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Coherent transients of localized triplet states in diamond

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Abstract

We report on time-resolved optically detected spin coherent transient measurements for the V–O center, in brown-colored diamond, in its photo-excited triplet state. Observed irreversible spin dephasing and spin diffusion are shown to arise from dynamical magnetic dipolar couplings with randomly distributed N–V centers which are characterized by an electron spin triplet ground state.

1. Introduction

Recently, we have reported optically detected magnetic resonance studies of a few point defects with optically active triplet states in brown-colored natural diamond crystals [1–3]. By means of two-laser hole-burning [4] and optically detected spin-locking [5] experiments one of these defects, the N–V center, has been shown to possess a triplet spin electronic ground state (3A). Optically detected spin coherence studies of the N–V center in its triplet ground state appeared possible because advantage could be taken of a large optically induced spin alignment in the triplet ground state [1]. Elaborate studies of the irreversible spin dephasing [1,2] and spin diffusion of the N–V centers in the triplet ground state have revealed that magnetic dipole–dipole interactions among the N–V centers on the one hand, and between N–V centers and P_1 centers (with $S = \frac{1}{2}$) on the other hand can account for the spin dynamics results.

The other localized triplet state in the brown diamond sample is accessible after photo-excitation

near 365 nm [3]. The triplet state gives rise to a long-living emission which is characterized by a zero-phonon transition peaking at 441 nm (2.818 eV) [6]. From ODMR experiments it has been inferred that the phosphorescent defect is the V–O center, i.e. the analogue of the V–O center in silicon [7]. For the V–O center in diamond, the phosphorescent triplet state has the following spin Hamiltonian parameters: $|D| = 924$ MHz, $|E| = 198$ MHz, and $g = 2.00$ [3]. In addition, it was found that for certain strengths and orientations of an externally applied magnetic field, the phosphorescence intensity of the V–O center exhibits abrupt changes due to cross-relaxation effects [3]. The cross-relaxation appeared to involve the resonant exchange of spin energy with N–V center triplet spins and P_1 -center spins.

Here, we report on optically detected Hahn echo amplitude decay and stimulated echo decay amplitude experiments performed for the diamond V–O center in its photoexcited triplet state. We find that pure dephasing and spin diffusion are present, which both originate in dynamical magnetic dipole–dipole interactions with surrounding electron spin systems.

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2. Experimental

Two brown-colored diamond crystals, samples I and II, were used in the experiments. The N–V center concentration in sample I is approximately ten times higher than in sample II, the latter sample being the same as used previously [3]. The crystal was mounted inside a slow-wave helix immersed in a pumped liquid helium bath ($T = 1.4$ K). Optical excitation was at 364 nm using a CW Ar⁺-ion laser with 200 mW output power. The phosphorescence emitted perpendicular to the excitation pathway was focused on the entrance slit of a Jobin–Yvon HR 1000 grating monochromator; photo-detection was at 490 nm. The ODMR spectrometer used to perform the optically detected spin coherence experiments has been described elsewhere [8]. In the spin coherence experiments, the duration of a π -pulse was typically 150 ns.

3. Results and discussion

Optically detected Hahn echo decays were measured by applying a $\pi/2$ – τ – π – τ – $\pi/2$ pulse sequence at one of the zero-field spin resonance microwave frequencies, while optically exciting the diamond V–O center. The pulse sequence probes irreversible dephasing as the time interval 2τ is scanned. In Fig. 1, the optically detected Hahn echo decay transients of the $|D| + |E|$ transition at 1122 MHz of the V–O center obtained for samples I and II are shown. As can be seen from the figure, the spin echo decay transients are different for the two samples. Fitting the two experimental decays to a monoexponential decay function yielded an estimated phase memory time, T_m , for sample I of 20 μ s and for sample II of 70 μ s. The triplet sublevel lifetimes are of the order of milliseconds [3], whereas the Hahn echo decays are two orders of magnitude faster. Thus in the Hahn echo decay experiment a pure spin dephasing process is probed. Analogous to the results obtained for the N–V center in the same samples, the spin dephasing of the photo-excited V–O center is explained in terms of magnetic dipolar interactions with surrounding electron spins in the crystal. In fact, for the N–V center it could be shown [1,2] that magnetic dipolar inter-

Fig. 1. Optically detected Hahn echo decay transients of the 1122 MHz transition of the V–O center in diamond samples I and II. Drawn curves represent best fits to Eq. (1) with $C = 90$ kHz and $R = 20$ kHz for sample I, and $C = 30$ kHz and $R = 5$ kHz for sample II. Microwave pulses as shown in the inset were applied at a repetition rate of 110 Hz.

