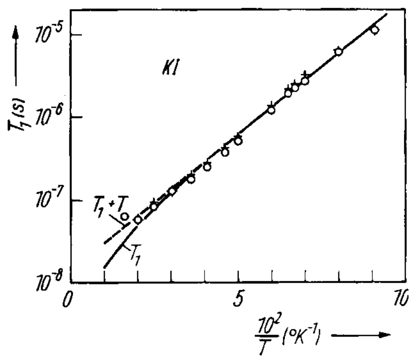

Fig. 6

Fig. 5. F centre relaxed excited state spin-lattice relaxation time versus reciprocal temperature in KBr for four different F centre concentrations (see also Fig. 4). ● concentrasition unknown. □ 1.5×10^{16} cm^{-3}, ○ 6×10^{16} cm^{-3}, △ 2×10^{17} cm^{-3}. The fitted straight line is a clear evidence for an Orbach process $T_1 \approx T_0 \exp(\Delta E/kT)$ with $\Delta E = 9.4$ meV and $T_0 = 2\times10^{-9}$ s

Fig. 6. F centre relaxed excited state spin-lattice relaxation time versus reciprocal temperature in KI (see also Fig. 3). + calculated values with the ground state resonance data. ○ calculated values with the relaxed excited state resonance data. The solid curve is an evidence for an Orbach process $T_1 = T_0\,(\exp(\Delta E/kT) - 1)$ with $\Delta E = 6.5$ meV and $T_0 = 15\times10^{-9}$ s

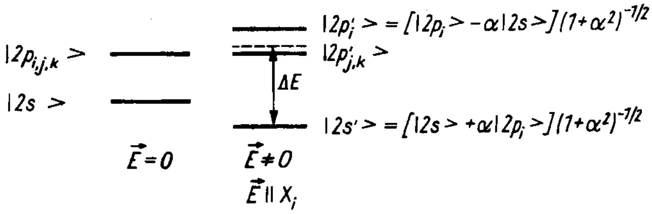

Fig. 7. F centre relaxed excited state level diagram proposed by Bogan and Fitchen [2]. α is the electronic state mixing parameter introduced to take into account the odd mode lattice vibrations

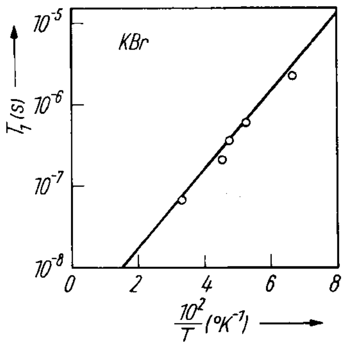

Fig. 8. F centre relaxed excited state spin–lattice relaxation time versus reciprocal temperature for KBr. ○ calculated values of $T_1(T)$ from the data of the non-resonant method [4, 7]. The straight line is from Fig. 5

Recently Ham [9] showed that this level ordering can be given a theoretical foundation by the exact vibronic solution of this model. However the only interaction which was taking into account was that of a triply degenerate $T_{1\text{u}}$ vibrational mode and it cannot give alone a complete answer to this relaxed excited state problem.

The field independence of T_1 which characterizes an Orbach type relaxation process has not been verified by EPR measurement but by a non-resonant method. In an earlier paper [4] we showed indeed that the important increase of the quantum luminescence yield η of the F centres observed when these crystals are placed in a magnetic field can be accounted for by the field dependence of the average tunnelling frequency. The analysis of the variation of η as a function of the applied field H and the temperature allows also to calculate $T_1(T)$.

In Fig. 8 the values obtained for T_1 by this method (extrapolation of η for $H \gg$ nuclear fields) are compared to the straight line obtained from the EPR results (Fig. 5). The agreement between both results is quite good; more detailed results will be published elsewhere [10].

6. Conclusion

The study of the F centre luminescence decrease in alkali halides crystals induced by microwave has been completed to give interesting details about the kinetics of the transitions between the spin levels of the F centre pairs.

1. The analysis of the resonance signals as a function of the incident r.f. power at constant optical excitation and temperature has allowed to calculate the time T_2 which characterizes the width of the elementary resonance line. For each crystal studied the T_2 values (Table 2) are found to be almost independent of the F centre concentration, the light excitation intensity, and the temperature. However in crystal having resonance lines well separated and associated to high values of the mean nuclear fields, the T_2 values differ for the ground and the excited state.

2. The analysis of the resonance signals as a function of temperature at constant microwave and optical pumping rates has allowed to determine the spin–lattice relaxation time $T_1(T)$ of the relaxed excited state of the F centre. For $T \gtrsim 10$ °K the relaxation mechanism is unambiguously described by an Orbach process: $T_1 = T_0(\exp(\Delta E/kT) - 1)$ (Table 3). For lower temperature, i.e. for the case of spin–lattice relaxation times larger than the lifetime of the F centre.

it was not possible to see with this kind of experiments if other relaxation mechanisms play a role or not.

Moreover the isotropy of the g-factor and the fact that an Orbach process requires the presence of at least two real energy levels suggest that the nature of the relaxed excited F centre consists of a lower level having essentially an s character (responsible for the relaxed excited state resonance) and a higher p-like level which is separated by just a few meV (responsible for the relaxation process). Both level are mixed by odd mode lattice vibrations. The experiments confirmed in a way the level scheme proposed earlier by Bogan and Fitchen [2] and Stiles et al. [5].

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