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Coherence dynamics of cross-relaxing triplet spins

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The dynamics of resonant cross relaxation between different electron-spin species, viz., the F_2^{2+} ($S=1$) and F^+ ($S=\frac{1}{2}$) defects in CaO, is studied by optical-spin-echo spectroscopy. For the F_2^{2+} center in the photoexcited $^3B_1$ state, the phenomenon of hole burning by resonant cross relaxation is inferred.

Spin dephasing due to spectral diffusion in ionic solids has been extensively discussed in the past.[1-3] The process is controlled by spin-spin interactions which, to be specific, are constrained to terms of the form, $S_{zA}S_{zB}(t)$, A and B being representative of the probed and fluctuating spin species, respectively. The approach is valid because the A- and B-spin resonances usually are sufficiently remote to ensure rapid averaging out of all other terms in the dipolar coupling. However, for the situation of comparable A and B splittings, an additional decay channel is opened up for the A spins. The phenomenon, well known as cross relaxation (CR), tends to establish a common spin temperature for the A- and B-spin ensembles. CR should be manifest in the coherence dynamics of A spins.

Relatively few experiments on CR *dynamics* in electron-spin systems have been reported. In part this is because of the fact that one cannot spectrally resolve either of the cross-relaxing species by standard magnetic resonance techniques. This difficulty may be overcome when double-resonance methods can be applied.[4,5] In this paper we report the first study of CR dynamics by using *optically* detected A-spin coherence as a probe. Our experiments concern the resonant energy exchange, in CaO crystals, between F_2^{2+} centers in the phosphorescent $^3B_1$ state, and F^+ centers in the spin doublet ground state. Here the triplet spins act as A spins, the doublet spins form the B spins; CR is achieved in the presence of an external magnetic field. The sensitivity of the method enables one to study the cross-relaxation process in some remarkable detail. For example, for the A-B system in this work, it is inferred that a hole is burnt in the inhomogeneously broadened A-spin signal as the A and B spins become resonantly coupled.

As shown recently,[6] in the presence of an external magnetic field along the crystallographic [100] direction, the $^3B_1 \rightarrow {}^1A$ no-phonon line emission at 683 nm, which is characteristic of the F_2^{2+} vacancy-pair, exhibits a sharp (polarized) intensity change when $H=H_{CR}\equiv 363$ G. The effect reflects an abrupt variation in the (non-Boltzmann) triplet spin alignment and occurs because rapid CR into the bath of abundant F^+ center spins (having $S=\frac{1}{2}$) is possible. Now, using the probe-pulse technique[7,8] at 1.2 K, optically detected Hahn-echo amplitude decays for the $|\beta\rangle \rightarrow |\gamma\rangle$ triplet spin transition were obtained as a function of the strength of the magnetic field, the latter being directed along the [100] axis. For H values between 200 and 400 G, the spin echoes showed a monoexponential decay. A plot of the characteristic decay time, T_M, vs H is given in Fig. 1(a). Typically, $T_M = 23 \pm 2$ μs, except for $H=363$ G: under CR conditions T_M becomes 13 ± 2 μs; i.e., *T_M is decreased by almost a factor 2.*

