ELECTRON-SPIN MEMORY IN THE OPTICAL-PUMPING CYCLE OF F CENTERS IN ALKALI HALIDES AND ELECTRON-SPIN RESONANCE OF THE RELAXED EXCITED STATE*

L. F. Mollenauer, S. Pan, and S. Yngvesson
Physics Department, University of California, Berkeley, California 94720
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The g factors and electron-spin resonance linewidths have been measured for the relaxed excited state of F centers in KCl, KBr, and KI by means of a special technique combining optical pumping, optical detection, and resonating microwaves. The technique is based upon the nearly complete electron-spin memory exhibited by these centers in an optical-pumping cycle.

For the F center in KCl, KBr, and KI we have detected EPR of the relaxed optically excited state by using a special optical double resonance technique. The method relies on the nearly complete electron-spin memory exhibited by the F center in an entire optical-pumping cycle. By subjecting the relaxed excited state to a resonant microwave (H_1) field while the F center is being continuously pumped with σ^+ or σ^- light, the spin memory can be partially erased. As a consequence, the (unsaturated) rate of pumping of the ground-state spin polarization is increased, and the equilibruim value of the polarization thereby changed. The ground-state polarization is measured (and hence the signal is detected) by continuous monitoring of the magnetic circular dichroism (MCD) of the absorption band.

The essential features of the optical pumping are indicated in Fig. 1. The ground-state populations ar; n^+ and n^-. To explain the experimental results obtained here, we need consider only the lowest lying component of the relaxed excited manifold. Accordingly, in the following we refer to "the" relaxed state, ρ, a Kramers doublet with populations n_ρ^+ and n_ρ^-; τ is the radiative lifetime of this state ($\tau \sim 1\times 10^{-6}$ sec). This and other transition rates are indicated beside each arrow in the figure: w is the transition rate induced by a field H_1 resonant with the splitting $g_\rho \beta H_0$; u^+ and u^- are the rates per F center for pumping into one of the dichroism peaks of the absorption band with (say) σ^+ light. For the F centers considered here, the fraction $(u^+-u^-)/(u^+ +u^-)$ is quite large, ranging from about 5% for KCl to 40% for KI.[1-3] In keeping with the known high quantum efficiency of luminescence[4] from the relaxed excited state, and consistent with the very large spin memory measured in these experiments, we assume the following: (1) Decay from the ^2P band is an extremely rapid, nonradiative process, taking place in a time quite short relative to ^2P-band radiative lifetime of $\sim 10^{-8}$ sec; (2) radiation from the ρ state to the ground state follows the strict selection rule $\Delta M_S = 0$; (3) the spin-lattice relaxation time $(T_1)_\rho$ for the relaxed excited state is long relative to τ.

According to the above model, the populations should be governed by the following rate equations:

$$\frac{dn^+}{dt} = -u^+n^+ + \frac{n_\rho^+}{\tau} - \frac{n^+}{T_1} + \frac{1}{T_1}\left(\frac{n^+ + n^-}{1+e^{\Delta}}\right), \quad (1)$$

$$\frac{dn^-}{dt} = -u^-n^- + \frac{n_\rho^-}{\tau} - \frac{n^-}{T_1} + \frac{1}{T_1}\left(\frac{n^+ + n^-}{1+e^{\Delta}}\right), \quad (2)$$

$$\frac{dn_\rho^+}{dt} = (1-\epsilon)u^+n^+ + \epsilon u^-n^- + w(n_\rho^- - n_\rho^+) - \frac{n_\rho^+}{\tau}, \quad (3)$$

$$\frac{dn_\rho^-}{dt} = (1-\epsilon)u^-n^- + \epsilon u^+n^+ + w(n_\rho^+ - n_\rho^-) - \frac{n_\rho^-}{\tau}. \quad (4)$$

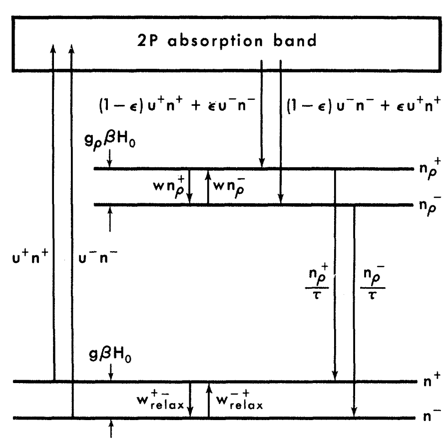

FIG. 1. Energy levels and transition rates for optical-pumping cycle of F center, including microwave-induced transitions in the state ρ and spin-lattice relaxation in the ground state.

