Optical detection of magnetic resonance in the photoexcited triplet state of a deep center in diamond

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From an optically detected magnetic resonance study of the 2.818-eV zero-phonon emission in brown diamond, direct evidence for the existence of a photoexcited phosphorescent triplet state in diamond has been obtained. The emission is attributed to a deep-center triplet state with spin-Hamiltonian parameters $|D|=924\pm2$ MHz, $|E|=198\pm2$ MHz, and $g=2.00$. The magnetic main axes are along [100], [011], and [01$\bar{1}$]. Time-resolved microwave recovery and microwave-induced delayed phosphorescence experiments at 1.4 K yield lifetimes of the radiative sublevels of 0.5 and 1.8 ms, whereas the nonradiative sublevel has a lifetime of 23 ms.

Color centers in solids are extensively studied nowadays, not only because of their intrinsic physical interest,[1,2] but also because of important technological applications, e.g., in materials for solid-state lasers[3,4] and optical data storage.[5] Natural diamond is known to contain a large variety of stable color centers; the optical and magnetic properties of the majority of these centers have been well documented.[6] In recent years studies of diamond color centers have been extended from colorless diamond samples to natural brown diamond crystals.[7] Photoluminescence studies of such crystals by Pereira and Santos[8-10] have shown the existence of many different luminescent centers for which the photoemission extends from the visible blue to the near infrared. Whereas in colorless diamond samples only defects with short-living luminescent states (with lifetimes typically of the order of nanoseconds) seem to be present, in brown diamond crystals several emissive states due to slowly decaying defects with lifetimes as long as milliseconds were found. The slowly decaying emissive states were identified with metastable states that undergo a spin-forbidden radiative decay to the ground state.[8-10] However, unambiguous evidence for the existence of such a spin-forbidden transition has not been given. In this paper we present results of a magnetic resonance study of a diamond color-center system that could be photo-excited into a long-living phosphorescent triplet state. In our experiments we apply optical detection of magnetic resonance (ODMR) to obtain unique information concerning the magnetic fine-structure splittings, the orientation of the magnetic main axes, and the radiative and nonradiative properties of the photoexcited triplet-state sublevels.

The experimental setup for performing the zero- and low-field ODMR experiments has been described in detail elsewhere.[11] Brown-colored diamond was mounted inside a slow-wave helix immersed in a pumped liquid-helium bath. All experiments were performed at 1.4 K. Optical excitation was by means of a cw Ar^+-ion laser, the excitation wavelength being 364 nm. When applying pulsed optical excitation, a XeCl excimer laser pumping a dye laser (*p*-terphenyl as a dye) was used. In the ODMR experiments the applied microwave power was square-wave amplitude modulated at 110 Hz. Phase-sensitive lock-in detection was applied to detect the microwave-induced changes in the emission intensity observed near 490 nm. Magnetic fields were induced by means of a pair of Helmholtz coils, fed by a regulated power supply. Signal averaging of microwave-induced phosphorescence transients was accomplished using a PAR model No. 4202 signal-averaging device.

The color center of concern in this paper has recently been reported by Pereira and Santos[10] and will henceforth be referred to as the 2.818-eV center. The defect is excited at 364 nm and gives rise to a long-living luminescence with a zero-phonon line (ZPL) peaking at 441 nm (2.818 eV). Upon pulsed optical excitation, the emission was found to decay with a characteristic time of about 1 ms. The long emissive lifetime is suggestive of a spin-forbidden transition to the ground state. To explore this further, we undertook zero-field ODMR experiments using microwave-frequency sweeps in the frequency range from 0.1 to 8 GHz. The observed zero-field ODMR spectrum is displayed in Fig. 1(a). The spectrum consists of two narrow transitions, the first peaks at 396 MHz and the second occurs at 1122 MHz, the linewidths [full width at half maximum (FWHM)] being 4.5 and 13 MHz, respectively. The optical spectral dependence of the ODMR signals was examined by scanning the detection wavelength while maintaining the microwave frequency on resonance. The resulting phosphorescence-microwave-double-resonance (PMDR) spectrum is given in Fig. 1(b). The PMDR spectrum is characterized by a narrow ZPL peaking at 441 nm and a weakly structured phonon sideband with a maximum near 500 nm. The PMDR spectrum is identical to the emission spectrum of the 2.818-eV center of Ref.10, showing that the ODMR signals peaking at 396 and 1122 MHz do indeed derive from the emissive state of this defect.