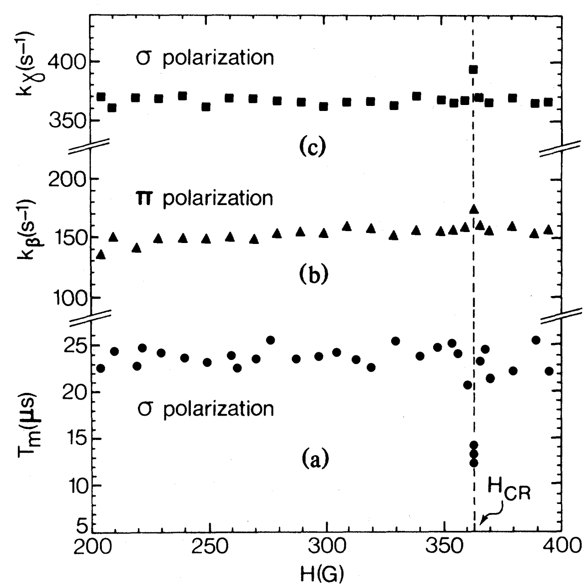

FIG. 1. Coherence- and population-decay characteristics for the F_2^{2+} center, in the $^3B_1$ state, in an applied magnetic field along a [100] axis of the CaO crystal. CR with F^+ centers occurs for $H=H_{CR}$. $T=1.2$ K. (a) Field dependence of the phase-memory time, T_M, as obtained for the $|\beta\rangle \rightarrow |\gamma\rangle$ (triplet) spin transition, (b) and (c) decay rate constants, k_β and k_γ, respectively, as a function of H, as determined after triggering a population inversion at $\omega_{\beta\gamma}$.

To discuss the shortening in the triplet spin dephasing, we recall that the time dependence of the echo amplitude, $S_1(t)$, is governed by the memory function, $K(t,t')$.[6] In the lowest Born approximation we have

$$K(t,t')=\frac{(S_1|\hat{\mathcal{H}}^*(t)(1-P)\hat{\mathcal{H}}^*(t')|S_1)}{(S_1|S_1)} \quad , \qquad (1)$$

where $\mathcal{H}^*(t)=U\mathcal{H}_{DD}^{AB}U^{-1}$, $U=\exp[i(\mathcal{H}^A+\mathcal{H}^B)t]$, $\mathcal{H}^A$ and $\mathcal{H}^B$ denote the spin Hamiltonians for the A- and B-spin ensembles (referring to F_2^{2+} and F^+ defects, respectively), and $\mathcal{H}_{DD}^{AB}$ represents the AB-dipolar interaction. P is a projection operator defined by $P=|S_1)(S_1|S_1)^{-1}(S_1|$; $\hat{\mathcal{H}}$ and P operate in Liouville space,[9] in which $|S_1)$ is a ket. For $H=H_{\rm CR}$, A and B spins exhibit equal energy eigenvalue splittings.

Then, $\mathcal{H}_{DD}^{AB}$ contains "static" *and* "dynamic" secular terms $\mathcal{H}_{DD}^{AB}(s)$ and $\mathcal{H}_{DD}^{AB}(d)$ respectively, which are characterized by $[\mathcal{H}^A,\mathcal{H}_{DD}^{AB}(s)]=0$, and

$$[\mathcal{H}^A,\mathcal{H}_{DD}^{AB}(d)]=-[\mathcal{H}^B,\mathcal{H}_{DD}^{AB}(d)]=\pm\omega_{\beta\gamma}\mathcal{H}_{DD}^{AB}(d) \quad ,$$

with $\hbar=1$. For the calculation of $K(t,t')$, only the secular terms in $\mathcal{H}^*(t)$ of Eq. (1) are retained. It follows, for the case of resonant coupling between A and B spins, that A-spin dephasing arises not only because of terms like $S_{zA}S_{zB}(t)$ in $\mathcal{H}_{DD}^{AB}(s)$, but also because of energy-conserving flip-flop terms as $S_{\beta\gamma}S_{+B}(t)$ or $S_{\gamma\beta}S_{-B}(t)$ in $\mathcal{H}_{DD}^{AB}(d)$. Explicit expressions for $\mathcal{H}_{DD}^{AB}(s)$ and $\mathcal{H}_{DD}^{AB}(d)$, in $\mathcal{H}_{DD}^{AB}=\mathcal{H}_{DD}^{AB}(s)+\mathcal{H}_{DD}^{AB}(d)$, were derived. The evaluation of $K^{\rm CR}(t,t')$ is then straightforward assuming uncorrelated A and B spins. The result is

$$K^{\rm CR}(t,t')=g_A^2g_B^2\mu_B^4\sum_{A,B}\frac{1}{n_A}\left[\frac{(1-3Z_{AB}^2)^2}{r_{AB}^6}\frac{z_l^2}{1+z_l^2}\langle S_{zB}(t)S_{zB}(t')\rangle + \frac{|3[z_l+(1+z_l^2)^{1/2}](X_{AB}-iY_{AB})^2-(1-3Z_{AB}^2)|^2}{4r_{AB}^6}\left(1-\frac{z_l}{(1+z_l^2)^{1/2}}\right)\langle S_{xB}(t)S_{xB}(t')\rangle\right] . \qquad (2)$$

