Magnetic Resonance and Related Phenomena

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SECTION E

Resonance Experiments Involving the Excited State

OPTICAL DETECTION OF NMR FOR CLOSE F CENTRE PAIRS IN KCL

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Abstract. The exchange interaction of close F centre pairs mixes strongly two electronic spin states. Their populations are disturbed by the optical pumping cycle. A r.f. field restores the equilibrium by nuclear flips together with change of the electronic spin state, appearing as a NMR spectrum in the luminescence.

1. Introduction. In alkali halides at low temperature, single F centers excited optically by light in the F-band return radiatively to the ground state with a luminescent quantum yield of unity. If their concentration is larger than 10^{16} cm^{-3}, some of them build up in pairs with a smaller quantum yield. The non-radiative transition is attributed either to formation of a transient F'+vacancy pair (Lüty, 1961) or to an instability of local vibrational modes leading to a radiationless disexcitation (Jaccard et al, 1973). Such mechanisms are effective only if the spin state of the pair contains a certain admixture on the singlet state. This has been shown by the magnetic field dependence of the luminescence at low temperature (1.5 K) due to the Boltzmann factor (Porret et al, 1971) or at higher temperature (up to 50 K) due to inhomogeneities of the nuclear magnetic fields (Jaccard et al, 1972). Electronic spin flips induced by a microwave field in the relaxed excited state show up as an EPR spectrum in the luminescence (Ruedin et al, 1972, 1973). The pairs giving rise to these effects are called "distant pairs", because their separation is relatively large (80 Å) and the electron spins interact weakly and only in the relaxed excited state.

2. NMR transitions in close pairs. If the crystal is irradiated briefly near RT with F light, the pair separation decreases, giving "close pairs" with quite different properties (Schnegg et al, 1974). These are explained by an exchange interaction which should be smaller than the hyperfine energy in the ground state, but much larger in the excited state. It mixes the electronic spin states in such a way that one of the spin populations is enhanced significantly at the expense of the other during the optical cycle. A microwave field induces then EPR transitions in the ground state (tending to restore the equilibrium) producing a luminescence increase. At strong microwave intensity the center of the inhomogeneous line can be saturated, and a r.f. field induces ENDOR-type transitions (without change of the electronic spin state) revealed also by the luminescence (Schnegg, 1974). Surprisingly, the ENDOR signal does not vanish if the microwave power is turned off, as it can be seen in Fig. 1. It only decreases by a factor of about 2. The luminescence measured as a function of the r.f. frequency at constant magnetic field (or vice-versa) gives exactly the same spectrum as in the ENDOR case (Fig. 2). This spectrum agrees also with conventional ENDOR measurements (Seidel, 1961). In a first attempt to explain this behaviour, we considered the fact that, if a pair is transfered from a triplet to the singlet state by the optical cycle, the conservation of the total spin should compensate a loss of the electronic spin by a gain of the nuclear spin, producing thereby a net nuclear polarization. This would decrease the nuclear field inhomogeneity and change the luminescence in the right direction, but the effect is quantitatively too small. On the other hand the asymmetry of the nuclear distribution as a result of this polarization gives an effect with the wrong sign in all the models studied so far. The approximate solution sketched in the following section explains the observation sucessfully and gives the right answer for the relative intensities with respect to ENDOR and EPR.

3. Behaviour of close pairs in the strong field case. The spin hamiltonian for the pair in its ground state takes the form

(1) $$H = g_e\beta_e\vec{H}_0(\vec{S}_1+\vec{S}_2) + J\vec{S}_1S_2 + \sum_k(A_{1k}\vec{S}_1 + A_{2k}\vec{S}_2 + g_k\beta_n\vec{H}_0)\vec{I}_k$$

expressing electronic Zeeman exchange, hyperfine and nuclear Zeeman energies. The symbols have their usual meanings. The sum over k extend over all nuclei interacting with a pair. For high temperature and strong fields :

(2) $$kT >> \beta_eH_0 >> A_{jk} \sim \beta_nH_0 \gtrsim J$$

In the base $|s_1,s_2;\{m_k\}>$ only the states $|\pm1/2,\mp1/2;\{m_k\}>$ are mixed significantly by the exchange; other admixtures are of the order of A_{jk}/β_eH_0 and therefore left out. The states are then

(3) $$|+1/2,+1/2;\{m_k\}> = |\sigma^+> \qquad |-1/2,-1/2;\{m_k\}> = |\sigma^->$$
$$|\psi^+;\{m_k\}> = \cos\phi\,|+1/2,-1/2;\{m_k\}> + \sin\phi\,|-1/2,+1/2;\{m_k\}>$$
$$|\psi^-;\{m_k\}> = \sin\phi\,|+1/2,-1/2;\{m_k\}> - \cos\phi\,|-1/2,+1/2;\{mk\}>$$
$$\mathrm{tg}\phi = (M^2/J^2+1)^{1/2} - M/J \;;\; M = \sum_k(A_{1k}-A_{2k})m_k$$

