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DIPOLAR-INDUCED DEPHASING OF TRIPLET ELECTRON SPINS

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In this paper, magnetic dipolar-induced spin dephasing is considered for localized electronic triplet spin states in solids. Using a projection operator formalism, expressions are derived to describe the Hahn-echo decay behavior for an ensemble of triplet spins at zero- and low-magnetic field strengths. For triplet states localized on non-axially symmetric molecules (or defects) it is shown that, at *zero* field, cross-relaxation with rapidly relaxing spins is essential in the dipolar-induced dephasing process; secular spin–spin interactions become important only in the presence of a static magnetic field or hyperfine couplings. The results are used to relate experimental dephasing data previously obtained for photoexcited triplet states of axially- and non-axially symmetric defects in CaO.

1. Introduction

Recently, spin relaxation within photoexcited triplet states of point defects randomly distributed in ionic solids has been extensively studied [1–6]. It was shown that, at liquid-helium temperatures, the spins are thermally isolated from the lattice and that relaxation of an ensemble of triplet spins (henceforth called A spins) excited into a coherent superposition state develops from magnetic dipolar coupling with fluctuating neighboring spins (called B spins).

In general, for triplet spins embedded in a non-axially symmetric crystal field, spin–spin couplings can contribute to spin dephasing in two ways. First, dephasing may arise from the presence of secular spin–spin coupling terms, i.e. dipolar interactions which commute with the zero-order A-spin hamiltonians. In this case, the A-spin resonance frequencies become randomly modulated with time (due to the time dependence of the B spins) and the A spins undergo random (irreversible) phase shifts. However, as was pointed out previously [1,2], in zero magnetic field the triplet spin angular momentum, S_i, with $i = x, y, z$ is quenched [7], so all secular AB-spin interactions are quenched also. Only when $H \neq 0$ or when detuning due to static other spins occurs, can one expect secular spin–spin interactions to produce triplet spin dephasing. An alternative way for spin–spin interactions to contribute to dephasing derives from the fact that most often localized electron spin triplet states exhibit an intrinsic fine structure (characterized by the zero-field splitting parameters D and E). It is then conceivable that triplet spin dephasing arises from *non*-secular spin–spin couplings. Especially at zero- or low-magnetic field strengths when, as already mentioned, secular dipolar interactions fail to cause dephasing, non-secular AB-spin dipolar interactions seem to be of importance. It is the purpose of this paper to investigate in a general fashion under what conditions the non-secular terms in the AB-spin interaction prevail in the spin dephasing mechanism. Despite extensive previous work concerning electron spin dephasing based on magnetic dipole–dipole interactions (see for excellent reviews refs. [8,9]), to our knowledge the problem as to how non-secular AB-couplings can cause triplet spin phase relaxation has still not been treated. From a physical point of view the problem is of interest because dephasing due to non-secular couplings is characteristic of energy exchange between A and B spins.

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To obtain the results we have applied a memory function formalism [2]. Expressions giving the explicit time dependence of the A-spin memory function as a function of the B-spin autocorrelation function and the strength of an externally applied magnetic field are presented; subsequently, the connection with the time behavior of the A-spin echo intensity in a Hahn-echo experiment is presented.

In section 3, it is discussed how the results are relevant for photoexcited triplet states of color centers in alkaline earth oxides. It is explained why spin dephasing as measured in zero-field for axially symmetric point defects is almost an order of magnitude faster than for low symmetry defects.

2. Theoretical

2.1. Coherence creation for triplet spins in a static magnetic field

Although the description of an optically detected Hahn-echo cycle for phosphorescent triplet states can be found at various places [10,11,2], in this section we briefly review the derivation to point out the new features due to the applied magnetic field. Spin coherence is created by strong microwave pulses resonant with the $|\beta\rangle \rightarrow |\gamma\rangle$ transition (cf. fig. 1) assuming thermal isolation among the triplet sublevels $|\alpha\rangle$, $|\beta\rangle$ and $|\gamma\rangle$. We write the spin hamiltonian as,

$$H = H_A + H_B + H_{AB} + V(t). \tag{1}$$

In eq. (1)

$$H_A = \sum_A \left(-X_A S_{xA}^2 - Y_A S_{yA}^2 - Z_A S_{zA}^2 + g_A \mu_B H_z S_{zA} \right), \tag{2}$$

where the summation is taken over all A spins excited by the microwaves; X_A, Y_A and Z_A denote the zero-field energies of the A-spin sublevels characteristic of the fine structure [12] (cf. fig. 1); the externally applied magnetic field, H_z, is directed along the molecular A-spin z-axis; H_B comprises all interactions involving the B spins except for the dipolar AB-spin couplings which are represented by H_{AB}; finally, $V(t)$ is the interaction of the A spins with the circularly polarized microwave field component suitable for

