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ELECTRON TRANSFER BY THE TUNNEL EFFECT AND ITS INFLUENCE ON THE F CENTER LUMINESCENCE IN ALKALI HALIDES

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ABSTRACT

Concentration quenching plays an important role in luminescence phenomena, and is generally accounted for by pair interactions. In alkali halides containing F centers, whenever a member of an F center pair is optically excited at low temperature, it can return to its ground state either radiatively or by the formation of an intermediate F' center. In this case, the excited electron is transferred by fast tunnelling to a neighboring center. This process depends on the spin symmetry of the pair, which is determined by the inhomogeneity of the hyperfine field. Effects of applied magnetic field, spin lattice relaxation and spin-spin interaction on the tunnelling probability are investigated. Experimental confirmation of the theory is presented for the case of KCl.

1. INTRODUCTION

The characteristic variations due to concentration effects of the emission properties of defects in insulating materials such as the quenching of the photoluminescence, the line broadening and the shortening of the radiative lifetime are now well-known experimental facts (1). For instance, the quenching interaction between similar activator ions occurs in many rare-earth activated crystals with increasing doping concentration. It affects strongly the emission states of these ions through multipolar or exchange interactions. Quenching interactions between dissimilar species are, however, generally associated with the mutual relationships of their energy levels. Energy may be transferred non-radiatively from a metastable state of an excited activator to a neighboring ion which has a lower energy level (ground state for instance) pro-

vided the rate of dissipation of the total electronic energy is increased.

The emission properties of F centers in alkali halide crystals (an electron trapped in an anion vacancy) have been studied quite intensively during the last two decades (2). Excitation of an isolated F center at low temperature leads after a local lattice relaxation to the emission of a photon with a luminescent quantum yield of unity. However, when the F center concentration is high enough, there is a finite probability that two centers form a pair within a certain critical distance R_t; in this case the electron of the relaxed excited center $\tilde{F}^*$ may be transferred via a tunnelling mechanism to a neighbor defect in its ground state F_o, thereby forming an F' center (two electrons located in an anion vacancy) and an α center (anion vacancy). The pair returns then to its ground state F_o-F_o by some non-radiative mechanism. The existence of this process was suggested twenty years ago by Markham et al (3) and confirmed later experimentally by Miehlich's measurements of the concentration quenching of the F center luminescent quantum yield (4).

The study of this important de-excitation process has been revived recently by two fundamental experiments. The first one has been performed in our laboratory (5, 6) and has shown that a first stage increase of the F center luminescent quantum yield η can be induced by an external magnetic field at low temperature. This effect, which is of the order of 40% for a concentration of 5×10^{17} F centers/cm^3, occurs at low magnetic field (H<4kG). It can be explained by the competing influence on the pairs of the applied field $\underline{H_o}$ and of the local nuclear fields $\underline{H_N}$ and $\underline{H_N^*}$. They modify the character of the defect wave functions and consequently change the tunnelling probability. At the same time Porret and Lüty (7) have shown that in a second stage, an increase of η (up to a value of η=1) can be observed for T<LHeT and high magnetic field (H>>10 kG). As the F' ground state must have antiparallel spins, the non-radiative transfer is in this case hindered because of the finite spin polarization attained under these experimental conditions. We see therefore that in both cases the symmetry of the spin wave function of the initial and final tunnelling state of the pair, taken as an entity, plays a fundamental role in the explanation of the physical nature of this tunnelling mechanism.

In the next section we present the experimental results of the luminescent quantum yield variation at low magnetic field, obtained with KCl crystals of different F center concentrations. These results will be compared with a theory developed earlier by Jaccard et al (6). We show in section 3 that the study of this phenomenon as a function of temperature may give important information concerning the spin-lattice relaxation time of the F centers

in their relaxed excited state. In the last section some new effects which occur when the spatial distribution of the defects is modified (formation of loose aggregates) will be presented and discussed.

