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Optical Detection of Nuclear and Electronic Magnetic Resonances of Close F-Center Pairs in KCl

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The luminescence of close F center pairs (produced by short F band irradiation near RT) is measured at LHeT in a static magnetic field (kG) under the influence of a microwave and/or a rf field of suitable frequency. EPR, revealed by an increase of the luminescence, is modulated by the rf, giving ENDOR spectra similar to those obtained for single centers by conventional methods. The rf alone induces also changes of the luminescence (up to 1%) giving NMR spectra with an intensity depending on the optical excitation and the rf power. The relaxation rate, extrapolated to zero light intensity, is equal to the inverse electronic spin-lattice relaxation time. These observations can be explained by a pair model with isotropic spin exchange, calculated in the high field limit (Zeeman energy \gg hyperfine energy \approx exchange energy). The states, characterized by electronic and nuclear quantum numbers, have different luminescent probabilities and the optical cycle transfers the pairs into the non-radiative states. Any magnetically induced transition tends to restore the population equilibrium and increases the luminescence. The calculated intensity ratio EPR:NMR:ENDOR agrees with the observations.

On mesure la luminescence de paires courtes de centres F (produites par une brève irradiation dans la bande F à température normale) en présence d'un champ magnétique statique (kG) et de champs h.f. et micro-onde de fréquence adéquate. La RPE se manifeste par une augmentation de la luminescence et elle peut être modifiée par le champ h.f., donnant des spectres ENDOR semblables à ceux obtenus pour des centres isolés. Le champ h.f. peut à lui seul produire des variations de la luminescence (jusqu'à 1%), donnant des spectres de RMN dont l'intensité dépend de l'excitation optique et de la puissance h.f. La fréquence de relaxation extrapolée à intensité lumineuse nulle est égale à l'inverse du temps de relaxation spin-réseau électronique. Ces observations peuvent être expliquées par un modèle de paires pourvues d'un échange de spin isotropique, et calculées à la limite des champs élevés (énergie Zeeman \gg énergie hyperfine \approx énergie échange). Les états, caractérisés par des nombres quantiques électroniques et nucléaires, ont différentes probabilités de luminescence et le cycle optique transfère les paires dans les états non radiatifs. Toute transition induite magnétiquement tend à rétablir l'équilibre des populations et augmente la luminescence. Le rapport calculé des intensités RPE:RMN:ENDOR est en accord avec les observations.

1. Introduction

At low temperature, the luminescent quantum yield of isolated F centers in alkali halides is unity. At high concentration ($\approx 10^{17}$ cm⁻³) part of the centers build up in pairs; their disexcitation occurs not only by photon emission with a decay time of ≈ 1 μ s, but also along a non-radiative path. This mechanism seems to imply a jump of the excited electron into the neighboring center, giving an F' center and an anionic vacancy, followed by a deformation of the lattice, then a jump of one of the electrons back into the vacancy and a second lattice relaxation [1]. A direct disexcitation with phonon emission can also be

considered [2]. However, this transition is possible only if the electronic spin state of the pair contains a sufficient amount of the singlet wave function. This explains quite well the effect on the luminescence of a magnetic field [3] and of the paramagnetic resonance [4, 5]. The properties of the pairs depend on their separation: in quenched concentrated crystals there are only "distant" pairs, with optical EPR signals showing up as a decrease of the luminescence [4], whereas the opposite is found with "close" pairs produced by a short illumination in the F band near RT [5].

In previous papers only the electronic resonance has been considered and the hyperfine interaction has been described by means of a classical nuclear field varying randomly in the crystal. This paper is concerned only with close pairs and mainly the luminescent response to magnetic resonance of the neighboring nuclei. These have therefore to be treated by quantum mechanics. In the next section, experiments of optically detected ENDOR and NMR in KCl are described. A model is established in Section 3 and the quantum problem is solved approximatively in the high-field case, i.e. when the electronic Zeeman energy is much larger than the hyperfine interaction. This yields the magnetic transition rates and their influence on the luminescence. Finally the calculations are compared with the experiments; the observed spectra and the intensity ratios NMR:ENDOR:EPR are accounted for.

2. Experiments

The KCl samples are the same which have been used for EPR experiments and their preparation is described together with the experimental procedure in a previous paper [5] and with more details elsewhere [6]. They contain about 10^{17} F centers per cm^3 , about 10% being associated in close pairs (the concentration of distant pairs is negligible). They are excited by light in the F band, and submitted to a static magnetic field and to X-band microwaves. For ENDOR experiments the cavity contains a four-turn coil parallel to the larger side of the crystal, and for NMR the crystal is in a sample holder with a copper coil of 50Ω at 5 MHz. The radiofrequency field (oscillator Wavetek 114, followed by a rf amplifier Power Lab FK 110-20) is chopped at 36 Hz and the nuclear resonance signal is detected from the luminescence through a narrow-band amplifier (PAR 110). The relaxation processes can be measured by means of a signal analyser (HP 5080 A).