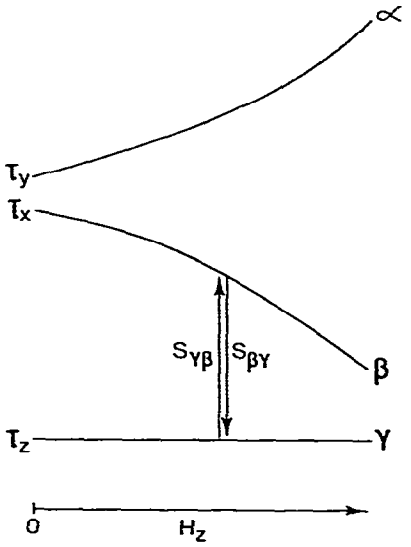

Fig. 1. Level splittings for an electron spin triplet state at zero field and in the presence of a magnetic field along the molecular z axis; $S_{\gamma\beta}$ and $S_{\beta\gamma}$ are raising and lowering operators for the transitions $\gamma \rightarrow \beta$ and $\beta \rightarrow \gamma$, respectively.

exciting the $|\beta\rangle \leftrightarrow |\gamma\rangle$ spin transition, hence

$$V(t) = \omega_1 \left[S_x \cos(\omega t) - S_y \sin(\omega t) \right], \tag{3}$$

where, as is done throughout this paper, we take $\hbar = 1$, and

$$S_x = \sum_A S_{xA}, \quad S_y = \sum_A S_{yA}.$$

The effects of the applied pulses in the echo-cycle are conveniently described in the A-spin interaction representation. We introduce

$$U = \exp(\mathrm{i} H_A t), \tag{4}$$

$$H^* = UHU^{-1} + \mathrm{i}(\partial U/\partial t)U^{-1}, \tag{5}$$

and

$$\rho^* = U\rho U^{-1}, \tag{6}$$

where ρ represents the density matrix, so that

$$\partial \rho^*/\partial t = \mathrm{i}\left[\rho^*, H^* \right]. \tag{7}$$

We now define

$$|\alpha\rangle = a_\alpha|+\rangle + b_\alpha|-\rangle, \quad |\beta\rangle = a_\beta|+\rangle + b_\beta|-\rangle, \quad |\gamma\rangle = |0\rangle, \tag{8}$$

where $|+\rangle$, $|-\rangle$, and $|0\rangle$ are the $m_s = 1$, -1, and 0 eigenfunctions of the S_{zA} operator. Retaining the time-independent effects of the microwave radiation field, one has

$$H^* = 2^{-1/2}\omega_1 \left(b_\beta^* S_{\gamma\beta} + b_\beta S_{\beta\gamma} \right) + H_{AB}(t) + H_B. \tag{9}$$

In eq. (9) we introduced the ladder operators $S_{\gamma\beta}$ and $S_{\beta\gamma}$, which have the following properties: $S_{\gamma\beta} = \Sigma_A S_{\gamma\beta A}$, $S_{\beta\gamma} = \Sigma_A S_{\beta\gamma A}$ and furthermore,

$$\langle \beta | S_{\gamma\beta A} | \gamma \rangle = \langle \gamma | S_{\beta\gamma A} | \beta \rangle = 1, \tag{10}$$

whereas all other matrix elements for these ladder operators are zero. $H_{AB}(t)$ in eq. (9) is given by

$$H_{AB}(t) = UH_{AB}U^{-1}. \tag{11}$$

To calculate the effects of high-power microwave pulses it is customary to rewrite eq. (7) in the Feynman, Vernon and Hellwarth (FVH) representation [10,11]. One obtains in the absence of relaxation

$$\partial \boldsymbol{r}^*/\partial t = \boldsymbol{\Omega}^* \times \boldsymbol{r}^*, \tag{12}$$