In a small externally applied magnetic field of 150 G, both transitions of Fig. 1(a) are seen to split. For an arbitrary orientation of the crystal with respect to the magnetic-field direction, a maximum number of six lines

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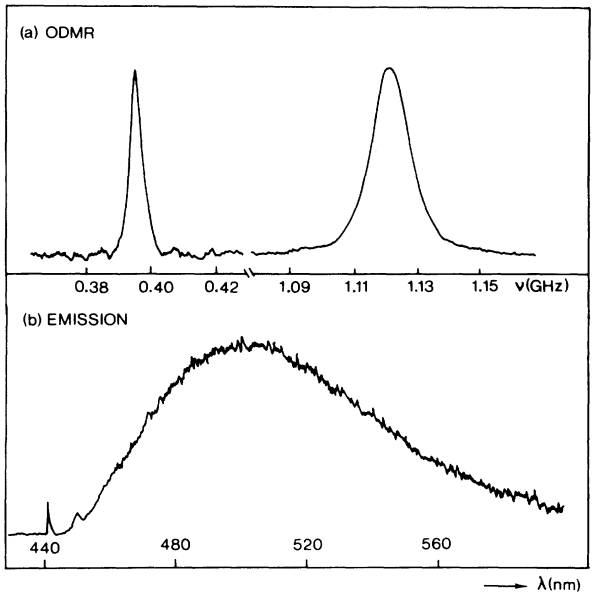

FIG. 1. (a) Zero-field ODMR spectrum as observed for the photoexcited triplet state of the 2.818-eV center in brown diamond at 1.4 K. (b) ODMR intensity as a function of the detection wavelength obtained by phase-sensitive detection of the microwave-induced emission changes of the 1122-MHz transition. cw optical excitation was at 364 nm.

is observed. The magnetic-field dependence and the angular variation of the ODMR peak positions were studied in detail using magnetic-field strengths up to 240 G. For field magnitudes larger than 350 G, the signal-to-noise ratio of the ODMR lines rapidly decreased and ODMR could no longer successfully be observed. The splittings and the shifts as a function of the magnetic-field strength (the field being along the [110] crystallographic axis) of the high-frequency ODMR transition (1122 MHz at zero field) is plotted in Fig. 2(a). In Fig. 2(b) we depict the angular variation of the lines deriving from the 1122-MHz resonance when the crystal is placed in a magnetic field of 175 G and rotated about its [110] axis. An accurate computer fit of the experimental results could be obtained using a spin Hamiltonian of the form

$$\mathcal{H}=g\mu_B\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2)\ , \quad (1)$$

with $S=1$ (characteristic of an electron-spin triplet state), $g=2.00$, $|D|=924\pm2$ MHz, and $|E|=198\pm2$ MHz. The principal axes of the fine-structure tensor were found to be along the [100], [011], and [01$\bar{1}$] directions. The results of the computer simulations are given as drawn lines in Figs. 2(a) and 2(b). Similarly, the influence of the magnetic-field strength and magnetic anisotropy was investigated for the low-frequency transition (396 MHz at zero field). Analysis of the experimental results for this ODMR transition yielded the same spin-Hamiltonian parameters and the same orientation of the main magnetic axes as obtained for the high-frequency transition. A general conclusion of the results is therefore that the defect characterized by a ZPL emission at 441 nm is photoexcited to a phosphorescent triplet state. From the orientation of the spin quantization axes (along [100], [011], and [01$\bar{1}$]), it is furthermore clear that the triplet state belongs to a defect of rhombic I symmetry in Kaplyanskii's notation.[12]

Previously, in the case of the N-V center diamond defect system, zero-, low-, and high-field ODMR data characteristic of a localized triplet state have been measured as well.[13,14] (The N-V center is a nitrogen-carbon vacancy pair defect, the nitrogen impurity being substitutional for a carbon atom.[15]) However, two laser hole-burning[16] and optically detected spin-locking experiments[17,18] proved independently that the probed triplet state of the N-V center is in fact the ground state of the defect. The ODMR results reported in this work for the 2.818-eV defect represent the first magnetic resonance study of a photoexcited triplet state in diamond.