The EPR of "close" pairs is characterized by an increase of the luminescence by about 8% giving a sharp peak at a field of 3.4 kG. For a microwave power higher than one μW , the signal amplitude grows very slowly with the power, indicating a saturation behavior. For the ENDOR experiments, the field is chosen in order to saturate the center of the EPR line (with 100 mW) and a rf current with a frequency between 0.1 and 100 MHz is injected into the coil in the cavity. This produces a further increase of the luminescence by about 0.5% when the resonance condition $h\nu_{\text{rf}} = |\frac{1}{2} W_{\text{hfs}} \pm g_k \beta_n H_0|$ is satisfied (Fig. 1). The spectrum as a function of ν_{rf} agrees with the one obtained by Seidel with a conventional ENDOR method [7] and it confirms the nature of the elements of the pairs.

If the microwave power is decreased, the ENDOR signal is reduced but it does not vanish completely; it merely drops by a factor of about 2 (Fig. 2). Without microwaves, the spectrum remains the same as before, and in this case we have optically detected pure NMR. Since the field needs not to be maintained

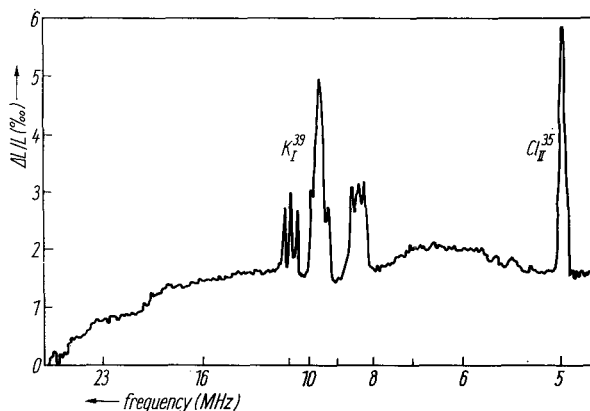


Fig. 1

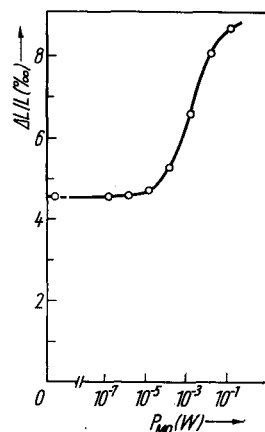


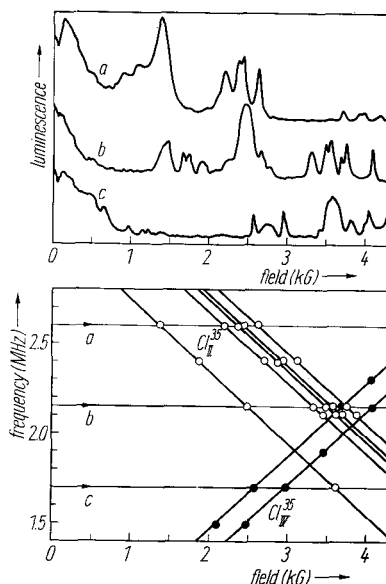
Fig. 2

Fig. 1. Part of optically detected ENDOR spectrum of close F pairs in KCl: relative change of the luminescence versus rf field frequency ($H_0 = 3440$ G, $T = 13.6$ K, microwave frequency 9.651 GHz)

Fig. 2. Relative height of the 5 MHz ENDOR peak of $\text{Cl}_{\text{II}}^{35}$ versus microwave power ($H_0 = 3440$ G, $T = 13.6$ K)

at its EPR value, it can be varied at will, together with the radio frequency. This gives different spectra (Fig. 3) but they all obey the resonance condition. In this case the luminescence increase appearing at low rf frequencies due to the modulation of the static field [8] is suppressed and the identification of the different peaks is easier. The height of the NMR peaks at constant rf power grows with the exciting light intensity but it is limited at high pumping intensity (Fig. 4). When the rf power is turned off, the luminescence goes back to its equilibrium level according to an exponential law provided the exciting light flux is homogeneous. The relaxation frequency is independent of the rf power but it is a linear function of the exciting light intensity (Fig. 5). Its value extrapolated to zero light intensity (5 s^{-1}) is the same as for the electronic resonance [5] and is equal to the electronic spin-lattice relaxation time. This indicates that, as in the case of the EPR, the nuclear resonance affects the different populations of the electronic spin levels and is effective only in the ground state