actions with nearby N–V centers caused the triplet spins to undergo fluctuations which are optimal when the interacting defects are resonant because then flip-flop processes come into play. Likewise, the flipping N–V center spins will contribute to the random modulation of the resonance frequency of the zero-field triplet spin transitions of the photo-excited V–O center. Taking into account the random spatial distribution of the interacting point defects, one may derive that the triplet spin echo decay varies as [9],

$$S(2\tau) \propto \exp[-C\sqrt{B(\tau)}] \quad (1)$$

with

$$C = d_B [\{8\pi\sqrt{3\pi}/27\} \{z/\sqrt{1+z^2}\} (g_A g_B \mu_B^2)].$$

Here, d_B is the density of spins giving rise to the dephasing, g_A and g_B are the g -factors of spins A (the probe spins) and spins B (the fluctuating N–V center spins), and $z = g_A \mu_B H_1 / |E|$ in which H_1 is the local magnetic field at the site of a probe spin A, produced by the surrounding spins. The function $B(\tau)$ is given by

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

In this expression, R represents the dephasing rate of the N–V center spins. The experimentally obtained Hahn echo decay transients have been computer fitted to Eq. (1) with C and R as parameters of the fit. The best fits (represented by the drawn curves in Fig. 1) yielded the parameter values: $C = 90$ kHz and $R = 20$ kHz for sample I, and $C = 30$ kHz and $R = 5$ kHz for sample II. These results are briefly discussed as follows. Firstly, by means of conventional X-band EPR experiments, it was verified that the N–V center concentration in sample I is larger than that in sample II. It is thus not surprising that the fitting procedure also yields a higher N–V center spin dephasing rate for sample I. Secondly, previous studies of the N–V center spin dephasing in sample I showed that the so-called static secular contribution to the dephasing rate constant is 50 kHz, which should be compared with the value of $R = 20$ kHz mentioned above. Considering the approximations made in the derivation of Eq. (1), it is concluded that satisfactory agreement between the experimental data and the above-mentioned extrapolated values for the N–V center spin dephasing has been obtained, thus confirming the magnetic dipolar mechanism for the V–O center spin dephasing.

By means of optically detected stimulated spin echo decay (SED) measurements we have also investigated spin diffusion on a longer time scale. In the SED experiment $\pi/2 - \tau - \pi/2 - T - \pi/2 - \tau - \pi/2$ microwave pulse sequences were applied at a frequency of 1122 MHz, while T was stepwise increased. As a result, a spectral grating is set up, which sinusoidally modulates the intensity of the inhomogeneously broadened zero-field ODMR transition with a periodicity of $1/\tau$ [1]. During the time T , the grating pattern becomes erased due to relaxation processes. In the event of a spin diffusion process, the SED rate will depend on the grating periodicity, $1/\tau$. In Fig. 2 SED transients as observed for the $|D| + |E|$ transition for various values of τ are shown. Comparison with the population decay rates of the sublevels involved in the ODMR transition ($K_x = 2$ ms⁻¹ and $K_z = 0.043$ ms⁻¹), shows that the SED is on a faster time scale (~ 10 ms⁻¹). Furthermore, the SED kinetics appears to be dependent on τ : as the grat-

Fig. 2. Optically detected stimulated spin echo decay transients as observed for the 1122 MHz transition of the V–O center in sample I, for (a) $\tau = 1$ μ s, (b) $\tau = 3$ μ s and (c) $\tau = 5$ μ s. Drawn curves represent best fits to Eq. (3) with $K_x = 2$ kHz, $K_z = 0.043$ kHz and (a) $R = 3.3$ kHz and $k(\tau) = 0.096$, (b) $R = 3.3$ kHz and $k(\tau) = 1.0$ and (c) $R = 3.3$ kHz and $k(\tau) = 3.24$. The inset shows $\sqrt{k(\tau)}$ as a function of τ . The drawn line is the least-squares fit to the data points and gives a slope of 340 kHz.

ing periodicity, $1/\tau$, increases, the decay rate slows down. The SED results show therefore the presence of spin diffusion. Fitting the SED function to the form [8],

$$I_{se}(T) \propto [\exp(-K_x T) + \exp(-K_z T)] \times \exp\{-k(\tau)[1 - \exp(-RT)]\}, \quad (3)$$

where the first factor between brackets accounts for the population decay out of the sublevels T_x and T_z , respectively, and the exponential factor is related to the diffusion kernel by a cosine Fourier transform. $k(\tau)$ is the rate at which the grating pattern is erased; $k(\tau)$ takes the form $a\tau$ in the case of a Lorentzian diffusion kernel or $b\tau^2$ in the case of a Gaussian diffusion kernel. The drawn curves in Fig. 2 represent the best fittings of the SED transients to Eq. (3). The inset of Fig. 2 shows the plot of $\sqrt{k}$, as obtained from the fittings, against τ . The linear dependence is characteristic of a Gaussian spin diffusion kernel. From the slope a stationary width of the diffusion kernel of $b \approx 340$ kHz is obtained.

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