In the above, Δ is $g\beta H_0/kT$, and $1/T_1$ is the spin-lattice relaxation rate for the ground state. ($1/T_1$ is now known[3] empirically for all fields up to $H_0 = 50$ kG.) For the maximum optical-pump power used here, $u^+ + u^- \ll 1/\tau$; and for all values of H_0, $1/T_1 \lll 1/\tau$. Then the rate equations have the steady-state solution

$$P_e \equiv \frac{n^+-n^-}{n^++n^-} = \frac{P_{e,s}-[T_p/T_1]\tanh(g\beta H/2kT)}{1+T_p/T_1}, \quad (5)$$

where $P_{e,s} = (u^- - u^+)/(u^- + u^+)$ is the value of P_e for saturated optical pumping, and where $1/T_p \equiv (\epsilon + w\tau)(u^+ + u^-)$ is the ground-state spin-flipping rate due to optical pumping and resonance in the relaxed excited state. Furthermore, for an experiment in which the optical pump is turned on suddenly, P_e rises exponentially from its thermal equilibrium value to its steady-state value under optical pumping at a characteristic rate $1/T_r = 1/T_p + 1/T_1$.

The above model has been given rather exhaustive experimental test for KCl: Both P_e and T_r were measured experimentally for the full range of fields $0 < H_0 \leq 50$ kG, and for various gross pump rates $(u^+ + u^-)$. The results fit Eq. (5) rather well in all cases. For KCl, we can estimate $u^+ + u^-$ from the absolute intensity of the pump light and the known oscillator strength of the F-center absorption. For the maximum light power, $u^+ + u^- \sim 100$/sec, yet the corresponding value of $1/T_p \sim 1$/sec; thus $\epsilon \sim 0.01$ for KCl. ϵ appears to increase rapidly with increasing spin-orbit splitting in the band, so that ϵ is roughly 0.06 for KBr and still larger for KI. These results are entirely consistent with the recent observation of Schmid and Zimmerman[5] on the optical pumping of the F center in KCl; earlier and less accurate experiments,[6,7] originally interpreted with the a priori assumption of zero spin memory, nevertheless show no essential inconsistency with the above.

For the detection of resonance of the relaxed excited state ρ, we are essentially interested in $\Delta P_e = (\partial P_e/\partial T_p)\Delta T_p$, where ΔT_p is brought about by application of a field H_1 resonant with $g_\rho \beta H_0$. If $w\tau \ll \epsilon$, it can be shown that

$$\Delta P_e \simeq \frac{T_p/T_1}{(1+T_p/T_1)^2}\left\{P_{e,s} + \tanh\left(\frac{g\beta H}{2kT}\right)\right\}\left(\frac{w\tau}{\epsilon}\right). \quad (6)$$

Thus, optimum sensitivity will be attained when the optical-pump power is reduced to the point where $T_p \simeq T_1$. [The required relation between optical-pump power and $1/T_1$ is similar to that required in ENDOR (electron-nuclear double resonance) between microwave power and $1/T_1$.] The above tacitly assumes a homogeneously broadened EPR line, when in fact the resonances in question represent an extreme of inhomogeneous broadening. Thus, the above expression for ΔP_e should probably be reduced by a factor on the order of $\Delta\omega_h/\Delta\omega$, where $\Delta\omega_h$ is the width of a homogeneous packet within the full linewidth $\Delta\omega$.