where the FVH space vectors, $\boldsymbol{\Omega}^*$ and $\boldsymbol{r}^*$, are defined by $\Omega_1^* = 2^{-1/2}\omega_1(b_\beta^* + b_\beta)$, $\Omega_2^* = 2^{-1/2}\mathrm{i}\omega_1(b_\beta^* - b_\beta)$, $\Omega_3^* = 0$ and $r_1^* = (\rho_{\beta\gamma}^* + \rho_{\gamma\beta}^*)$, $r_2^* = \mathrm{i}(\rho_{\beta\gamma}^* - \rho_{\gamma\beta}^*)$, $r_3^* = \rho_{\beta\beta}^* - \rho_{\gamma\gamma}^*$, whereas $\rho_{\beta\beta}^* + \rho_{\gamma\gamma}^*$ is a constant. Solution of eq. (12) yields

$$\begin{aligned} r_1^*(t) &= 2^{-1/2}\mathrm{i}(\omega_1/\omega_R)\left(b_\beta^* - b_\beta \right) r_3^*(0) \sin(\omega_R t), \\ r_2^*(t) &= -2^{-1/2}(\omega_1/\omega_R)\left(b_\beta^* + b_\beta \right) r_3^*(0) \sin(\omega_R t), \\ r_3^*(t) &= r_3^*(0) \cos(\omega_R t), \end{aligned} \tag{13}$$

where ω_R, the Rabi frequency characteristic of the nutation of the pseudo-magnetization r_3^*, is given by

$$\omega_R = \omega_1\left[1 + z/(1+z^2)^{1/2}\right]^{1/2}, \tag{14}$$

with

$$z \equiv g_A\mu_B H_z/(Y_A - X_A). \tag{15}$$

Thus, in the presence of an external static magnetic field, H_z, a $\pi/2$ pulse resonant with the $|\beta\rangle \leftrightarrow |\gamma\rangle$ transition produces

$$\begin{aligned} r_1^*(\pi/2) &= 2^{-1/2}\mathrm{i}(\omega_1/\omega_R)\left(b_\beta^* - b_\beta\right)r_3^*(0), \\ r_2^*(\pi/2) &= -2^{-1/2}(\omega_1/\omega_R)\left(b_\beta^* + b_\beta\right)r_3^*(0), \\ r_3^*(\pi/2) &= 0. \end{aligned} \tag{16}$$

In zero field, $z = 0$ and $b_\beta = 1/2^{1/2}$ so that $r_1^*(\pi/2) = 0$ and $r_2^*(\pi/2) = -r_3^*(0)$ *.

As is well known, in the optically detected Hahn-echo experiment the microwave pumping cycle is characterized by $\pi/2$–τ–π–τ–$\pi/2$, where τ is the time interval between the $\pi/2$ and π pulses. By studying the behavior of $r_2^*(\tau)$ as τ increases, one obtains the information concerning the coherence decay due to the combined effect of H_{AB} and H_B in eq. (9).

2.2. Coherence decay due to dipolar spin–spin interactions

We will now consider the relaxation of $r_2^*(t)$ for the A spins dipolar coupled to the B spins using, as before [2], the Zwanzig–Mori projection operator formalism [13,14]. In this approach we write the operator associated with the observable r_2^* as S_2^*, where

$$\langle\overline{S_2^*}\rangle = \mathrm{Tr}\left(\rho S_2^*\right) = r_2^* = \mathrm{i}\left(\rho_{\beta\gamma}^* - \rho_{\gamma\beta}^*\right). \tag{17}$$

In Liouville space the equation of motion for $\langle\overline{S_2^*}\rangle$ becomes [15],

$$\begin{aligned} \partial\langle\overline{S_2^*}\rangle/\partial t = &-\mathrm{i}\left(S_2|\hat{H}^*\hat{P}|\rho^*(t)\right) - \mathrm{i}\left(S_2|\hat{H}^*\hat{S}(t,0)(\hat{1}-\hat{P})|\rho^*(0)\right) \\ &- \int_0^t \mathrm{d}t'\left(S_2|\hat{H}^*(t)\hat{S}(t,t')(\hat{1}-\hat{P})\hat{H}^*(t')\hat{P}|\rho^*(t')\right), \end{aligned} \tag{18}$$

where we have used the notation customary in the formalism, i.e.,

$$(A|B) = \mathrm{Tr}(A^+B),$$

A^+ being the adjoint of A,

$$\hat{O}A = [O, A],$$

and finally,

$$\mathrm{e}^{\mathrm{i}\hat{O}}A = \mathrm{e}^{\mathrm{i}O}A\,\mathrm{e}^{-\mathrm{i}O}.$$

