Spin Dynamics and Electronic States of N-*V* Centers in Diamond by EPR and Four-Wave-Mixing Spectroscopy

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We applied a new phase-modulation technique for nonlinear laser spectroscopy with sub-Hz relative resolving power to measure fundamental relaxation processes of the N-*V* center in diamond. Complementary EPR experiments versus temperature establish the ground-state spin character in the absence of optical illumination and show that spin-lattice decay occurs via two-phonon processes involving the dominant vibrational mode. The combined results permit deduction of reliable fine-structure assignments for three states of the center and accurate values for zero-field intersystem crossing and spin-lattice relaxation rates from linewidths of individual resonances in the four-wave-mixing spectrum.

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Nearly degenerate four-wave-mixing (NDFWM) spectroscopy with 1-Hz resolution based on acousto-optic frequency-modulation techniques has previously been applied to frequency-domain measurements of slow relaxation processes in impurity-doped solids [1] and point-defect systems [2]. This coherent spectroscopy has proven very useful for precise measurements of decay processes too slow for effective signal averaging in real time. Here we introduce a new optical technique for the performance of NDFWM with much higher resolution (10 mHz), and apply it in concert with double-cavity EPR experiments to resolve the controversy over the energy-level scheme of the N-*V* center in diamond and to study system dynamics. We provide evidence for a hypothesized metastable state and demonstrate that precise measurements of intersystem crossing and spin-lattice relaxation rates can be obtained from linewidth measurements of individual, ultranarrow resonances in the four-wave-mixing spectrum recorded with sub-Hz resolution.

The N-*V* center is a product of irradiation and annealing processes in diamond crystals containing nitrogen [3] and exhibits a zero-phonon line at 637 nm assigned by uniaxial stress measurements [4] to an $A \rightarrow E$ electric-dipole transition at a site of trigonal symmetry. It consists of substitutional-nitrogen–vacancy pairs oriented along equivalent (111) directions, and exhibits triplet spin resonance which was first attributed to a metastable excited state [5] because it required optical illumination in the N-*V* absorption band. This conclusion and even the existence of a metastable state was challenged recently in a series of papers reporting hole burning [6], optically detected magnetic resonance [7], and Raman heterodyne experiments [8], which indirectly suggested that the triplet state occurs in the ground-state manifold rather than the metastable manifold. However, these experiments were performed with optical illumination of the centers, and are consistent with alternative explanations based either on absorption at 637 nm by a metastable excited triplet population or on a third possible energy-level structure of the center. To examine these possibilities, the current work was undertaken to determine fine-structure assignments directly from simple Curie-law behavior of the susceptibility in unilluminated samples, and to apply NDFWM spectroscopy to measure electronic and spin decay processes from linewidths of frequency-domain NDFWM resonances.

Three possible energy-level schemes for the N-*V* color center are shown in Fig. 1. Figures 1(a) and 1(b) show diagrams considered in earlier work [5,6]. The chief difference between them lies in their assignments of triplet spin character to the excited- and ground-state manifolds, respectively. Loubser and van Wyk [5] did not report N-*V* EPR signals in unilluminated samples and concluded from strong, slowly decaying signals in illuminated samples that their signals originated from a metastable triplet level, as in Fig. 1(a). This conclusion cannot explain the strong EPR signal that we have observed in complete darkness in samples with large enough N-*V* concentrations, shown in Fig. 2. The EPR spectrum also exhibited spin polarization in the illuminated samples, indicating optical pumping between the spin sublevels of the triplet (see upper trace Fig. 2). More recently, Reddy, Manson, and Krausz [6] attributed the asymmetry of the strength of antiholes observed in the optical hole-burning spectrum to this pumping process. However, the structure of the hole-burning spectrum and the temperature dependence of magnetic circular dichroism signals were consistent with a ground-state triplet [Fig. 1(b)].

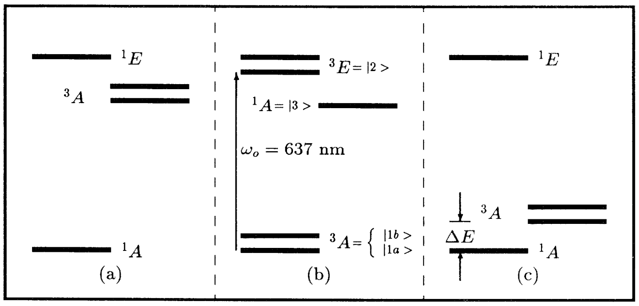

FIG. 1. Possible energy level schemes of the N-*V* center in diamond.