Fig. 3. Upperpart: NMR spectra obtained from the luminescence versus magnetic field at three frequencies (a) 2.6 MHz; (b) 2.15 MHz; (c) 1.7 MHz. Lower part: line frequencies versus magnetic field



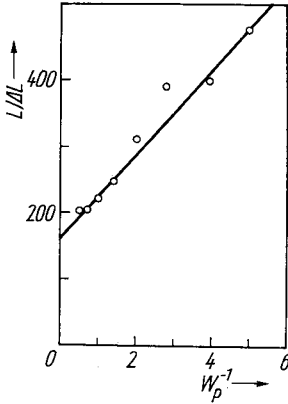


Fig. 4

Fig. 4. Dependence of the inverse of the relative NMR signal on the inverse of the excitation light intensity (in arbitrary units)

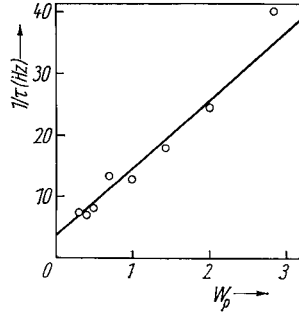


Fig. 5

Fig. 5. Relaxation frequency of the luminescence versus excitation light intensity (arbitrary units), for ENDOR peak of $\text{Cl}_{\text{II}}^{35}$ at 5 MHz, measured after the microwaves are switched off

of the pair. Indeed it cannot be effective in the relaxed excited state because of the short lifetime.

All these properties can be accounted for with the model developed in the next section, provided certain relations between Zeeman, hyperfine, and exchange energies are satisfied.

3. Pair Model

We consider a system composed of a pair of F centers with two electrons and a large number of surrounding nuclei labelled by k (spin I , Landé factors g_k) interacting with the electrons (hyperfine coupling energies A_{1k} and A_{2k}). Since we want to consider magnetic transitions between well-defined nuclear levels, it is not possible to reduce the hyperfine interaction to classical random magnetic fields of nuclear origin as it was the case in [3]. The quantum properties of the nuclear moments must be retained, at least initially. The pair being of the close type, we introduce as in [5] an isotropic exchange interaction J between the electrons. With the static magnetic field \mathbf{H}_0 the energy of the spin system in the symmetrical ground state is given by

$$\begin{aligned} \mathcal{H} = & g_e \beta_e \mathbf{H}_0 \cdot (\mathbf{S}_1 + \mathbf{S}_2) + J \mathbf{S}_1 \cdot \mathbf{S}_2 + \sum_k (A_{1k} \mathbf{S}_1 + A_{2k} \mathbf{S}_2) \cdot \mathbf{I}_k - \\ & - \sum_k g_k \beta_n \mathbf{H}_0 \cdot \mathbf{I}_k. \end{aligned} \quad (1)$$

The effect of spin-orbit coupling is included in g_e . The natural energy unit of the system is taken as

$$A \equiv \left(\sum_k A_{1k}^2 \right)^{1/2} = \left(\sum_k A_{2k}^2 \right)^{1/2}. \quad (2)$$

With the axis of quantization parallel to the static field, the basis for the spin states is chosen as $|s_1, s_2, \{m_k\}\rangle$ where $s_{1,2} = \pm \frac{1}{2}$, $m_k = -I, -I+1, \dots, I-1, I$.

The non-diagonal part of the Hamiltonian mixes together all the states with $s_1 + s_2 + \sum_k m_k = \text{const}$. Since the number of the nuclei is very large, an exact

diagonalization is impossible. Therefore we shall limit ourselves to the strong field condition $\beta_e H_0 \gg A$, which is relevant for NMR and EPR experiments. In this case, the states $|\pm \frac{1}{2}, \pm \frac{1}{2}, \{m_k\}\rangle$, which represent also the electronic triplet $|\sigma^\pm, \{m_k\}\rangle$, are well separated from the middle states $|\pm \frac{1}{2}, \mp \frac{1}{2}, \{m_k\}\rangle$, which are mixtures of the triplet and singlet states $|\sigma^0, \{m_k\}\rangle$ and $|\alpha, \{m_k\}\rangle$. A perturbation calculation to the first order shows that the two middle states are strongly mixed by the exchange interaction (they are nearly degenerated) but that the admixture of the outer states is of the order of $A/\beta_e H_0$ and therefore much smaller. In the following we shall neglect terms of this order so that only the central part of the Hamiltonian has to be diagonalized exactly, for an exchange energy J smaller than the electronic Zeeman energy. We define

$$x_1 \equiv \frac{\sum_k A_{1k} m_k}{A}, \quad x_2 \equiv \frac{\sum_k A_{2k} m_k}{A}, \quad x \equiv x_1 - x_2, \quad (3)$$

$$h_n \equiv \sum_k g_k \beta_n H_0 m_k. \quad (4)$$

Because of the large number of parameters m_k , the new variables defined by (3) have nearly Gaussian distributions $g_j(x_j)$ of widths

$$\langle x_{1,2}^2 \rangle^{1/2} = \left(\frac{1}{3} I(I+1)\right)^{1/2}, \quad \langle x^2 \rangle^{1/2} = (2\langle x_{1,2}^2 \rangle)^{1/2}. \quad (5)$$