2. QUANTUM YIELD DEPENDENCE OF CONCENTRATION

In a recent paper (6), we have shown that the spin state of an electron pair $\tilde{F}^*$-F_o, i.e., an F center in its relaxed excited state, $\tilde{F}^*$, neighboring an F center in its ground state, F_o can be described by a four level scheme, equally populated for low magnetic field and for temperatures down to liquid helium temperature with the following energies:

$$\varepsilon_{1,4} = \pm\{(1/2)g^*\beta H^* + (1/2)g\beta H\},\ \varepsilon_{2,3} = \pm\{g^*\beta H^* - (1/2)g\beta H\}$$

β is the Bohr magneton, g the Landé factor of the F_o ground state and $|\underline{H}| = |\underline{H_o}+\underline{H_N}|$ the value of the local magnetic field at the site of the defect. The index * describes the same quantities for the relaxed excited state. Recalling that in the final state of the tunnelling process both electrons of the F' center must have the same orbital wave function but antisymmetric spin wave functions, it is possible to give an expression for the tunnelling probability of such a pair. Assuming that the spatial distribution of defects is random and that the nuclear fields $\underline{H_N}$ and $\underline{H_N}^*$ are not correlated and have an isotropic space distribution, the radiative quantum yield can be expressed by

$$\eta = \exp(-nV_t\langle P_t\rangle)$$

n is the F center concentration, V_t a critical spherical volume in which the tunnelling occurs (in this model independent of n) and $\langle P_t\rangle$ an average of the tunnelling probability. It is worth recalling that if $\langle P_t\rangle$ can be calculated exactly for the two special cases $|\underline{H_o}| = 0$ and $|\underline{H_o}| \gg |\underline{H_N}|, |\underline{H_N}^*|$ the averaging must be computed for intermediate values of $|\underline{H_o}|$.

An experimental check of this result is a very difficult task because of the determination of the absolute luminescent quantum yield. However, the luminescence intensity is proportional to η, the multiplicative constant containing geometrical factors and the excitation intensity; its logarithm therefore is linear in $\langle P_t\rangle$. In this way an "a posteriori" determination of η can be obtained and the slope of the straight line gives the value of nV_t. For this purpose thirteen ultra pure KCl crystals have been additively colored by the van Doorn technique with $2\times10^{16} < n < 1.4\times10^{18}$ F centers/cm^3. These crystals have been carefully quenched between two copper blocks and mounted under safe light in an Andonian variable temperature cryostat. The optical excitation device consisted of a quartz iodine lamp filtered by two broad band filters: a $CuSO_4$