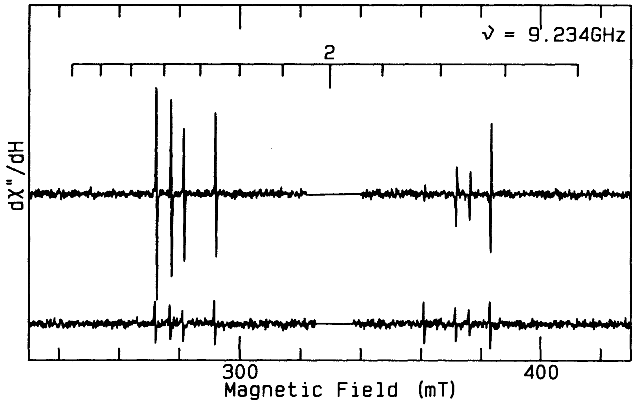

FIG. 2. Room-temperature electron-paramagnetic-resonance signals of the N-*V* center in a sample containing approximately 220-ppm N-*V* centers: lower trace, in complete darkness; upper trace, with illumination in the absorption band of the N-*V* center ($\lambda = 632.8$ nm). In both traces, the large signal due to single substitutional nitrogen atoms at $g = 2.0023$ has been omitted for clarity. Phase reversal of high-field lines occurs upon illumination.

Additional work [7,8] was also consistent with this assignment, but was performed with continuous optical illumination which could have sustained a sizable population in a metastable excited state having an overlapping absorption spectrum. Alternatively, an energy-level scheme like that of Fig. 1(c), with a small ΔE to permit substantial thermal population of the metastable manifold at accessible temperatures could also account for their observations. Consequently, we performed additional experiments to obtain direct evidence of the correct state assignments, intersystem crossing rates, and spin dynamics.

For NDFWM measurements we used high-quality synthetic single crystals with dimensions of $3.5 \times 3.5 \times 1.75$ mm^3 containing 220-ppm substitutional nitrogen atoms. The crystals were irradiated with 1.7-MeV electrons and heated to 820 °C for 4 h in argon. For a dosage of $1.94 \times 10^{18} e^-/\mathrm{cm}^2$, 20% conversion of nitrogen to N-*V* centers was attained for an optical density at 637 nm of 0.25 at room temperature. This corresponds to the "thin sample" regime ($\alpha L < 1$). Samples were subjected to three beams from a DCM [9] single-mode, cw dye laser: two counterpropagating pump waves of identical frequency along the [100] direction and a third tunable probe wave, incident at an angle of 0.5° in the sample relative to the forward pump. Tunability on the sub-Hz scale at a center wavelength of 637 nm was achieved by applying a variable-slope, linear ramp voltage to the phase-modulation input of the frequency synthesizer driving the acousto-optic modulator which controlled the probe frequency. The intensity of the phase-conjugate backward wave was then recorded as a function of detuning. Under these conditions, ultranarrow resonances due to the slow recovery of the ground-state population can be observed in multilevel systems with metastable states [10]. The detailed resonant response may be calculated from the quantum-mechanical Liouville equation by third-order perturbation theory [10], and for the scheme of Fig. 1(b) yields the following polarization:

$$\mathbf{P}^{\mathrm{nl}} = \left(\frac{1}{2\hbar}\right)^3 \rho_{11}^{(0)} |\tilde{\mu}|^4 \left\{ \frac{A}{\gamma_3 + i\delta} + \frac{B}{\gamma_2 + i\delta} + \frac{C}{\gamma_{1b,1a} + i\delta} \right\} \tilde{E}_f \tilde{E}_b \tilde{E}^*_{\mathrm{pr}} e^{i(2\omega_p - \omega_{\mathrm{pr}})t} + \mathrm{c.c.} \qquad (1)$$

Here *A*, *B*, and *C* are constants, the laser frequency detuning is $\Delta = \omega_0 - \omega$, the rate of relaxation out of level *i* is γ_i, and we have assumed $\gamma_{21} \gg \gamma_{31}, \gamma_{23}$. Excited-state triplet structure is ignored because of the rapid *E*-state population decay [11]. Zero-field triplet sublevels of the ground state have been designated by indices *a* and *b*, with *b* being the doubly degenerate level. From this expression it can be seen that the theoretical NDFWM spectrum is expected to consist of additive resonances with Lorentzian line shapes furnishing intersystem crossing, excited-state, and spin-lattice relaxation rates γ_3, γ_2, and $\gamma_{1a,1b}$ directly.

The observed spectrum is presented in Fig. 3(a), where the insets show wide scans over 2 kHz and the main figure shows the high resolution obtained using phase modulation. Individual data points in the latter are separated by 200-mHz steps over a 10-Hz range. The spectrum consists of an extremely narrow spike of width 1.2 Hz on top of a broader resonance of width 272 Hz at 80 K. Thus two resonances, corresponding to two distinct relaxation processes with rates of $\gamma_3 = 0.61$ s^{-1} and $\gamma_{1b,1a} = 136$ s^{-1}, as determined by Lorentzian best fits, are observed in this system. The fact that this spectrum is indeed due to the N-*V* center is confirmed by its excitation spectrum [Fig. 3(b)] which exhibits the N-*V* zero-phonon resonance at 637 nm.