The partial Hamiltonian for the states $|\pm \frac{1}{2}, \mp \frac{1}{2}; \{m_k\}\rangle$ becomes then

$$\mathcal{H}' = \begin{pmatrix} -\frac{J}{4} + \frac{1}{2}Ax - h_n & \frac{J}{2} \\ \frac{J}{2} & -\frac{J}{4} - \frac{1}{2}Ax - h_n \end{pmatrix}. \quad (6)$$

The energy eigenvalues and the eigenstates are

$$\varepsilon^\pm = -\frac{J}{4} \pm \frac{1}{2}(A^2x^2 + J^2)^{1/2} - h_n, \quad (7)$$

$$|\psi^+, \{m_k\}\rangle = \cos \varphi |+\frac{1}{2}, -\frac{1}{2}, \{m_k\}\rangle + \sin \varphi |-\frac{1}{2}, +\frac{1}{2}, \{m_k\}\rangle, \quad (8)$$

$$|\psi^-, \{m_k\}\rangle = \sin \varphi |+\frac{1}{2}, -\frac{1}{2}, \{m_k\}\rangle - \cos \varphi |-\frac{1}{2}, +\frac{1}{2}, \{m_k\}\rangle, \quad (9)$$

$$\tan \varphi = \left(\frac{A^2x^2}{J^2} + 1\right)^{1/2} - \frac{Ax}{J}, \quad \tan 2\varphi = \frac{J}{Ax}. \quad (10)$$

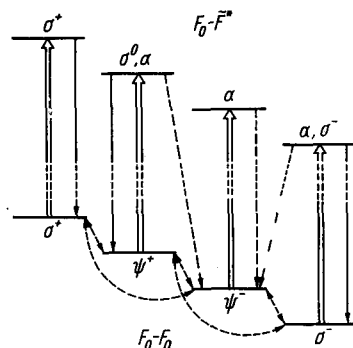


Fig. 6. Transitions between the ground states ($F_0 - F_0$) and the relaxed excited states ($F_0 - \tilde{F}^*$). ——— optical pumping; ——— radiative decay; - - - - non-radiative decay; spin-lattice relaxation.

For a pair in its ground state (F_0-F_0) the wave function overlap is small and consequently $J < A$, so that either $\sin \varphi$ or $\cos \varphi$ is small (depending on the x). When sign of excited optically by light in the F band, the pair is transferred rapidly into the relaxed excited state ($F_0-\tilde{F}^*$) (Fig. 6). There, the overlap is much larger, J becomes larger than A and the sine and cosine approach the value $1/\sqrt{2}$. $|\psi^+\rangle$ is then mainly a triplet state $|\sigma^0, \{m_k\}\rangle$ but since it still has a small singlet admixture, it can return to the ground state radiatively or non-radiatively, depending on the amount of this admixture and on the ratio of the two decay frequencies. On the other hand, $|\psi^-\rangle$ is nearly a pure singlet $|\alpha, \{m_k\}\rangle$ and it decays non-radiatively. What happens to the outer states $|\pm \frac{1}{2}, \pm \frac{1}{2}, \{m_k\}\rangle$ can be taken from a previous paper [5]: $|+\frac{1}{2}, +\frac{1}{2}, \{m_k\}\rangle$ has only a very small singlet component and decays radiatively: $|-\frac{1}{2}, -\frac{1}{2}, \{m_k\}\rangle$ is mixed weakly with $|\alpha, \{m_k\}\rangle$ for $A < J \ll \beta_e H_0$ and it decays mainly radiatively.

The effect of the optical cycle is therefore to populate preferentially the state $|\psi^-\rangle$ which is non-luminescent at the expense of $|\psi^+\rangle$. Any resonant transfer in the ground state increases then the observed luminescence. Resonance in the relaxed excited state (like the EPR of distant pairs) would produce the inverse effect, but it should not be effective: the distribution of the pair separations smears out the exchange interaction and with it the energy difference for resonance.