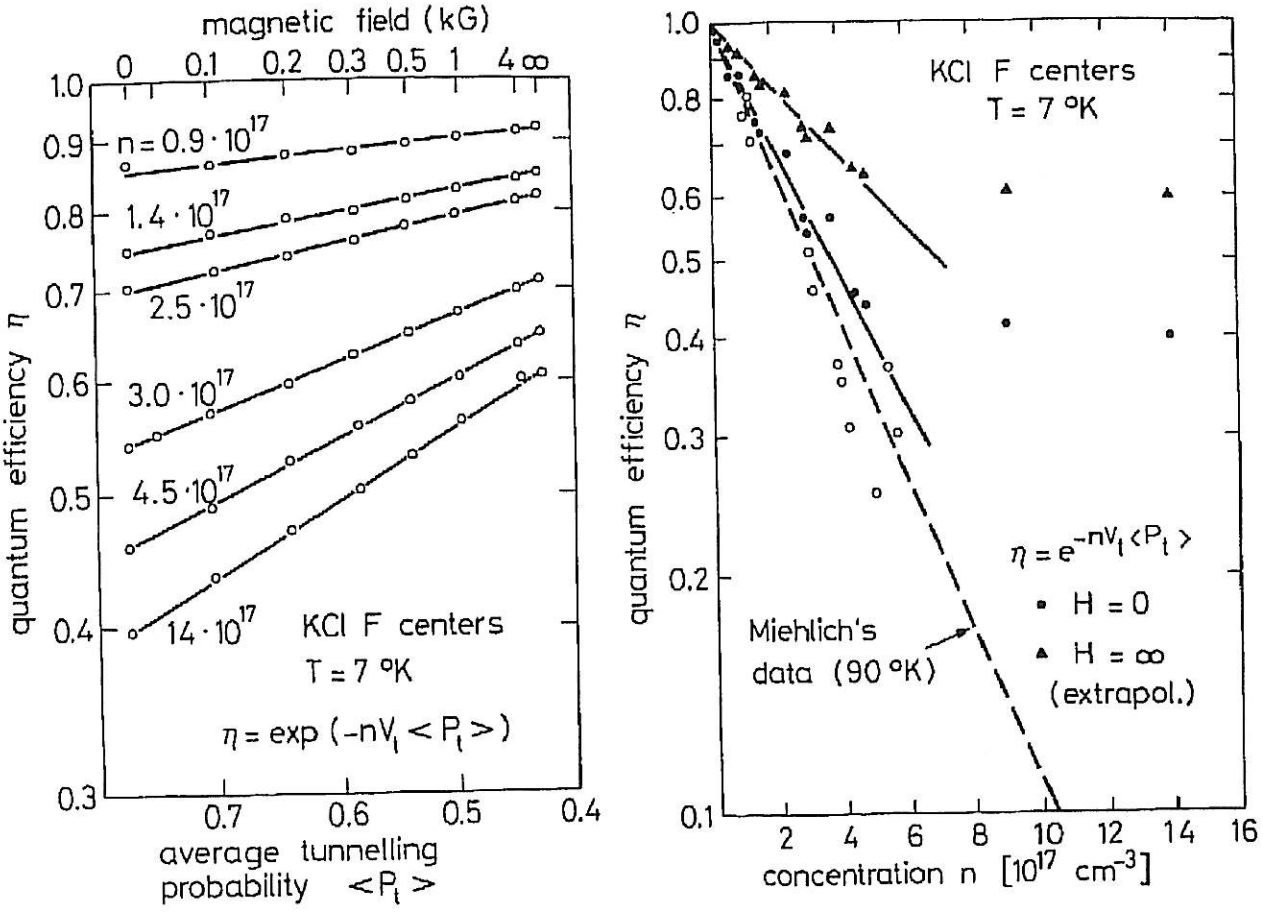

Fig. 1 Experimental radiative quantum yield of F centers versus computed average tunnelling probability P_t in KCl at 7 K for different concentrations. W = 8 ±1; R_t = 85 A (see (6)).

Fig. 2 Experimental radiative quantum yield η versus concentration n of F centers in KCl at 7K for zero • and infinite (extrapolated values ▲) magnetic field. Miehlich's data o, taken at 90K for H = 0, are also shown.

solution and an anticalorific Calflex B_1K_1 filter. In this way the F centers were essentially excited in their main transition. The F center luminescence was first filtered (Schott RG 715) in order to eliminate completely the light excitation and then detected with a PbS photoresistor (Mullard 119 CPY). The output signal was selectively amplified (PAR 110 and JB5) and recorded.

In Fig. 1 the calculated values of the luminescent quantum yield η at 7K are plotted for six crystals in a logarithmic scale versus the computed values of the average tunnelling probability. The fitted straight lines are in good agreement with our model for

all concentrations. In Fig. 2 the same ordinate is plotted for $H = 0$ and $H = \infty$ ($>>H_N$) in a logarithmic scale versus the macroscopic concentration of F centers (measured with a double beam spectrophotometer). For comparison some of Miehlich's data, measured at 90K for $H = 0$ are also shown. We can see that for concentrations up to 5×10^{17} F centers/cm^3 both results are in good agreement too. From the slope of the straight lines and with the knowledge of the corresponding values of the average tunnelling probability, we have determined that the critical radius R_t of the spherical volume in which tunnelling is possible is of the order of 85 A. For higher concentrations we observe systematic deviations from the straight lines. In the calculation of the luminescent quantum yield we have assumed that the tunnelling probabilities for different centers are independent; this is true for well-separated defects only. Jaccard et al (6) have shown that correlation effects affect the values of the radiative quantum yield by a multiplicative factor smaller than unity in the exponent $nV_t\langle P_t\rangle$. On the other hand, the optical density of these crystals around the main absorption band of the F centers was larger than 5 and no special effort was made to depress the intensity of the broad spectrum of excitation. For these experimental conditions an appreciable depopulation of the ground state may become important, especially if the average time required for a cycle F_o-$\tilde{F}^*$-F_o is of the order of 10^{-3} sec (see section 5). It will again affect the exponent of η by a multiplicative factor smaller than unity (6). Therefore, we see that in both cases these second order corrections have an effect similar to the reduction of the macroscopic concentration of defects. This shifts the calculated values of η towards the left of Fig. 2. It will generally be difficult to take quantitative account of these effects; but they can practically be eliminated by choosing more adequate experimental conditions.