Assignment of these decay measurements to internal processes of the N-*V* center requires firm evidence of the energy-level structure. To provide correct assignments, we undertook measurements of EPR temperature dependence in unilluminated samples. These measurements have not previously been reported for the N-*V* center because of weak signals in the absence of light and the extremely low saturation intensity of this center at low temperatures. The experiment is further complicated by the necessity of comparing the signal strength to a fixed reference in a dual-cavity configuration. Our measurements were all carefully verified to be unsaturated in complete darkness throughout the temperature range 100–500 K and revealed the behavior displayed in Fig. 4(a). A second, separate set of decay measurements, in which the disappearance of optically enhanced signals was observed after blocking illumination, is shown in Fig. 4(b).

The EPR measurements clearly establish in the most

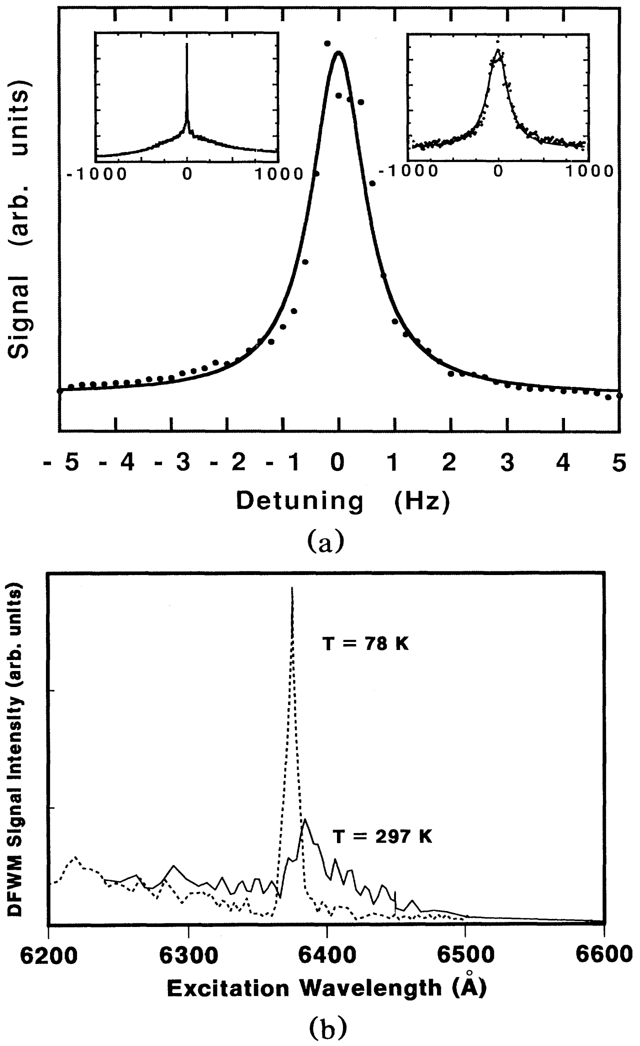

FIG. 3. The NDFWM spectrum of the N-*V* center in diamond. (a) The main figure shows the central detuning region covering a range of 10 Hz, obtained using a novel phase-modulation technique. The left inset covers a detuning range of 2 kHz, revealing a broad resonance topped with a spike at zero detuning. The right inset shows a low-intensity scan of the wide component obtained by intermodulation chopping which eliminates the narrow central feature. (b) The four-wave-mixing excitation spectrum, showing NDFWM response in the region of the N-*V* center zero-phonon transition at 637 nm.

direct way possible that the spin triplet occurs in the ground state. Curie-law behavior of the susceptibility is observed at all temperatures in the experiment below 500 K, ruling out all but a metastable triplet state with $\Delta E < 8.6$ meV, a maximum energy splitting which is much smaller than even the dominant phonon energy (67 meV) of the N-*V* center. Consequently we take this as good, direct evidence of a ground-state triplet. The *E* state must also be of triplet character in view of the spin selection rule for allowed optical transitions. The metastable state is taken to be a singlet in view of its slow decay. Notice, however, that the EPR measurements have no bearing on the existence, location, or decay of a singlet metastable level.