4. Transition Rates

For pairs in the orbital ground state (F_0-F_0), a microwave field H_{ex} induces transitions between the states $|\pm \frac{1}{2}, \pm \frac{1}{2}, \{m_k\}\rangle$ and $|\psi^\pm, \{m_k\}\rangle$. The energy difference $E_{MW} = g_e \beta_e H_0 + A x_{1,2} \pm J/2$ depends on the random variables x_1 and x_2 , the distribution of which appears in the inhomogeneous lineshape.

The transition rate is also a function of these variables. However, if $J \ll A$, the integral over H_0 of the transition rate reduces to

$$\bar{P}_E \equiv \int P_E dH_0 = \frac{\pi}{2\hbar} g_e \beta_e H_{ex}^2 \quad (11)$$

for any pair (i.e. for any $x_{1,2}$). At low microwave power (far from saturation) \bar{P}_E is proportional to the integrated EPR line intensity.

For nuclear transitions we consider a transversal rf field H_{nx} with such a frequency that it affects only a particular nucleus with index K . The optically detectable transitions concern the states $|\psi^\pm, m_K\rangle$ and they are divided in two classes. In the first one, only the nuclear quantum state changes and they lead to states $|\psi^\pm, m_K \pm 1\rangle$. These "horizontal" transitions appear only in ENDOR spectra. In the second class, the electronic quantum state changes simultaneously and they lead to states $|\psi^\mp, m_K \pm 1\rangle$. These "diagonal" transitions appear in ENDOR and in NMR spectra. In the latter case, the golden rule applied to (8) and (9) yields a transfer rate given by

$$P_{NK}^\pm = \frac{2\pi}{\hbar} |\langle \psi^\mp, m_K | \frac{1}{2} g_K \beta_n H_{nx} I_K^\mp | \psi^\pm, m_K \pm 1 \rangle|^2 \varrho_K = \frac{2\pi}{\hbar} \left(\frac{1}{2} g_K \beta_n H_{nx} \right)^2 \times \\ \times [I(I+1) - m_K(m_K \pm 1)] \varrho_K p_{NK}^\pm, \quad (12)$$

where ϱ_K is the nuclear density of states, and

$$p_{NK}^\pm = \sin^2 [\varphi(Ax) - \varphi(Ax \pm A_{1K} \mp A_{2K})]. \quad (13)$$

With $(A_{1K} - A_{2K})/A \equiv a_K$, the factor p_{NK}^{\pm} is unity between $x = 0$ and $x = \mp a_K$, and zero elsewhere, provided $J \ll |A_{1K} - A_{2K}|$ (the relevant case for the experiments). With this condition, the energy difference for the transition

$$E_{NK}^{\pm} = \frac{1}{2} \sqrt{A^2(x \pm a_K)^2 + J^2} + \frac{1}{2} \sqrt{(Ax)^2 + J^2} \mp g_K \beta_n H_0 \quad (14)$$

possesses in the same range a very flat minimum, i.e. an appreciable number of pairs with $|x| < |a_K|$ have the same energy difference $|\frac{1}{2}(A_{1K} - A_{2K}) \pm g_K \beta_n H_0|$ and produce a sharp peak, just at the same position as for standard NMR if the considered nucleus interacts mainly with one electron only ($A_{1K} \gg$ or $\ll A_{2K}$).

As in the case of EPR, an average transition rate for any pair \bar{P}_{NK} can be defined from the rate integrated over the field. Near equilibrium (i.e. for Gaussian distributions in x_1 and x_2) it amounts to

$$\begin{aligned} \bar{P}_{NK} &= \int dH_0 \iint dx_1 dx_2 g_1(x_1) g_2(x_2) (P_{NK}^+ + P_{NK}^-) \approx \\ &\approx \frac{\sqrt{\frac{\pi}{3} I(I+1) |a_K| g_K \beta_n H_{nz}^2}}{\hbar} \end{aligned} \quad (15)$$

when m_K and m_K^2 are replaced by their average values.

For horizontal transitions, the transfer rate is given by

$$P_{ENK}^{\pm} = \frac{2\pi}{\hbar} \left(\frac{1}{2} g_K \beta_n H_{nz} \right)^2 [I(I+1) - m_K(m_K \pm 1)] Q_K (1 - p_{NK}^{\pm}). \quad (16)$$

With a small exchange energy, the last factor is near unity only for $|x| > |a_K|$ and otherwise zero. The energy difference

$$E_{ENK}^{\pm} = \frac{1}{2} \sqrt{A^2(x \pm a_K)^2 + J^2} - \frac{1}{2} \sqrt{(Ax)^2 + J^2} \pm g_K \beta_n H_0 \quad (17)$$

has the constant value $|E_{ENK}^{\pm}| = |\frac{1}{2}(A_{1K} - A_{2K}) \pm g_K \beta_n H_0|$ for $|x| > |a_K|$ provided $J \ll |A_{1K} - A_{2K}|$. The same consideration as above can be applied: all pairs with an inhomogeneous nuclear field and a small exchange energy have the same resonance frequency, and they give rise to a sharp peak in the spectrum. In a way, horizontal transitions are complementary to the diagonal ones.