* Note that a change of the phase of the microwave field causes $r_2^*(\pi/2)$ and $r_1^*(\pi/2)$ to be non-zero. However, since by definition pure dephasing is characteristic of the relaxation of the off-diagonal elements in the density matrix, the decay with time is alike for the r_1- and r_2-components. Thus in discussing phase relaxation it is sufficient to consider the time behavior of either r_2 or r_1 (as was done in refs. [1–4]).

In eq. (18), the Liouville operator $\hat{S}(t, t')$ is defined by

$$\hat{S}(t, t') = T\exp\left[-\mathrm{i}\int_{t'}^{t}(\hat{1}-\hat{P})\hat{H}^*(\tau)\mathrm{d}\tau\right], \tag{19}$$

in which T is the time-ordering operator which places operators with a larger time argument to the left. $\hat{P}$ is a projection operator which for the echo-experiment takes the form

$$\hat{P} = |S_2)(S_2|/(S_2|S_2), \tag{20}$$

where the Hilbert operator S_2 is defined by

$$S_2 = US_2^*U^{-1} = -\mathrm{i}S_{\gamma\beta} + \mathrm{i}S_{\beta\gamma}. \tag{21}$$

For $\hat{P}$ as given by eq. (20) and since S_2 is hermitian, the first two terms on the right-hand side of eq. (18) become zero. To evaluate the remaining term of eq. (18) we first consider the propagator $\hat{S}(t, t')$. In a Magnus expansion up to first order [16] one has,

$$\hat{S}(t, t') \approx \exp\left[-\mathrm{i}\int_0^{t_c}\mathrm{d}\tau(\hat{1}-\hat{P})\hat{H}^*(\tau+t')\right], \tag{22}$$

where $t_c = t - t'$. Note that

$$H^*(\tau+t') = H_{AB}(\tau+t') + H_B. \tag{23}$$

The time average of $H_{AB}(\tau+t')$ in eq. (22) is practically zero because on the one hand the non-secular terms contained in $H_{AB}(\tau+t')$ rapidly die out (e.g., on the time scale of 20 ns when an inhomogeneous distribution of A spins was excited by microwaves with a H_1 component of ≈ 1 G), and on the other hand, the time-independent secular terms of H_{AB}, are averaged out by the pulse sequence applied in the echo experiment. Thus,

$$\hat{S}(t, t') \approx \exp(-\mathrm{i}\hat{H}_B t_c). \tag{24}$$

By substitution of eq. (24) into eq. (18) and making use of the fact that $b_\beta^* = b_\beta$ at all strengths of the magnetic field H_z one readily finds,

$$\partial\langle\overline{S_2^*}(t)\rangle/\partial t = -\int_0^t \mathrm{d}t'\, K(t, t')\langle\overline{S_2^*}(t')\rangle, \tag{25}$$

where the memory function is given as

$$K(t, t') = (S_2|\hat{H}^*(t)\hat{S}(t, t')\hat{H}^*(t')|S_2)/(S_2|S_2), \tag{26}$$

or, equivalently,

$$K(t, t') = \mathrm{Tr}\{[S_2, H^*(t)]\exp(-\mathrm{i}H_B t_c)[H^*(t'), S_2]\exp(\mathrm{i}H_B t_c)\}/\mathrm{Tr}(S_2^+ S_2). \tag{27}$$

To evaluate the memory function further, it is noted that

$$H^*(t) = H_{AB}(t) + H_B, \tag{28}$$

with

$$H_{AB}(t) = \sum_{A,B} h_{AB}(t) \tag{29}$$

and

$$h_{AB}(t) = (g_A g_B \mu_B^2 / r_{AB}^3)\{ S_{xA}(t) S_{xB}(1 - 3X_{AB}^2) + S_{yA}(t) S_{yB}(1 - 3Y_{AB}^2) + S_{zA}(t) S_{zB}(1 - 3Z_{AB}^2) - 3[S_{xA}(t) S_{yB} + S_{yA}(t) S_{xB}] X_{AB} Y_{AB} - 3[S_{yA}(t) S_{zB} + S_{zA}(t) S_{yB}] Y_{AB} Z_{AB} - 3[S_{zA}(t) S_{xB} + S_{xA}(t) S_{zB}] Z_{AB} X_{AB}\}, \quad (30)$$

where X_{AB}, Y_{AB} and Z_{AB} denote the direction cosines of the AB axis with respect to the A-spin triplet fine structure axes.