To investigate why the third zero-field transition (anticipated at a frequency of 726 MHz) is missing in the zero-field ODMR spectrum, a detailed study of the populating and depopulating kinetics of the triplet-state sublevels was performed. To this end, time-resolved microwave recovery[19] and microwave-induced delayed phosphorescence (MIDP) (Ref. 20) experiments were conducted. In the microwave recovery experiment a microwave pulse (with a duration of 2 μs) resonant with ei-

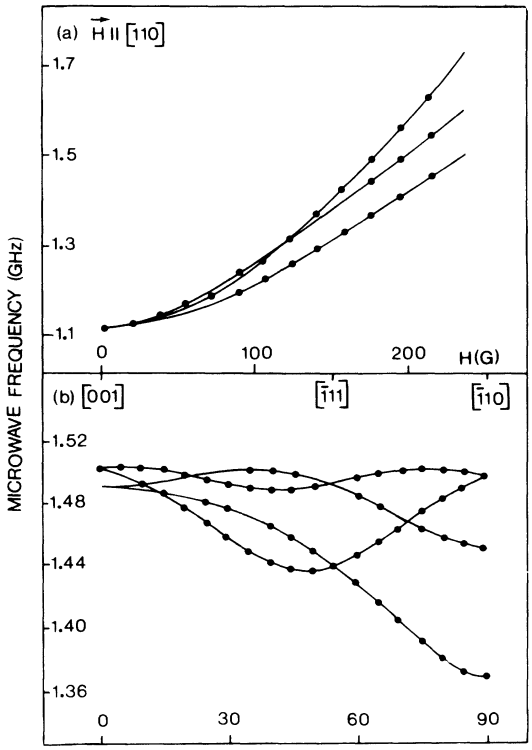

FIG. 2. (a) Magnetic-field dependence of the "high"-frequency ODMR transitions, for a magnetic field applied along a crystallographic [110] direction. (b) Angular dependence of the ODMR peak positions derived from the high-frequency ODMR transitions when a magnetic field of 175 G is rotated in the plane perpendicular to the [110] axis. Dots represent experimental data; drawn curves were computer simulated with $|D|=924$ MHz, $|E|=198$ MHz, and $g=2.00$ for a ⟨110⟩ center.

ther the $2|E|$ transition at 396 MHz or the $|D|+|E|$ transition at 1122 MHz was applied while maintaining the cw optical excitation conditions for populating the triplet state. The subsequent phosphorescence transient, characteristic of the relaxation of the system to steady state, was monitored. The transients observed for both zero-field transitions fitted a biexponential function of the form

$$f(t)=A\exp(-k_1t)+B\exp(-k_2t)\ .$$

The biexponential decay behavior is anticipated when the spin-lattice relaxation is absent. Then, k_1 and k_2 denote the total decay rate constants of the resonantly pumped levels and the ratio A/B is representative of the ratio of the radiative decay constants of the two levels involved.[21] The values for the parameters that yield the best fit to the experimental decay curves are presented in Table I. The T_z level is thus found to be the long-living substate. Also, T_z is almost nonradiative (see the discussion below). Consequently, when the $|D|+|E|$ transition is pulsed, the ensuing phosphorescence transient shows only very weak biexponential behavior since the second term in $f(t)$ becomes relatively small. It was felt therefore that the lifetime of the T_z substate should be determined more accurately by means of a MIDP experiment. In this experiment, the defect was optically excited by means of a laser pulse delivered by the excimer-pumped dye-laser system. At a time t_d following the optical pulse, a microwave pulse at a frequency of 1122 MHz was applied. The amplitude M of the induced phosphorescent transient was determined (see inset, Fig. 3). The experiment was repeated for a series of stepwise increased values of t_d. Figure 3 shows a semilog plot of M as a function of t_d. From the slope of the plotted line it is confirmed that the characteristic decay time of T_z is 23 ms.

The results of Table I show that two levels, the T_x and T_y substates, have decay times an order of magnitude shorter than the lifetime of the longest living sublevel, T_z. From Table I it is also seen that the T_x and T_y levels are most radiative and that the radiative character of the T_z level is less by at least an order of magnitude. It is thus likely that the population decay of the T_x and T_y levels is largely due to radiative decay and that, by contrast, the T_z level decays predominantly radiationless.