5. Effect on the Luminescence

We consider a crystal containing isolated F centers (N_i) and a smaller number of pairs (N_p). The total number of pairs with nuclear parameters x_1 and x_2 is $g_1(x_1) g_2(x_2) N_p$. At or near equilibrium (without resonances), $g_1 g_2$ is a two-dimensional Gaussian distribution. We call $n_1, n_2, n_3,$ and n_4 the fraction of pairs with given x_1 and x_2 in the electronic states $|\sigma^+\rangle, |\psi^+\rangle, |\psi^-\rangle,$ and $|\sigma^-\rangle$, respectively. The luminescent probabilities depend on the absolute singlet content $|\langle \alpha | \psi \rangle|$ of the wave function $|\psi\rangle$ in the optically excited state, as described at the end of Section 3, and they have the approximate values 1, $1 - t$, 0 and 1, respectively. If W_p is the optical pumping rate, the luminescence of the crystal, expressed as the number of photons emitted per unit time, is given by

$$L = W_p N_i + W_p N_p \iint [n_1 + n_4 + n_2(1 - t)] g_1 g_2 dx_1 dx_2. \quad (18)$$

The transitions induced by alternative magnetic fields which affect only the luminescence of the pairs can be described generally by transition rates P_r , where r stands for EPR, NMR, or ENDOR. When the considered resonance is

far from saturation, the change of luminescence is linear in P_r

$$\Delta L_r = P_r W_p N_p \iint \frac{\partial}{\partial P_r} [n_1 + n_4 + n_2(1 - t)] g_1 g_2 dx_1 dx_2. \quad (19)$$

It is then convenient to introduce a dimensionless linear response by

$$\mathcal{L}_r = \frac{\Delta L_r}{L} \frac{N_1}{N_p} \frac{W}{P_r} = W \iint \frac{\partial}{\partial P_r} [n_1 + n_4 + n_2(1 - t)] g_1 g_2 dx_1 dx_2, \quad (20)$$

where W is the known electronic spin-lattice relaxation rate.

With optical pumping the pairs are distributed unevenly between the electronic states. As it can be seen from Fig. 7, the second level is depleted because of the unilateral transfer W_p (optical pumping rate); the occupations of the other levels are then above their equilibrium values. However, the population distribution within each electronic state is not changed with respect to the nuclear coordinates x_1 and x_2 . This situation is maintained if microwave- or rf-induced transition rates (P_E or P_N) are small. In this case, it is not necessary to consider the dependence in x_1 and x_2 , provided the rates are averaged over these variables as in Section 4. The four relative populations $n_1, n_2, n_3,$ and n_4 take the following values

$$n_1 = n_4 = \frac{1}{4}, \quad n_2 = \frac{1}{4} \frac{W + P_E + P_N}{W + P_E + P_N + \frac{1}{2} t W_p}, \quad n_3 = \frac{1}{2} - n_2. \quad (21)$$

If $p \equiv W_p/W$ is the relative pumping rate, the luminescence can be calculated according to (18) and the linear responses defined by (20) are then equal for EPR and NMR:

$$\mathcal{L}_E = \mathcal{L}_N = \frac{1}{2} \frac{(1 - t) tp}{(2 + tp)^2}. \quad (22)$$

In the case of ENDOR, the microwave field saturates the pairs situated (in the $x_1 x_2$ plane) in a cross-shaped zone of width x_c . In order to simplify the analytical treatment, we assume that the saturation is complete inside the zone (in which all the relative populations are equal to $\frac{1}{4}$) and zero outside the zone, where the populations are not perturbed by the microwave field; moreover the zone width should be comprised between $(A_{1k} + A_{2k})/A$ and $(\langle x_{1,2}^2 \rangle)^{1/2}$. Because of the population inequalities, the rf field induces horizontal transfers into the saturated zone. The change of the nuclear coordinate $\Delta m_K = \pm 1$ produces changes $\Delta x_1 = \pm A_{1K}/A$ and $\Delta x_2 = \mp A_{2K}/A$. Therefore, the transfer is possible