We rewrite h_{AB} as

$$h_{AB} = d_{xB} S_{xA}(t) + d_{yB} S_{yA}(t) + d_{zB} S_{zA}(t), \quad (31)$$

with

$$d_{xB} = [(1 - 3X_{AB}^2) S_{xB} - 3X_{AB} Y_{AB} S_{yB} - 3Z_{AB} X_{AB} S_{zB}](g_A g_B \mu_B^2 / r_{AB}^3),$$

and analogous expressions for d_{yB} and d_{zB}. The explicit time dependence of the A-spin operators is given by,

$$\begin{aligned} S_x(t) &= 2^{-1/2}[(a_\alpha + b_\alpha) e^{-i\omega_{\alpha\gamma} t} S_{\alpha\gamma} + (a_\alpha^* + b_\alpha^*) e^{i\omega_{\alpha\gamma} t} S_{\gamma\alpha} + (a_\beta + b_\beta) e^{-i\omega_{\beta\gamma} t} S_{\beta\gamma} + (a_\beta^* + b_\beta^*) e^{i\omega_{\beta\gamma} t} S_{\gamma\beta}], \\ S_y(t) &= -2^{-1/2} i[(b_\alpha - a_\alpha) e^{-i\omega_{\alpha\gamma} t} S_{\alpha\gamma} + (a_\alpha^* - b_\alpha^*) e^{i\omega_{\alpha\gamma} t} S_{\gamma\alpha} \\ &\quad + (b_\beta - a_\beta) e^{-i\omega_{\beta\gamma} t} S_{\beta\gamma} + (a_\beta^* - b_\beta^*) e^{i\omega_{\beta\gamma} t} S_{\gamma\beta}], \\ S_z(t) &= (a_\alpha^* a_\alpha - b_\alpha^* b_\alpha)(S_\alpha - S_\beta) + (a_\alpha^* a_\beta - b_\alpha^* b_\beta) e^{i\omega_{\alpha\beta} t} S_{\beta\alpha} + (a_\beta^* a_\alpha - b_\beta^* b_\alpha) e^{-i\omega_{\alpha\beta} t} S_{\alpha\beta}, \end{aligned} \quad (32)$$

where in all spin operators the label A (as e.g. in $S_{\alpha\gamma A}$) has been omitted. S_α and S_β are short for $S_{\alpha\alpha}$ and $S_{\beta\beta}$. Substitution of eqs. (28) through (32) into eq. (27) leads after some algebra to the following expression for the memory function $K(t, t')$.

$$\begin{aligned} K(t, t') = (S_z|S_z)^{-1} \sum_{A\,B} \{ &\langle d_{xB}^+ d_{xB}(t_c)\rangle \{[1 + (1 + z^2)^{-1/2}] \cos \omega_{\alpha\gamma} t_c + 2[1 - (1 + z^2)^{-1/2}] \cos \omega_{\beta\gamma} t_c\} \\ &+ \langle d_{yB}^+ d_{yB}(t_c)\rangle \{[1 - (1 + z^2)^{-1/2}] \cos \omega_{\alpha\gamma} t_c + 2[1 + (1 + z^2)^{-1/2}] \cos \omega_{\beta\gamma} t_c\} \\ &+ \langle d_{zB}^+ d_{zB}(t_c)\rangle \{2z^2/(1 + z^2) + 2[1 - z^2(1 + z^2)^{-1/2}] \cos \omega_{\alpha\beta} t_c\} \\ &+ \{\langle d_{yB}^+ d_{xB}(t_c)\rangle - \langle d_{xB}^+ d_{yB}(t_c)\rangle\} \{z(1 + z^2)^{-1/2} \sin \omega_{\alpha\gamma} t_c - 2z(1 + z^2)^{-1/2} \sin \omega_{\beta\gamma} t_c\}\}. \end{aligned} \quad (33)$$

