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Optically detected spin coherence of the diamond N–V centre in its triplet ground state

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Abstract. For the N–V centre in type Ib diamond the optical detection of spin coherence in
the 3A state is reported. The 3A-state lifetime is studied as a function of the light intensity
used for the optical excitation of the N–V centre by means of spin-locking experiments. The
shortening of the lifetime at higher excitation intensities provides evidence for the previously
proposed idea that the 3A state of the N–V centre is the ground state.

1. Introduction

The N–V centre in type Ib diamond consists of a substitutional nitrogen atom adjacent
to a carbon atom vacancy containing one electron (Davies and Hamer 1976, Loubser
and van Wyk 1977, 1978). The defect is produced after radiation damage and annealing
in vacuum of the diamond sample (du Preez 1965). Characteristic of the N–V centre is
a zero-phonon line (ZPL), in the absorption and emission spectrum, at 637 nm. Uniaxial
stress experiments have shown that the 637 nm ZPL originates from an A → E transition
at a trigonal centre (Davies and Hamer 1976). EPR measurements performed under
continuous optical excitation of the diamond crystal have revealed the presence of an
electron spin triplet state of axial symmetry with a zero-field splitting given by |D| =
2.88 GHz (Loubser and van Wyk 1977, 1978). As the lifetime of the radiative E level is
13 ns (Collins et al 1983), it has been suggested that the 637 nm ZPL is an allowed transition
between 1A and 1E states, whereas the EPR signal has been attributed to a metastable
3A state (Loubser and van Wyk 1977, Bloch et al 1985). Persistent spectral hole burning
has also been reported for the N–V centre (Harley et al 1984). Laser irradiation of the
637 nm ZPL was found to produce unusual side-hole patterns in addition to the central
hole. The side holes were proposed to originate in splittings of the excited E state.
Recently, however, two laser hole-burning experiments established the presence of side
holes shifted to the low- and high-energy sides of the central hole by 2.88 GHz (Reddy
et al 1987). The latter results were interpreted as arising from the 3A state and it was
proposed that the 3A state is in fact the N–V ground state. Accordingly, the 637 nm ZPL
was re-assigned as corresponding to a 3A → 3E optical transition. In this paper, we report
on optically detected magnetic resonance (ODMR) and spin-coherence experiments conducted for the N–V centre in zero magnetic field. The experiments allow for a new approach, based on spin-locking techniques, for establishing that the ground state of the N–V centre is indeed a triplet state. In addition, we have been able to perform two- and three-pulse spin-echo decay experiments for the N–V centre in zero field. The results provide us with information on the dynamics in the ground-state triplet system. Spin diffusion is established, possibly being predominantly due to dynamical magnetic dipole–dipole couplings to the electron and nuclear spins of the randomly distributed substitutional nitrogen impurity present in the lattice.

2. Experimental details

The diamond type Ib crystal is the same as used in previous experiments (Reddy et al 1987). The crystal was mounted inside a slow-wave helix immersed in a pumped liquid helium bath at a temperature of 1.3 K. Optical excitation near 450 nm was by means of the filtered light from a 100 W PEK mercury lamp. In the ODMR experiments, the microwave power was amplified using a 20 W travelling-wave-tube amplifier; the microwaves were square waves, amplitude-modulated at 10 Hz. Phase-sensitive lock-in detection of the 637 nm ZPL emission was applied. Spin coherence was optically detected following the probe-pulse method (Breiland et al 1975, Harris and Breiland 1978, Brenner 1982). Details of the spin-echo spectrometer have been described elsewhere (Glasbeek and Hond 1981, Gravesteijn and Glasbeek 1979).

3. Results and discussion

The zero-field ODMR spectrum of the N–V centre is given in figure 1. The transition, peaking near 2.88 GHz, is found to be weakly structured. A similar structure has been observed in high-resolution studies pumping the zero-phonon line, although then the signal has the opposite sign (Harley et al 1984). The structure is presumably associated

![Figure 1](image)

**Figure 1.** The optically detected magnetic resonance spectrum at zero field of the N–V centre in type Ib diamond. The broad-band excitation is peaked near 450 nm. The detection wavelength is at 637 nm. Phase-sensitive detection is at 10 Hz. $T = 1.3$ K.
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Evidence for a coherent coupling of the N–V centre triplet spin system to the $H_1$ component of the driving microwave field was obtained from a transient nutation experiment. In this experiment the ZPL emission intensity at 637 nm is monitored as a function of the duration ($t$) of applied microwave pulses at a repetition rate of 10 Hz. The signal displayed in figure 2 shows the lock-in-detected ZPL emission as $t$ is increased. The damped oscillatory behaviour is indicative of induced spin coherence (Glasbeek 1983). From the periodicity of the damped oscillation it is indicated that, for the microwave power used in the experiments, the Rabi frequency is 3 MHz.

Concerning the question of the spin multiplicity of the ground state of the N–V centre, it is first remarked that in the case where the ground state is a triplet, cw optical excitation of the N–V centre would diminish the ground-state lifetime. On the other hand, in the case where the triplet state is a metastable excited state, its lifetime is not affected by optical excitation of the system from the ground state. Therefore, the method of deciding on the spin multiplicity of the ground state is to measure the triplet-state lifetime as a function of the intensity of the exciting light. It is pointed out, however, that for our purposes the desired information cannot be obtained from optically detected microwave recovery transients—the reason being that following a microwave pulse under conditions of cw optical excitation, the steady-state spin alignment is restored through population decay and feeding processes. Consequently, in the microwave recovery experiments one cannot select out the kinetics solely associated with the spin-level population decay. The influence of the feeding processes on the triplet spin dynamics was eliminated by performing optically detected spin-locking experiments (Slichter 1978, Vreeker et al 1986). In these experiments, an initial $\pi/2$ microwave pulse is...
applied to produce spin coherence in the ensemble of N–V centres in the triplet state. Immediately thereafter, by controlled switching of the phase of the microwave field over 90°, the coherent state vector becomes aligned parallel to the exciting microwave field vector. For this spin-locked state it can be derived (see, e.g., Sleva et al 1986) that interactions that normally contribute to pure dephasing or spin-diffusion effects become (partly) averaged (coherent averaging). As a result, measurement of the relaxation of the locked state provides us with the lifetime of the coherent triplet state.