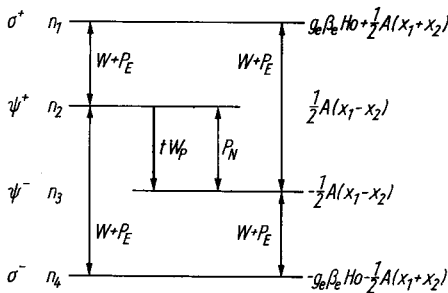
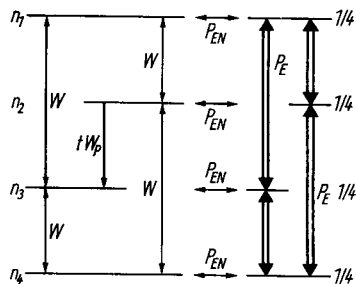


Fig. 7. Low-power EPR and NMR: electronic levels, populations and energies. W spin-lattice relaxation rate, W_p optical pumping rate, t probability of non-radiative decay, P_E, P_N electronic and nuclear transition rates, respectively (for other symbols see text)

Fig. 8. ENDOR case: electronic levels and populations (saturated zone of the right side). P_{EN} nuclear transition rate. Other rates as in Fig. 7



only for pairs with $|x_c + A_{1, 2K}/A| > |x_{1, 2}| > x_c$. The average transfer rate is then

$$P_{ENK} = \int dx_2 \left(\int_{-x_c - A_{1K}/A}^{-x_c} dx_1 P_{ENK}^+ + \int_{x_c}^{x_c + A_{1K}/A} dx_1 P_{ENK}^- \right) g(x_1) g(x_2) + \int dx_1 \left(\int_{-x_c - A_{2K}/A}^{-x_c} dx_2 P_{ENK}^- + \int_{x_c}^{x_c + A_{2K}/A} dx_2 P_{ENK}^+ \right) g(x_1) g(x_2). \quad (23)$$

Using (16), replacing m_K and m_K^2 by their mean values, and integrating over the field, one obtains

$$\begin{aligned} \bar{P}_{ENK} &\equiv \int P_{ENK} dH_0 = \sqrt{\frac{2\pi}{3}} I(I + 1) g_K \beta_n H_{nz}^2 \frac{A_{1K} + A_{2K}}{A\hbar} = \\ &= \sqrt{2} \bar{P}_{NK} \left| \frac{A_{1K} + A_{2K}}{A_{1K} - A_{2K}} \right|. \end{aligned} \quad (24)$$

But almost every nucleus is nearer to one of the electrons, and if the pair separation is not too small, one has either $A_{1k} > A_{2k}$ or $A_{1k} < A_{2k}$. Therefore the last factor of (24) is somewhat larger than unity and $\bar{P}_{ENK} \gtrsim \sqrt{2} \bar{P}_{NK}$. The system, represented in Fig. 8, can be solved in the steady state and the values for the n_j introduced in (20) yield

$$\mathcal{L}_{EN} = \mathcal{L}_N \quad (25)$$

6. Comparison with Experiments and Discussion

The model yields signal intensities for EPR and NMR which are proportional to the exciting light flux as long as its pumping rate is small with respect to the spin-lattice relaxation frequency. This behavior is verified as it can be seen for NMR in Fig. 4, where the inverse of the luminescent signal (proportional to \mathcal{L}_N^{-1}) is a linear function of the inverse pumping rate (proportional to p^{-1}). For EPR, Fig. 5a of [5] shows the same dependence. However, for high pumping rates, formula (36) indicates for \mathcal{L}_E a proportionality to p^{-1} . This shows up also in Fig. 5a of [5]: at small p^{-1} a significant increase of the inverse signal is observed. This reverse trend has not been found in NMR because the light intensity has been kept there under the critical value.

The pair concentration has not yet been determined by an independent method, and it is not possible to check quantitatively the theoretical results. But this parameter is eliminated if the intensities of the different resonances are compared. A spectrum has been measured, in which the radio frequency is chosen in order to separate EPR from NMR peaks of the second nearest neigh-

bor $\text{Cl}_{\text{II}}^{35}$. From Seidel's values [7] the KCl parameters are for this nucleus

$$\begin{aligned} N_K &= 12, & A_K &= 6.9 \text{ MHz}, & A &= 56.1 \text{ MHz}, \\ a_K &= 0.178, & g_K &= 0.549, & I &= \frac{3}{2}. \end{aligned}$$

With transverse magnetic field intensities of 0.5 G for NMR and 12 mG for EPR, the intensities of all the lines integrated on the spectrum are, respectively,

$$\int \Delta L_N dH_0 = 38 \text{ cm}^2, \quad \int \Delta L_E dH_0 = 12.5 \text{ cm}^2.$$

The ratio (EPR):(NMR) is therefore near $\frac{1}{3}$. From (20) we obtain

$$R(\text{E/N}) = \frac{\int \Delta L_E dH_0}{\int \Delta L_N dH_0} = \frac{\mathcal{L}_E \bar{P}_E}{\mathcal{L}_N \bar{P}_N} \frac{1}{2N_K}. \quad (26)$$