Figure 2 shows the apparatus used for these experiments. The arrangement is essentially the same as that used in Ref. 3, except for the addition here of a microwave cavity. Since the cavity configuration is a bit unusual, it is detailed in Fig. 2(b). The microwave frequencies used were in the neighborhood of 52 GHz; thus both ground-state and excited-state resonances ($g \sim 2$) occurred for H_0 on the order of 20 kG. A maximum of about $\frac{1}{2}$ W of microwave power was available at the cavity. As in Ref. 3, a narrow

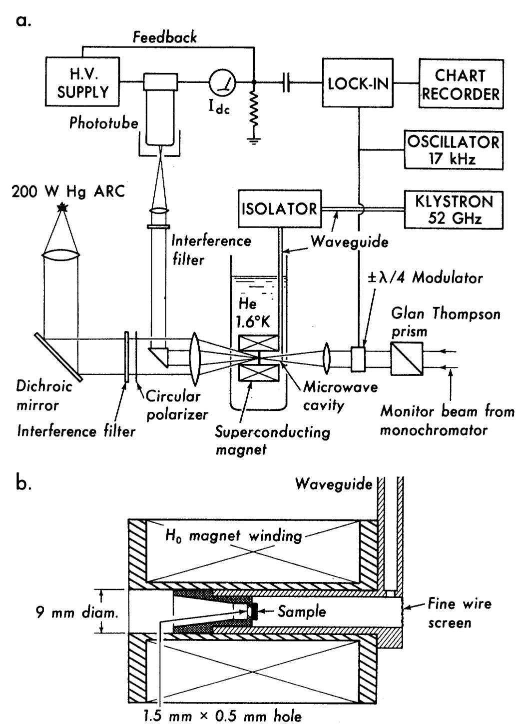

FIG. 2. (a) Block diagram of the apparatus. (b) Detailed view of microwave cavity and superconducting magnet. TM_{11n} modes were excited in the cylindrical cavity. Monitor-beam cross section at sample was approximately 0.4 mm × 0.8 mm; sample thickness ranged from 0.5 to 1 mm. Over this volume of sample, H_0 is constant to within a few G in 20 kG.

band of wavelengths near one dichroism peak of the absorption band was used for pumping, while a low-intensity, narrow band of wavelengths at the other dichroism peak was used for monitoring the MCD. Neutral density filters in the pump beam allowed control over T_p.

The nature of the dichroism signal S and the sensitive technique used in its measurement have been detailed in Ref. 3. For some of the experiments here, where we are interested in having an absolute measure of P_e, it is important to realize that the MCD signal S is the sum[2] of a paramagnetic part (S_p) and a diamagnetic part (S_d). S_d is independent of P_e and depends only on the Zeeman splitting of the $2P$ band, and is thus linearly dependent on the magnetic field, whereas S_p depends on the field-independent spin-orbit splitting of the band and on P_e. Thus we have $P_e = KS_p = K(S-S_d)$. It is easy to discover experimentally what fraction of the signal is S_d: With the optical pump turned off, the system is allowed to reach thermal equilibrium at a large field H_0'. Then the field is switched to a low value H_0'' in a time very short relative to the value of T_1 at any field $\leq H_0'$. The discontinuous jump in S is then S_d for a field $H_0'-H_0''$; the remaining part (immediately after the jump) is S_p for the thermal equilibrium value of P_e at H_0'. Using the above information, one can then always calculate S_d for any field and subtract this from the measured S to obtain the desired S_p.

Figure 3 shows behavior of the resonances in KBr for various levels of optical-pump power. Note that although the ground-state resonance signal always points towards $P_e = 0$, the excited-state resonance always points towards increasing P_e, even when P_e itself is inverted; this constitutes the most dramatic proof that the second resonance signal is indeed due to an excited state of the F center. As a further check, the excited-state resonance signal ΔP_e, when plotted versus the parameter $X/(1+X)^2$ ($X \equiv T_p/T_1$), makes a good fit to a straight line, in conformity with Eq. (6). Finally, with only the monitor beam itself acting as a very low-level pump, the excited-state resonance signal disappears entirely into the noise, again as expected.