3. SPIN-LATTICE RELAXATION TIME T_1

At temperatures higher than 10K the spin-lattice relaxation time of the relaxed excited state decreases and mixes up the population of the different pair states within the radiative lifetime. Consequently the average tunnelling probability is changed. According to our earlier paper (6) the measurements of η as a function of temperature can give the values of this spin-lattice relaxation time since all the other parameters are known. It is worth noting that such information is usually obtained by EPR measurements. The usefulness of this optical non-resonant method is somewhat limited since the temperature variation of η is not very important. Our first measurements only qualitatively agree with those obtained by EPR-OD with a better accuracy (5, 6). For most alkali halide crystals, the observed spin-lattice relaxation time is characteristic of an Orbach process $T_1 = T_o\{\exp(\Delta E/kT)-1\}$. The values for KCl are $T_o = 2.5$ nsec, $\Delta E = 14.2$ meV.

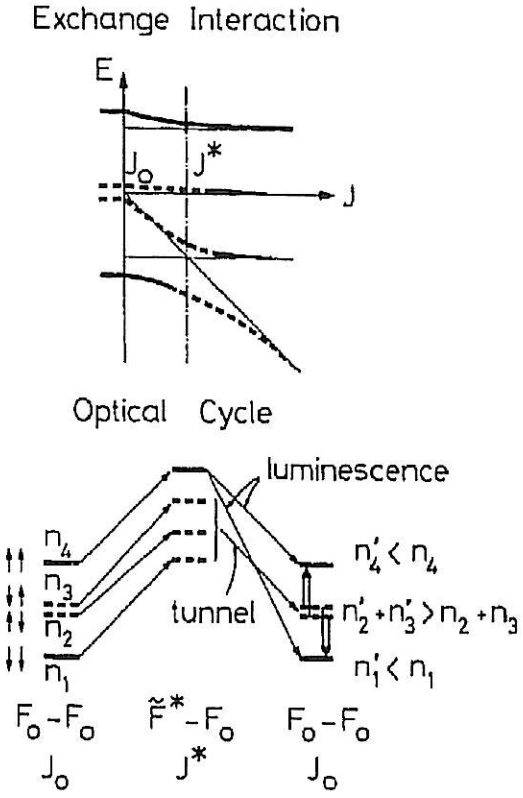

Fig. 3 a) (upper figure) Level scheme of a loose aggregate F center pair in its relaxed excited state as a function of exchange energy $J \cdot \underline{S}_1 \cdot \underline{S}_2$; b) (lower figure) Optical cycle for such a pair showing the change of the radiative mechanism, the tunnelling character and the population of each level. The levels drawn in heavy line have a low tunnelling probability while dashed lines represent levels with a high tunnelling probability.

4. AGGREGATION EFFECTS

Light irradiation in the F band at room temperature is known to favor aggregation of F centers, which eventually form aggregates of 2,3, etc. F centers called F_2, F_3, etc. (2). The mechanism of the aggregation is still not well understood. The new optical properties of these defects outlined in this report, together with the technique of optical detection of the EPR in the ground and the relaxed excited state performed in our laboratory (5, 6, 8) promise to shed some light on this subject.

The positive variation of the luminescent intensity with increasing magnetic field is found to diminish gradually and eventually to become negative when the F light irradiation at RT stretches out. This can be explained by taking account of an exchange term of the form $J \cdot \underline{S}_1 \cdot \underline{S}_2$ in the magnetic Hamiltonian. Fig. 3 shows the

result of this calculation. In an external magnetic field the energy of the four levels of a relaxed excited pair and the tunnelling probabilities are gradually modified, as the members of the pair become closer to each other. For a J* value, for instance, we see that only one level can radiate; the other three levels de-excite non-radiatively by tunnelling. This explains why the F centers radiative quantum yield decreases as a function of the aggregation. Moreover a check of the kinetics of the F luminescent intensity under rectangular pulse excitation (rise time $\nu 1\mu$sec, length 2 sec) indeed shows a fast rise time followed by a partial diminution (time constant of 0.5 sec under our experimental conditions). It can be accounted for by the change in the level population occurring during the optical cycle.

5. CONCLUSION

The study of the variation of the luminescence intensity of F centers induced by a low magnetic field in KCl crystal has allowed a clarification of the mechanism of concentration quenching of the radiative quantum yield. The agreement between theory and experimental results is good. The measurement of this property as a function of temperature should also give the characteristic values of the spin-lattice relaxation time of the relaxed excited state, which are usually determined by resonant methods. Moreover, one of the most interesting features of this phenomenon lies in the possibility to understand better the physical nature of the aggregation mechanism of these defects in alkali halide crystals.

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