The factor $1/2N_K$ has to be added because there are in each pair $2N_K$ equivalent nuclei which contribute to the same lines. Introducing (11) and (15) the ratio becomes

$$R(\text{E/N}) = \frac{\mathcal{L}_E}{\mathcal{L}_N} \frac{1}{4} \sqrt{\frac{3\pi}{I(I+1)}} \frac{g_e \beta_e}{g_K \beta_n} \left(\frac{H_{ex}}{H_{nx}} \right)^2 \frac{1}{a_K N_K}. \quad (27)$$

Using the parameters given above, we obtain

$$R(\text{E/N}) = \frac{\mathcal{L}_E}{\mathcal{L}_N} 0.27 = 0.27, \quad (28)$$

a value which agrees with the observation if the inaccuracy of the model is taken into account.

The ENDOR signal can also be compared to the NMR signal. This appears directly in Fig. 2, which indicates a ratio $R(\text{EN/N})$ of about 0.9. From (25) one obtains

$$R(\text{EN/N}) = \frac{\int \Delta L_{\text{EN}} dH_0}{\int \Delta L_N dH_0} = \frac{\mathcal{L}_{\text{EN}}}{\mathcal{L}_N} \frac{\bar{P}_{\text{EN}}}{\bar{P}_N} \approx \frac{\mathcal{L}_{\text{EN}}}{\mathcal{L}_N} \sqrt{2} \approx 1.4. \quad (29)$$

The discrepancy with the experimental value can be explained by the fact that we have oversimplified the distributions with EPR saturation: we have assumed a discontinuity at the edge of the saturated zone. Since the distribution varies smoothly, the real population difference for part of the pairs is smaller than assumed, and this reduces the ENDOR signal.

From NMR experiments some information can be obtained on the size of the close pairs. In the spectra, the lines of the fourth nearest neighbor $\text{Cl}_{\text{IV}}^{35}$ are still well resolved. This implies that the integral of p_K^{\pm} should not be smaller than a_K . This means that the exchange energy is near the hyperfine energy of the considered nucleus ($J/A_K \lesssim 2$). This gives $J \lesssim 0.2$ MHz. From a calculation by Schwörer and Wolf [9] the average pair size can then be estimated to be around seven interionic distances. This is much less than the separation of the distant pairs [3] estimated to range up to 25 interionic distances. Since these distant pairs are characterized by equal non-radiative probabilities for both states $|\psi^+\rangle$ and $|\psi^-\rangle$, the close pairs should have themselves a smaller non-radiative probability for $|\psi^+\rangle$ than for $|\psi^-\rangle$, in order that the optical pump can establish a population difference between these two states. Inspection of the formulae of Section 5 shows that the exchange energy in the excited state, J^* , should then be near

the total hyperfine energy: $J^* \gtrsim A$. If J^* were known as a function of the distance, this would allow to estimate the upper limit for the close-pair size.

Another question is why the close pairs do not show any EPR signal in the excited state, characterized by a decrease of the luminescence as in the distant pairs. If such an effect is included in the scheme of Fig. 7, one finds that the EPR transition rate P_E has to be multiplied by the ratio W_p/W_r of the pumping rate to the radiative disexcitation rate. The latter parameter, being >1 MHz, makes the ratio much smaller than unity, because in our conditions the pumping rate is at most 1 kHz. This makes any EPR transfer in the excited state very inefficient and completely overwhelmed by the transfers in the ground state. Moreover, the pair separation is certainly not unique, so that the exchange is somewhat distributed and produces a broadening of the line.

7. Conclusion

Illumination of a KCl crystal containing F centers, performed during a short time at room temperature can reduce the distance between neighboring centers, producing close pairs of F centers. Their separation is such that the exchange energy is near 0.2 MHz in the ground state and near 50 MHz in the optically relaxed excited state. Their luminescence probability depends on the spin state, and in a static magnetic field of a few kG it can be modified by a transverse magnetic field of suitable frequency, giving rise to EPR, NMR, and ENDOR spectra. These are almost the same as those obtained by a conventional detection method. These properties can be explained by the following mechanism: under light excitation in the F band, pairs are transferred via the excited state preferentially into an almost pure singlet state, which is non luminescent. The population differences established this way are restored by the transitions due to the transverse field and they all produce an increase of the luminescence when the resonance conditions are satisfied. A Hamiltonian containing two electronic and many nuclear spins with isotropic interactions can be treated approximately in the high-field case (Zeeman energy \gg hyperfine energy \gtrsim exchange energy) and it accounts qualitatively for the observed spectra and quantitatively for their relative intensities.

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