

## OPTICALLY DETECTED NMR AND ENDOR WITH F CENTER PAIRS IN KCl

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F centres, paired by bleaching near RT and excited by F-band light, experience an exchange interaction favoring a non-radiative disexcitation. In a magnetic field at 10°K, the luminescent intensity shows EPR, ENDOR and NMR, from changes of the spin populations induced by microwave and r.f. fields.

At high concentration, an appreciable fraction of the F centers are paired with a relatively small separation. If the crystal is optically excited in the F band ( $F_0 \rightarrow \tilde{F}^*$ ), the radiative quantum yield for luminescence is lower than unity because of the non radiative decay path  $\tilde{F}^* + F_0 \rightarrow F' + \alpha \rightarrow F_0 + F_0$  (electron transfer within a pair). We have shown that at low temperature a moderate magnetic field reduces this transfer by decreasing the antisymmetric part of the spin functions (Jaccard et al. [1]) and in a recent paper that spin resonance in the ground and in the excited state can be detected by observing the luminescence intensity (Ruedin et al. [2]).

In the experiments discussed below, KCl crystals with an homogeneous F centre concentration of  $5 \cdot 10^{17} \text{ cm}^{-3}$  have been bleached slightly with F light at 283°K. This treatment renders the centers mobile, and decreases the average separation in the pairs, eventually leading to the transformation of the pairs into  $F_2$  centers. When excited with F light at 10°K these crystals show a luminescence which decreases with magnetic field (instead of increasing as in Ruedin's case). With applied microwaves in the X band, the EPR in the ground state can be detected optically too, showing up as an increase of the luminescence (instead of a decrease in Ruedin's case) with a g-factor of 2.001 and a FWHM of 64 G. Moreover, this signal possesses a relatively long relaxation time, varying between  $10^{-3}$  and  $10^{-1}$  s, depending upon the incident light intensity. ENDOR has been tried and yields optical signals of the same sign and order of magnitude as the EPR signal, the spectrum corresponding closely to the one observed by Seidel [3] with a conventional purely electrical method. If the microwave power is turned off, the luminescence displays as a function of the radio frequency the same

spectrum, which is then even better because the low frequency shift of the baseline disappears (fig. 1). This optical detection of NMR is in a way similar to the one recently discovered by Ekimov and Safarov [4], but in our case it applies to localized electrons pairs and to their nuclear environment.

These results can be explained by the following mechanism. When the pair separation is within a critical range, the wave function overlap is quite small in the ground state, but it becomes appreciable if one of the electrons is in the relaxed excited state. This introduces an exchange interaction, which in a first approximation can be assumed to be of the form  $J \cdot S_1 \cdot S_2$ , with  $|J| \lesssim g\beta H_0$ . Its major effect is to change the spin symmetry: whereas there are in the ground state two symmetrical spin states  $\psi_1$  and  $\psi_4$  (luminescent) and two antisymmetrical spin states  $\psi_2$  and  $\psi_3$  (non-luminescent), there is in the excited state only a single symmetrical spin state  $\psi_1^*$ , the other one  $\psi_4^*$  receiving an appreciable part of antisymmetry to make it partially non-luminescent ( $\psi_2^*$  and  $\psi_3^*$  remain mainly antisymmetrical). The net effect of the exciting light

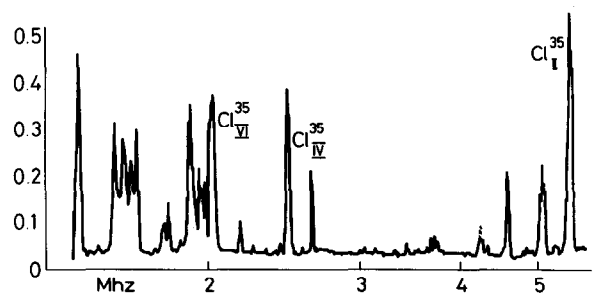


Fig. 1. Optical detection of NMR with F-pairs in KCl at 9.5°K. Abscissa: radiofrequency; ordinate: percent change of the luminescence ( $H_0 = 5 \text{ kG}$ ,  $n_F \approx 10^{17} \text{ cm}^{-3}$ ).

is then to populate especially  $\psi_2$  and  $\psi_3$  at the expense of  $\psi_4$ , thereby decreasing the luminescent quantum yield [5]. If microwaves are applied in a magnetic field, they transfer back part of the pairs into the luminescent state  $\psi_1$ , whenever the resonance condition is satisfied. As it has been shown by Ruedin [2], the homogeneous EPR line width is much smaller than the observed one. At high intensity, the microwaves "burn a hole" in the line. The projection  $m_I$  along the applied field of all the neighbouring nuclear magnetic moments can be considered as the abscissa of the line. Since the r.f. field at resonance equalizes the distribution over  $m_I$ , it does in the ENDOR experiment refill the burned hole, thereby enhancing the transfer toward the luminescent state and consequently the luminescent quantum yield. The case with the microwaves turned off (pure NMR) is more subtle and its explanation requires the following hypothesis: During the non-radiative electron transfer  $F_0 + \tilde{F}^* \rightarrow F' + \alpha \rightarrow F_0 + F_0$ , the total spin  $z$ -component of the pair and its neighbourhood is preserved. An electronic flip-down  $\Delta m_s = -1$  is compensated by some nuclear flip-up  $\Delta m_I = +1$ . This latter process is quite possible for a nuclear configuration with a negative  $m_I$  in which a large number of nuclei are able to flip-up. But it is quite improbable for a large positive  $m_I$ , in which the number of nuclei able to flip-up is small, and it is impossible if the nuclear neighbourhood is completely polarized with  $m_I$  at its maximum value. The effect of the exciting light is then not only to change the total populations, but also to shift the distributions over the nuclear magnetic states and make them skew. Since the r.f. field tends to restore the equilibrium distribution, it brings back part of the pairs into a nuclear environment which favors the transfer into luminescent states.

If the crystals are subjected to the same treatment

but for a longer lapse of time, another EPR peak appears near the half value of the applied static field. ENDOR experiments on this peak reveal the same spectrum as found by Seidel [6] for the  $F_2(M)$  centre. We have then obviously to deal with  $F + F_2$  pairs, and the resonance at half field is for a spin  $S = 1$  with  $g = 2.009$  (FWHM 37 G.). Another peak at a third of the field shows up after a long bleaching time and is due to pairs  $F + F_3$ , resulting of the resonance of a spin  $S = 3/2$ , as it has also been revealed by the ENDOR spectrum. We have found also under special conditions an EPR resonance of the opposite sign (i.e. showing up as a decrease of the luminescence) with a  $g$ -factor slightly larger than 2 and a long relaxation time, but no explanation has been found as yet.

This method is the first one which does not use the light polarization to detect optically the different types of magnetic resonances. It is simpler than the other methods because it does not require a sophisticated equipment and is also quite sensitive.

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