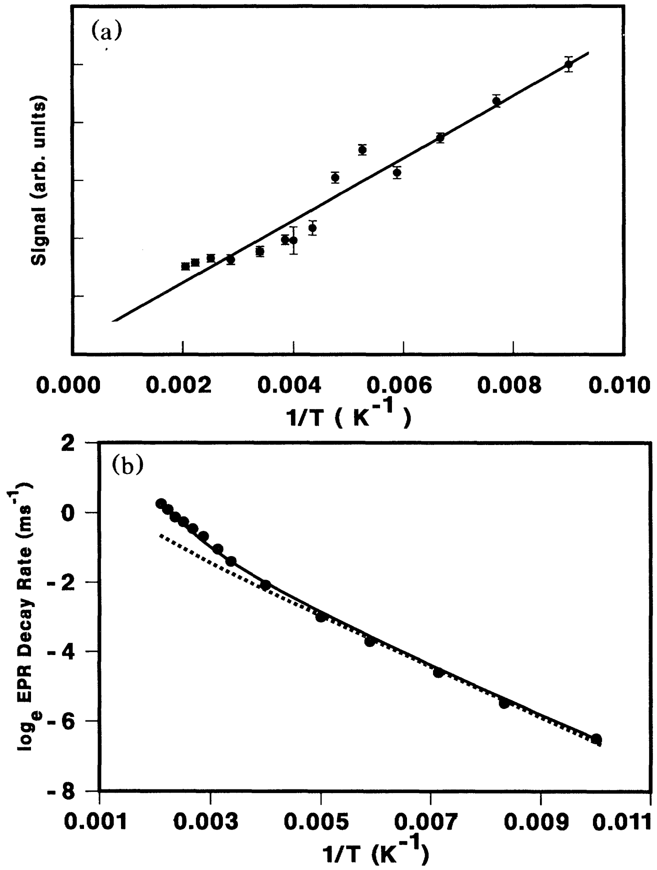

FIG. 4. (a) Electron-paramagnetic-resonance signal strength as a function of inverse temperature in complete darkness. Measurements at each temperature were compared to a Varian Associates strong pitch reference (No. 06226-A) in a dual-cavity configuration and were verified to be unsaturated. Error bars reflect signal-to-noise ratio alone. (b) Temperature dependence of single exponential decay constants of the EPR signal observed by blocking optical illumination. The size of the data points is indicative of experimental uncertainties.

There are only three possible relaxation processes into the triplet ground state: radiative decay from the *E* state, decay from the hypothesized metastable ^1A state, and spin-lattice relaxation. The fast decay time (13.3 ns) of the ^3E state [11] corresponds to an NDFWM resonance of width 23.9 MHz, which is much wider than the kHz scale of our experiments. This contributes only to background levels. Hence it remains to assign the two NDFWM resonances of Fig. 3 to electronic state decay and spin dynamics. EPR saturation data, not shown here for brevity, provide an upper limit for the spin-lattice relaxation time when the value $T_2 = 1/g\beta\Delta H_{1/2}$ is inserted into the power-broadening formula. At room temperature, a value of $T_1 < 40$ ms is obtained in this way, clearly identifying the broad NDFWM resonance as originating from spin-lattice relaxation with $T_1 = (2\pi\gamma_{1b,1a})^{-1} = 1.170 \pm 0.003$ ms and the narrower resonance revealing intersystem crossing from a metastable ^1A state with a crossing time $\tau_{IC} = (2\pi\gamma_3)^{-1} = 265.3 \pm 0.6$ ms. The mechanism of spin-lattice relaxation in the ground state was revealed by the temperature dependence of the decay of the optically enhanced EPR signal, shown in Fig. 4(b). The low-temperature behavior follows the exponential behavior characteristic of a two-phonon Orbach process [12]. A best fit by a dependence of the form

$$\frac{1}{T_1} \propto \frac{R_0 \Delta^3}{\exp(\Delta/k_B T) - 1} \tag{2}$$

yields an activation energy $\Delta = 62.2 \pm 0.1$ meV, in close agreement with the energy of the dominant phonon of the N-V center, namely, 63 meV at liquid-nitrogen temperature [4,13]. Above room temperature, a T^5 dependence begins to dominate in a fashion consistent with a second-order Raman process [14].

In summary, new direct evidence from the Curie-law behavior of the EPR of the N-V center indicates that the ground state of this center is a triplet [see Fig. 1(b)], in agreement with recent proposals. The resulting fine-structure designations for the lowest three energy levels of the center have permitted definite assignments in the present work of accurate, zero-field relaxation rates measured using a new method of NDFWM spectroscopy. Spin-lattice relaxation occurs at a rate $\gamma_{1b,1a} = 136$ s^{-1} by a two-phonon process at low temperatures. The existence of a metastable ^1A state is confirmed by the presence of an ultranarrow Lorentizian-shaped resonance in the NDFWM spectrum, with a corresponding decay time of $\tau = 265$ ms, or an intersystem crossing rate of $\gamma_{IC} = \gamma_3 = 0.61$ s^{-1}.

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