Experimentally, a π/2–90°–τL–90°–π/2 microwave pulse sequence (at a repetition rate of 10 Hz) for pumping the Tz→Tx, Ty spin transition is applied while continuously optically pumping the N–V centre near 450 nm. The microwave-induced changes in the emission intensity at 637 nm are monitored using phase-sensitive lock-in detection techniques. Note that to probe the residual coherence after a locking time τL, the microwaves are back-shifted in phase with the initial pulse and that the final π/2 pulse serves to convert the residual coherence into an optically detectable population difference between the Tz and T+, Ty sublevels (Harris et al 1973). Figure 3(a) displays the experimental result for the spin-locked signal as τL is scanned. The characteristic decay time is found to be near 1.5 ms. On the other hand, as detailed below, the phase memory time (TM) and the stimulated-echo decay (SED) times turned out to be near 40 μs and about 150 μs, respectively. It follows that the signal in the spin-locking experiments decays on a much longer timescale, and spin locking has indeed been accomplished.

Of great interest are the results obtained when the spin-locking experiment is repeated utilising different intensities of the illuminating light. As illustrated in figure 3(b), we find that the spin-locking decay slows down as the optical excitation intensity is decreased. The decay rate constant appears to be linearly proportional to the optical excitation intensity. Obviously we find that optical pumping of the N–V centre (near 450 nm) causes a depletion of the locked coherence in the triplet system. A major conclusion from the spin-locking experiment is therefore that the N–V centre does possess an electron spin triplet ground state.

We now turn to the results of the optically detected two-pulse and three-pulse spin-echo experiments. Figure 4 shows a typical optically detected Hahn echo decay. The
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Figure 4. The optically detected Hahn echo decay for the N–V centre in the \( ^3A \) state. Microwave pulse cycles of the form \( \pi/2 - \tau - \pi - \tau - \pi/2 \) were applied at a repetition rate of 10 Hz. The microwave frequency is 2880 MHz. \( T = 1.3 \) K. The smooth curve is the exponential fit with \( T_M = 41 \) ps.

signal is obtained by the application of a pulse cycle of the form \( \pi/2 - \tau - \pi - \tau - \pi/2 \), where it is understood that the emission intensity is detected while sweeping the time interval, \( \tau \). The experimental decay was fitted to an exponential (see the smooth curve), yielding a phase memory time \( (T_M) \) of 41 \( \mu s \) at 1.3 K. This value for the N–V centre compares very well with the dephasing times reported previously for a number of F-type defects, in ionic solids, in the triplet state (Glasbeek and Vreeker 1984, Glasbeek and Hond 1981). For the latter, irreversible spin dephasing was shown to arise from magnetic dipolar couplings to flipping spins that are randomly dispersed in the crystal. The data for the N–V centre do not permit further specification as regards the nature of the flipping spins. It is possible that magnetic dipole–dipole couplings between the triplet spins and the electron as well as the nuclear spins of the randomly distributed nitrogen atoms in the diamond lattice are effective here.

Finally, the results of the optically detected stimulated-spin-echo experiments are briefly mentioned. Stimulated spin-echo decays were measured by means of microwave pulse trains of the form \( \pi/2 - \tau - \pi - 2 \tau - \pi/2 \), while sweeping \( T \). The first two pulses introduce a spectral grating (with a periodicity of 1/\( \tau \)) across a part of the inhomogeneously broadened ODMR transition (Mims 1972, Vreeker and Glasbeek 1987). Because of population relaxation and/or spectral diffusion, the grating pattern will become erased. After a time \( T \) has elapsed, the residual ordering is measured as a stimulated echo by means of the final two pulses. Figure 5 shows the observed stimulated-echo decays for different choices of the experimental parameter \( \tau \). The observations are summarised as follows. Firstly, the decay time of the SED signals varies from about 120 \( \mu s \) to 260 \( \mu s \)—i.e., the decays are slower, by at least a factor three, than the Hahn echo decays. This result shows that the irreversible phase relaxation, as probed in the ‘two-pulse’ echo experiment, is not due to population relaxation or spin diffusion and therefore must involve a pure dephasing process, in full agreement with the dipolar coupling mechanism suggested above. Secondly, the decay of the SED signal slows down as the grating periodicity (1/\( \tau \)) increases. This is unambiguous evidence for a spin-diffusion process involving the N–V centre triplet spins. Experiments that study the spectral diffusion behaviour in the presence of an external magnetic field are currently in progress in our laboratories.
In summary, optical detection of spin coherence for the N–V centre in the triplet state has been feasible. Optical excitation of the defect is found to shorten the coherent-state lifetime. The results provide independent support for the previously proposed (Reddy et al 1987) triplet spin character of the ground state of the N–V centre. Furthermore, information on the spin dynamics in the triplet ground state, at 1.3 K, has been obtained from spin-echo and stimulated-echo-decay experiments. The data are representative for spin diffusion that is most probably caused by magnetic dipole–dipole couplings to flipping electron and nuclear spins at nitrogen sites in the crystal.

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