In Eq. (2), X_{AB}, etc., is the direction cosine of r_{AB}, with respect to the x, etc., axis of the A-spin fine-structure tensor; $z_l=g_A\mu_BH_z'|E|^{-1}$, $H_z'=(H_l^2+H^2)^{1/2}$, H_l being the local field for an A spin as produced by a nearest (*non*fluctuating) B spin which effectively lifts the zero-field quenching of the A-spin magnetic moment; n_A is the number of probed triplet spins, and, finally, $\langle S_{iB}(t)S_{iB}(t')\rangle$ is the autocorrelation function for B-spin component i. Subsequently, $K^{\rm CR}(t,t')$ was inserted in the Volterra-type equation of motion for $\langle S_{1l}^*(t)\rangle$, where $S_{1l}(t)$ is the spin-echo amplitude of A spins having a local field H_l. Integration was accomplished assuming (i) an isotropic Markoffian relaxation of the B spins, i.e., $\langle S_{iB}(t)S_{iB}(t')\rangle \propto \exp(-R|t-t'|)$ for $i=x,y,z$, (ii) rapid averaging out of the dipolar coupling between A and *fluctuating* B spins, and (iii) the applicability of the statistical averaging procedure of Ref. 2. Finally, the $\langle S_{1l}^*(t)\rangle$ are weighted because of the inhomogeneous distribution in H_l. For our purposes, it is not necessary to specify the distribution function for H_l; we simply introduce an effective parameter, z, for which $H_z=(H_{\rm loc}^2+H^2)^{1/2}$, where $H_{\rm loc}^2$ is the weighted average of H_l^2, $\langle H_l^2\rangle$. As a final result, the A-spin-echo amplitude is calculated to decay according to

$$\langle\langle S_{1l}^*(2\tau)\rangle\rangle_{\rm av}\propto\exp[-p(H)g_Ag_B\mu_B^2d_BB(\tau)^{1/2}] \quad , \qquad (3)$$

where d_B is the B-spin density,

$$B(\tau)=R^{-2}\{R\tau-[1-\exp(-R\tau)]-\tfrac{1}{2}[1-\exp(-R\tau)]^2\} \quad ,$$

and the function, $p(H)$, is representative of the static AB-dipolar interaction in a magnetic field of strength H. Evidently, for $H=H_{\rm CR}$, the computation of $p(H)$ must be performed using the complete expression of $K^{\rm CR}(t,t')$ in Eq. (2). On the other hand, for $H\neq H_{CR}$, the memory function consists only of the first term on the right-hand side of Eq. (2), and $p(H)$ will vary as $z/(1+z^2)^{1/2}$.[6] For the $^3B_1$ state of the F_2^{2+} center in CaO, $|E|=179$ MHz and $H_{\rm loc}\simeq 15$ G, so one has for $H>200$ G, $z>>1$. Consequently, $p(H)$ is almost constant for H between 200 and 400 G [we calculate $p(H)=4.0$], except, of course for H equal to $H_{\rm CR}$. In the latter instance, the calculation yields $p(H_{\rm CR})=9.1$, i.e., $p(H)$ is expected to increase by a factor of 2.3 because of CR.

The experimental A-spin-echo decay curves were computer fitted to a function of the form $\exp[-C(z)B(\tau)^{1/2}]$. The numerical values for $C(z)$ and R, obtained as a function of H, are plotted in Fig. 2. Note that no appreciable change in $C(z)$ occurs until, at $H=H_{\rm CR}$, its value is enhanced by a factor of 1.7, i.e., somewhat lower than our earlier prediction. Furthermore, the B-spin dephasing rate, R, remains constant, even when $H=H_{\rm CR}$. Apparently, it is legitimate to adopt isotropy in the B-spin dephasing, a result which further substantiates the previously invoked phenomenon of exchange narrowing by random B-spin flip-flops.[6]

Since for the photoexcited triplet spins of the F_2^{2+} center the characteristic cross-relaxation time is short (~30 μs) on the time scale of the $^3B_1$ state lifetime