In eq. (33), the autocorrelation function of d_{xB}, $\langle d_{xB}^+ d_{xB}(t_c)\rangle$ is given by $\mathrm{Tr}[d_{xB}^+ \exp(-iH_B t_c) d_{xB} \exp(iH_B t_c)]$; for d_{yB} and d_{zB} analogous expressions apply. Remark the appearance in the memory function of oscillatory terms due to non-secular interactions. The effects of these terms on the echo-decay have so far not been considered before. To calculate the echo-decay in a Hahn-echo pulse cycle, we have to include into eq. (25) the step function, $s(t)$, such that

$$\partial \langle \overline{S_z^*}(t)\rangle / \partial t = -s(t) \int_0^t dt' s(t') K(t, t') \langle \overline{S_z^*}(t')\rangle, \quad (34)$$

with $s(t) = 1$ for $t < \tau$ and -1 for $t > \tau$. In the event that the memory function decay is much faster than

the characteristic decay of the A spins, we may write,

$$\langle\overline{S_2^*(2\tau)}\rangle \propto \exp\left[-\int_0^{2\tau} dt \int_0^t dt' s(t)s(t')K(t,t')\right]. \tag{35}$$

Evidently, the oscillatory terms in eq. (33) become important for the irreversible A-spin relaxation when the Fourier transform of the B-spin correlation functions has appreciable spectral density at the resonance frequencies $\omega^{\wedge}_{\alpha\beta}$, $\omega^{\wedge}_{\alpha\gamma}$ or $\omega^{\wedge}_{\beta\gamma}$. Note from eq. (33) that at zero-field the memory function contains only oscillatory terms and that the decay of S_2^* due to secular interactions is quenched.

As an illustrative example, we will now examine the case that the B-spin spectrum in *zero-field* is resonant only with the $\alpha \leftrightarrow \beta$ A-spin transition. We consider the simple case that

$$\langle d^+_{z\mathrm{B}} d_{z\mathrm{B}}(t_c)\rangle = \langle d^2_{z\mathrm{B}}(0)\rangle \exp(-R|t_c|), \tag{36}$$

where R is the characteristic B-spin dephasing rate. Then substitution of eqs. (36) and (33) into eq. (35) for $z = 0$ yields,

$$\langle\overline{S_2^*(2\tau)}\rangle \propto \exp\left\{-a\left[(2R\tau)/\left(R^2+\omega^2_{\alpha\beta}\right) + \left(R^2-\omega^2_{\alpha\beta}\right)\mathrm{e}^{-2R\tau}/\left(R^2+\omega^2_{\alpha\beta}\right)^2 + \text{oscillatory terms}\right]\right\}, \tag{37}$$

a being a constant.

It is understood that the frequency of the oscillatory terms in eq. (37) is $\omega_{\alpha\beta}$. However, as is well known, in the Hahn-echo experiment one typically probes the echo response of a number of spin packets, excited by the strong microwave field. Thus, the echo-amplitude, $\langle\overline{S_2^*(2\tau)}\rangle$, as measured in the experiment involves a summation of exponential terms of the type given by eq. (37) and having oscillatory terms at a frequency around $\omega_{\alpha\beta}$. As a result the oscillatory factors in eq. (37) are averaged out and one is left with,

$$\langle\overline{S_2^*(2\tau)}\rangle \propto \exp\left[-\frac{1}{N_\mathrm{A}}\sum_{\mathrm{A,B}}\langle d^2_{z\mathrm{B}}(0)\rangle\left(\frac{2R\tau}{R^2+\omega^2_{\alpha\beta}} + \frac{\left(R^2-\omega^2_{\alpha\beta}\right)\mathrm{e}^{-2R\tau}}{\left(R^2+\omega^2_{\alpha\beta}\right)^2}\right)\right], \tag{38}$$

where

$$\langle d^2_{z\mathrm{B}}(0)\rangle = \tfrac{1}{4} g^2_\mathrm{A} g^2_\mathrm{B} \mu^4_\mathrm{B}\left[\left(1-3Z^2_{\mathrm{AB}}\right)^2 + \left(3Y_{\mathrm{AB}}Z_{\mathrm{AB}}\right)^2 + \left(3X_{\mathrm{AB}}Z_{\mathrm{AB}}\right)^2\right]/r^6_{\mathrm{AB}}. \tag{39}$$