In the excited state J is large, ϕ is near $\pi/4$ and $|\psi^+>$ has only a very small singlet component : pairs in this state can be radiative or not. In the latter case they disexcite to the state $|\psi^->$, which is almost a non-radiative pure singlet. The optical pumping populates then $|\psi^->$ at the expense of $|\psi^+>$ and also of $|\sigma^->$ as it has been shown (Schnegg et al, 1974). A r.f. field with a suitable frequency can then flip a certain nucleus K by inducing transitions $|\psi^+> \leftrightarrow |\psi^->$

(4) $$|<\psi^+;m_K|I_K^{\pm}|\psi^-;m_K\mp1>|^2 \sim \sin^2[\phi(m_K)-\phi(m_K\mp1)]$$

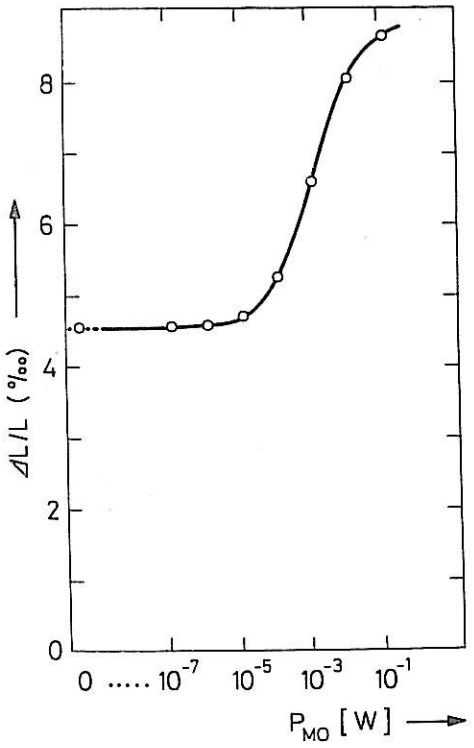

Fig. 1. Height of optically detected Cl^{35}_{II} ENDOR peak vs. microwave power (H_0 = 3440 G, f_{MW} = 9619 MHz, f_r = 5 MHz, T = 13.6 K)

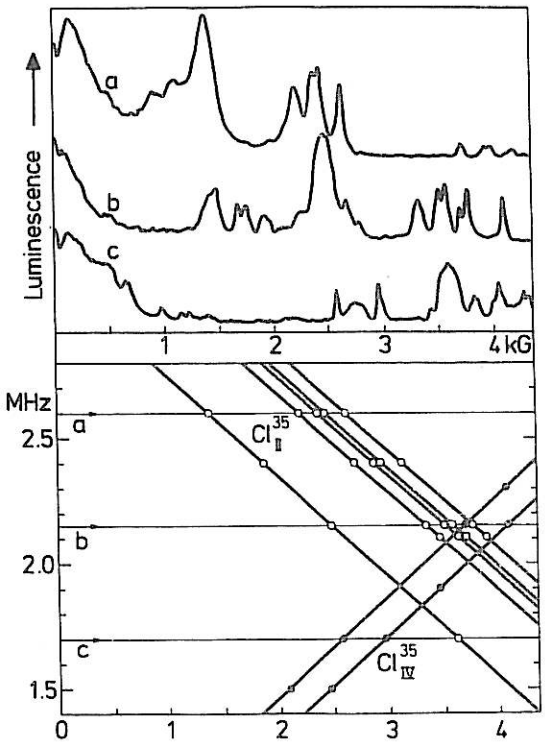

Fig. 2. NMR spectra detected optically at 13.6 K without microwaves at different radio-frequencies

According to equ. 3 this last expression is near unity for J << M and (±M) between zero and A_{1K}-A_{2K}. Therefore, r.f. transitions are possible with a frequency $|(A_{1K}-A_{2K})/2 \pm g_K\, n^H_0|/h$ involving nuclear spin flip together with change of the electronic spin state. They transfer pairs from the non-radiative state $|\psi^-\rangle$ back into the partly radiative state $|\psi^+\rangle$, increasing the luminescence. Moreover one has either $A_{1K} \cong A_K$, $A_{2K} \cong 0$, or vice-versa, except for nuclei lying near the median plane between the vacancies. The NMR spectrum reproduces therefore the standard ENDOR spectrum of single centers, with somewhat broadened lines.

A detailed analysis (to be published) yields correct values for the integrated ratios (NMR): (ENDOR):(EPR) = 1:1:3 obtained with H_x (microwave) = 0.5 G and H_x(r.f.) = 0.9 G. Absolute determination is not yet possible, the concentration of close pairs being not known with a sufficient accuracy.

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