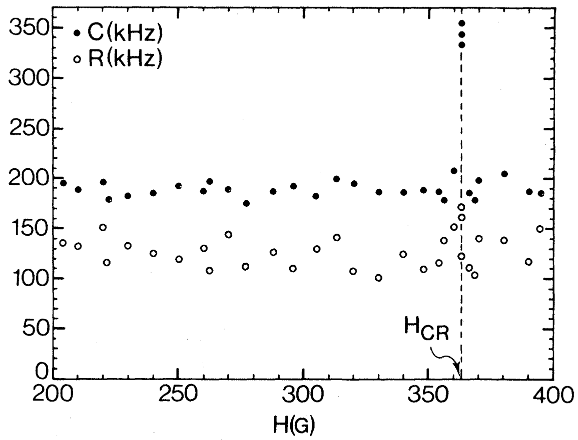

FIG. 2. Magnetic field dependence of $C(z)$ (●) and R (○) as obtained from fitting the F_2^{2+}-center echo decay curves to the form $\exp[-C(z)B(\tau)^{1/2}]$, as explained in the text. The sharp rise for $H=363$ G in $C(z)$ is representative of CR between F_2^{2+} and F^+ centers.

(3 ms), thermalization among A and B spins is rapid. In addition, the heat capacity of the F^+-center spin ensemble is almost infinitely large compared with that for the F_2^{2+} center spins [note that $d_B \simeq 10^{17}$ cm^{-3} and $n_A \simeq 10^4$ (Ref. 6)]. For the cross-relaxing A spins we anticipate, therefore, a Boltzmann population distribution, whereas, outside the CR regime, the anomalous spin alignment is preserved. However, this reasoning is, for the system studied here, too loose and should be refined, as can be seen from the population-decay kinetics.

Population-decay rate constants, k_β and k_γ, were determined from the time evolution of π- and σ-polarized intensity changes in the phosphorescence, that arise upon the application of a strong microwave (180°) pulse of frequency $\omega_{\beta\gamma}$. Figures 1(b) and 1(c) show the behavior of k_β and k_γ as a function of H. A striking feature is that k_β and k_γ still differ when $H=H_{\rm CR}$, a result which points to spin isolation. The apparent disparity in the outcome of the coherence- and population-relaxation experiments, is readily understood, however, on the basis of the significant difference in linewidth for A- and B-spin resonances. The characteristic width [full width at half maximum (FWHM)] for the inhomogeneously broadened $|\beta\rangle \rightarrow |\gamma\rangle$ transition is $\sim$15 MHz, whereas the width for the homogeneously broadened $|-\frac{1}{2}\rangle \rightarrow |+\frac{1}{2}\rangle$ B-spin transition of the F^+ center has previously been shown to be ultimately 100 kHz.[6] Thus, when the F_2^{2+}- and F^+-defect resonances exhibit overlap, only a small portion of the A-spin ensemble will be in thermal equilibrium with the B-spin bath or, equivalently, CR effects hole burning in the A-spin resonance.[10] Consequently, in experiments where high-power resonant microwaves are applied to measure CR dynamics, an inhomogeneously broadened set of A spins is excited (of 5–10-MHz width) which, for the larger part, comprises of A spins that are nonresonant with B spins. Clearly, the disperse excitation is expected to reduce effectively the value predicted for $p(H_{\rm CR})$, as indeed found experimentally. Likewise, the thermal isolation of the $|\beta\rangle$ and $|\gamma\rangle$ levels at $H=363$ G as concluded from the distinct values for k_β and k_γ, basically reflects that the microwave pulse predominantly excited A-spins nonresonant with B spins. Note that in the experiments of the latter type, the microwave pulse does not thermally separate the cross-relaxing A and B spins; instead, the temperature of the combined AB system with respect to that of the phonon reservoir is elevated. The slight increase in k_β and k_γ, by 25 s^{-1}, when $H=H_{\rm CR}$, is characteristic therefore of the B-spin spin-lattice relaxation rate at 1.2 K.

In summary, we have demonstrated that the rate for resonant energy exchange between different A and B spins can be determined in a direct manner from the (optically detected) coherence decay of the A spins. For the specific color-center system studied here, a comparison of the phase- and population-decay dynamics shows that CR generates hole burning in the inhomogeneously broadened A-spin signal.

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