Note that the echo amplitude as given by eq. (38) corresponds to the situation that the A spins undergo dephasing due to B spins in a well-defined single spatial configuration. For randomly distributed B spins in the lattice, however, one still has to average $\langle\overline{S_2^*(2\tau)}\rangle$ in eq. (38) to take into account the variation in the B-spin configuration around the A spins. Under these circumstances,

$$\langle\langle\overline{S_2^*(2\tau)}\rangle\rangle_{\mathrm{conf}} = \int P_\mathrm{B}\langle\overline{S_2^*(2\tau)}\rangle\, \mathrm{d}V, \tag{40}$$

where P_B is the statistical distribution function for the B spins. When the lattice is considered as a continuous medium and the B spins are allowed to occupy all positions in space, then one has [17],

$$\langle\langle S_2^*(2\tau)\rangle\rangle_{\mathrm{conf}} \propto \int^V \prod_\mathrm{B} \frac{\mathrm{d}V_\mathrm{B}}{V}\langle\overline{S_2^*(2\tau)}\rangle, \tag{41}$$

where $\mathrm{d}V_\mathrm{B}$ is the volume element of a B spin in the sample of total volume V. The integral of eq. (41) can

be evaluated using the statistical averaging procedure of refs. [17,2]. The result is

$$\langle\langle S_2^-(2\tau)\rangle\rangle_{\text{conf}} \propto \exp\left[-kd_B B(\tau)^{1/2}\right], \tag{42}$$

where d_B is the density of B spins, k is a constant,

$$k = \left[2/3 + (1/3\sqrt{3})\ \ln(2+\sqrt{3})\right]\pi\sqrt{\pi}\, g_A g_B \mu_B^2, \tag{43}$$

and $B(\tau)$ is given by

$$B(\tau) = 2R\tau/\left(R^2+\omega_{\alpha\beta}^2\right) + \left(R^2-\omega_{\alpha\beta}^2\right) e^{-2R\tau}/\left(R^2+\omega_{\alpha\beta}^2\right)^2 + 3\left(\omega_{\alpha\beta}^2 - R^2\right)/\left(R^2+\omega_{\alpha\beta}^2\right)^2. \tag{44}$$

3. Discussion

3.1. Influence of local symmetry

As already noted in section 2, at zero field (i.e. when $z=0$) the memory function given by eq. (33) contains only terms that oscillate at the A-spin resonance frequencies. From eq. (35) it follows then that at zero field only non-secular interactions denoting resonant cross relaxation between the A spins and the B spins can contribute to the irreversible triplet spin dephasing. Put in other words, one cannot expect the A spins to dephase on account of AB spin–spin interactions unless the A-spin and B-spin spectra show some resonant overlap. This result is of major importance in the understanding of triplet spin dephasing times measured for a number of defects in the photoexcited triplet state in ionic solids [1–4]. For example, in CaO a very slow dephasing is exhibited by the F_2^{2+} center (i.e., an oxygen divacancy containing two electrons) in the $^3B_1$ state ($T_M = 200$ μs [2]). For this system it was demonstrated [2] that dephasing is caused by spin–spin dipolar couplings, the B spins comprising an ensemble of randomly dispersed $S = 1/2$ spins due to F^+ centers (which consist of single oxygen vacancies each having one electron trapped). At zero field, however, the spectrum of the F_2^{2+}-center triplet spins peaks at $2|E| = 360$ MHz, $|D|-|E| = 1870$ MHz, and $|D|+|E| = 2230$ MHz, whereas the F^+-center spectrum peaks at $\omega = 0$ with a typical width of ≈ 20 kHz [2,5]. Consequently, at *zero* field the dipolar interactions between the F_2^{2+}-center triplet (A) spins and the F^+-center doublet (B) spins cannot possibly explain dephasing among the A spins. It is for this reason that one has to invoke a static magnetic hyperfine coupling between the probed F_2^{2+}-center spins and nearby *non*-fluctuating F^+-center spins, that are detuned from the bulk of F^+-center spins. In higher order this coupling introduces a lifting of zero-field quenching of the triplet spin magnetic moment thus making possible secular couplings with surrounding fluctuating B spins. It may be said then that the F_2^{2+}-center spins experience a net local field which was extracted to be 15 G [2]. It is of interest to note that the idea of detuning of nearby "B" spins and the importance of second-order hyperfine interactions for triplet spin dephasing have been recognized previously for organic crystals [18,19].