The resonance signals in Fig. 3 become distorted as the optical-pump power is increased, due to cross relaxation between F centers in the ground state. As this cross relaxation is strongly dependent on the frequency separation of the interacting centers, the low-field side of the excited-state resonance is affected more than the high-field side. Thus the low-field side of the signal begins to turn downward at high pump-power levels, while the high-field side continues to point upward. The cross relaxation is much stronger in KCl, where the g factors of the excited and ground states are much closer together. In fact, for KCl the entire excited-state resonance becomes inverted (points towards $P_e = 0$) at the highest pump-power levels. Except for the increased prominence of cross-relaxation effects, the excited-state resonance signal in KCl displays a behavior qualitatively the same as that of the excited state in KBr.

The excited-state g factors are 1.976, 1.862, and ~1.62 for KCl, KBr, and KI, respectively; the corresponding linewidths are 55, 270, and 700 G, respectively. Within the limits of experimental error, the excited-state g factors are isotropic. The result listed for KI is only tentative, since increased excited-state linewidth and decreased electron-spin memory make the resonance difficult to detect and measure accurately. To compare with ground-state g factors, see the table in Seidel and Wolf.[8]

A number of theoretical models have been proposed for the relaxed excited state.[9-11] In view of the isotropic g factor found here, two of these models would seem to be most promising. In

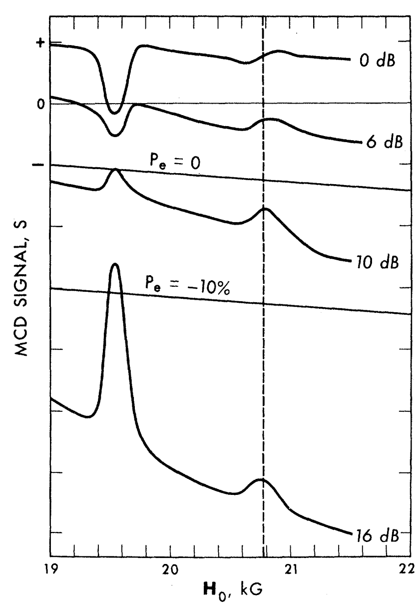

FIG. 3. MCD signal versus H_0 for various optical-pump powers. Ground-state resonance at left. Dashed vertical line shows center of excited-state resonance; cross relaxation distorts line shape at high pump powers (see text).

the first of these a $2P$ state is split by a strong, dynamic Jahn-Teller effect into three Kramers doublets. Presumably, the lowest-lying of these would be the relaxed excited doublet seen here. In the second, the doublet seen in these experiments would be a $2s$ state lying underneath a $2p$ manifold. A rather strong admixture of the $2p$ into the $2s$ would be required to explain the large g shifts. Somewhat bound up with the above problem of model selection is the question of the diffuse or compact nature of the wave function. It may not be possible to decide the latter question on the basis of the g shifts and linewidths measured here, since no unambiguous relation is known to exist between these factors and the physical extent of the wave function. In any case, it would be highly desirable to know the excited-state ENDOR behavior as well.

It is possible that the experiments described above may be extended to include detection of ENDOR in the relaxed excited state. By applying a second H_1 field at an ENDOR frequency, one may be able to increase the total number of electron spins affected by the microwave H_1 field. That is, the ENDOR field would tend to tie together two previously isolated, homogeneous, spin packets. If so, the microwaves would become more effective in erasing electron-spin memory, and the optically detected, excited-state resonance signal of the kind described above would be enhanced. For a number of reasons, ground-state ENDOR signals may appear mixed in with those of the excited state; however, as the former frequencies are already known,[12] the difficulty would not be insurmountable. We are presently modifying our apparatus to attempt such an experiment.

The nearly complete spin memory measured in these experiments may have a number of important theoretical implications about the unrelaxed excited state. For example, it may imply an extremely short lifetime for this state ($T^{-1} > \hbar^{-1}\Delta E_{\text{spin-orbit}} \sim 3\times10^{12}$/sec). Despite the large spin memory, we have recently been able to produce spin inversion in KCl and KBr for fields H_0 well in excess of 30 kG; thus these F centers may be useful as optically pumped maser materials for frequencies as high as 100 GHz.

The experiments described here may well represent a record for EPR sensitivity.[13] In KBr, the smallest measurable excited-state population was about 3×10^5 excess spins (integration time ~1 sec), or a mere 1000 spins per gauss of EPR linewidth.

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