Despite the fact that the T_z and T_y sublevels show an appreciable disparity in their radiative character, it appeared impossible to detect the $T_z\leftrightarrow T_y$ zero-field ODMR transition at a frequency of 726 MHz. Consequently, the absence of the latter transition must be due to the presence of equal steady-state populations of the T_z and T_y levels in the optical pumping cycle. (This, in turn, implies that the ratio of the feeding rate constants of these levels equals that for the decay rate constants.) By means of a slightly modified ODMR experiment using pulsed optical excitation, however, it appeared possible to probe optically the $|D|-|E|$ zero-field transition. In such a "gated" ODMR experiment, the microwave pulse is applied with a fixed delay time τ after each optical pulse. During the time interval τ, due to the difference in the decay kinetics of the T_z and T_y levels, a population difference among the level pair will be built up and ODMR becomes observable. Figure 4 displays the experimentally obtained "gated" ODMR signal near 726 MHz as probed for a waiting time of $\tau=6$ ms.

From the fact that the defect is of the rhombic I type (with main axes along [100], [011], and [01$\bar{1}$]), it seems

TABLE I. Lifetimes and relative radiative decay constants of the triplet sublevels of the 2.818-eV center in brown diamond.

Sublevel	τ (ms)	$k_i^{\rm rel}$
T_x	0.5	1.0
T_y	1.8	0.45
T_z	23	<0.01

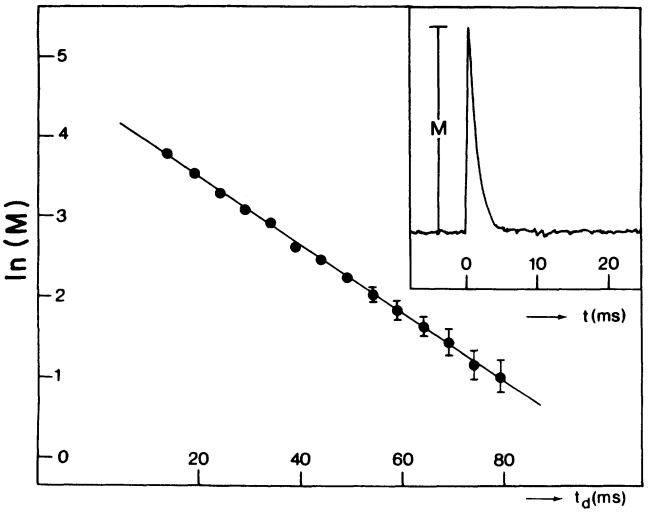

FIG. 3. Semilogarithmic plot of the amplitude M of the microwave-induced phosphorescent transient (inset) vs the delay time t_d. Dots represent experimental values; drawn curve represents the least-squares fit yielding a lifetime of 23 ms for the T_z sublevel.

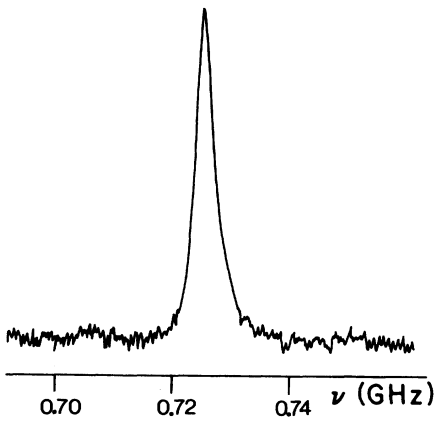

FIG. 4. Gated ODMR spectrum showing the $|D|-|E|$ zero-field transition at 726 MHz of the 2.818-eV defect in the triplet state. Microwave pulses (of 2-ms duration) were applied with a fixed delay time of 6 ms after each optical pulse.

likely that the defect structure involves impurity atoms and/or vacancies occupying at least three neighboring carbon sites coplanar in the (110) plane. The lack of hyperfine structure precludes that nitrogen, the dominant impurity in most diamond crystals,[6] is involved in the defect structure. The relatively long triplet-state sublevel lifetimes of the order of milliseconds and a value of almost exactly 2 for the g factor are typical for small spin-orbit couplings within the defect. A deep center involving a transition-metal impurity is therefore not likely. Possibly, the defect may comprise impurity oxygen atoms substitutional for carbon, as, for instance, in the O-C-O defect center in the (110) plane. Currently, optically detected spin coherence and optically detected Stark experiments, analogous to those for the N-V center,[22] are in progress to obtain more detailed information on the 2.818-eV defect.

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