A different situation is met when the triplet spins belong to a probe possessing axial local symmetry. In such an event, $|\alpha\rangle$ and $|\beta\rangle$ in fig. 1 become degenerate (provided, of course, H_z remains zero) and the triplet state fine structure is characterized by a single zero-field splitting parameter (D) only. Taking $\omega_{\alpha\beta} = 0$, it is immediately apparent from eq. (33) that now the memory function contains non-oscillatory terms expressing the fact that for axially symmetric species secular dipolar couplings exist even at zero field. The property is nicely demonstrated by the spin dephasing behavior in CaO of the F_A center which has C_{4v} local symmetry [20]. For the F_A center, photoexcited into its $^3B_{1u}$ state, the phase memory time was measured to be 30 μs which should be compared with the much different value of 200 μs measured for the F_2^{2+} center in the same crystal. Simulation of the experimental Hahn-echo decay curve for the F_A center using eq. (37)

yields $d_B = 2.0 \times 10^{17}/cm^3$ and $R = 36$ kHz. The good agreement between these values and those obtained from the spin-echo experiments on the F_2^{2+} defects in the same CaO crystals shows indeed that (i) spin–spin coupling with F^+ defects is important for the triplet spin interaction of both the F_A and F_2^{2+} defects, and (ii) the almost order of magnitude difference in the zero-field dephasing rates for the F_2^{2+} and F_A defects is caused by the almost complete quenching of the magnetic moment of the F_2^{2+} center in the triplet state.

3.2. Site-selective homogeneous dephasing

In section 2 it was shown (vide supra eq. (40) and from thereon) that for randomly distributed spins the A-spin dephasing is calculated from a statistical averaging over all relevant B-spin distributions. To simplify the approach the B spins were allowed to occupy any position in a continuous medium assuming an average density, d_B. This view must be handled with care as was very recently demonstrated by us for the photoexcited F_2^{2+} centers in CaO [5]. For this system the spin dephasing rate appeared very sensitive to the wavelength used for optical excitation of the phosphorescent $^3B_1$ state.

From the site-selective homogeneous broadening it was inferred [5] that the mean density (d_B) of the F^+ centers surrounding the probed triplet spins is not very well defined: d_B exhibits some inhomogeneous dispersion. This in turn means that at zero field the F^+-center spin spectrum is inhomogeneously broadened and is comprised of spin packets peaking at $\omega = 0$ but differing in their spectral width (the latter being characteristic of the dipolar interaction among the F^+-center doublet spins within the cluster).

It is noteworthy that for the triplet spins of F_A centers in CaO site-selective dephasing nor thermally induced dephasing could be observed [21]. Apparently, whereas for the F_2^{2+} divacancy centers an appreciable inhomogeneity exists due to density fluctuations of the surrounding F^+ centers, the F_A monovacancy centers are embedded in more homogeneously dispersed F^+ center distributions.

4. Conclusion

For localized electron spin triplet states in solids, phase relaxation due to dipolar spin–spin interactions has been examined. Using a memory function approach, it is possible to separately consider the contributions of the secular and non-secular terms in the dipolar interactions. Generally, at zero field, the triplet electron spin magnetic moment is quenched and it appears that under these conditions the influence of (oscillatory) non-secular terms in the memory function remains (cf. eq. (33) for $z = 0$). The effectiveness of the non-secular terms for dephasing depends on the behavior with time of the B spins that cause the relaxation: only if the B-spin time autocorrelation functions contain Fourier components resonant with the triplet state eigenfrequencies can one expect spin dephasing at zero field. This is the phenomenon of resonant cross-relaxation. Upon the application of a static magnetic field spin dephasing is enhanced because the magnetic field lifts the quenching of the secular spin–spin interactions.

The results are relevant when reviewing the dephasing rates observed recently for photoexcited defects in CaO and MgO. Whereas for photoexcited triplet states localized on non-axially symmetric point defects one typically measures (at 1.2 K) a phase memory time of 150–200 μs, a value of ≈ 30 μs is found for the dephasing time of a triplet state involving a point defect of axial symmetry.

In evaluating the magnetic dipolar interaction in the memory function one has to consider explicitly the spatial distribution of the interacting spins. A homogeneous random distribution of all spins participating in the dephasing process in a continuous medium was assumed for the color center systems. The observations made very recently of site-selective spin dephasing [5] show however that, at least in CaO, the point defects are not homogeneously but inhomogeneously distributed in the crystal.

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