Origin of persistent hole burning of N–V centers in diamond

D. Redman,* S. Brown, and S. C. Rand

Division of Applied Physics, University of Michigan, Ann Arbor, Michigan 48109-2122

Received October 16, 1991

New satellite features and antiholes in the persistent hole-burning spectrum of N–V centers in diamond, as well as their dependences on applied electric fields and frequency within the inhomogeneous absorption line, are reported. These results, together with reassignments of spin states of this center, permit an understanding of the origin of the satellite holes as well as of possible mechanisms for the persistent hole-burning phenomenon itself. In addition we report narrow optical interference fringes in heterodyne-detected spectra of persistent spectral holes in the N–V defect center in diamond and discuss a recent suggestion for high-resolution Ramsey-fringe hole-burning spectroscopy of solids based on phase-separated fields.

INTRODUCTION

Persistent hole burning in diamond was first reported by Harley *et al.*[1] in 1984 at wavelengths corresponding to zero-phonon resonances of several simple point defects, namely, the N3, H4, N–V, and GR1 centers. Detailed measurements reported for the GR1 and N–V centers are readily accessible to study by tunable laser sources, and in the inhomogeneous profile of the absorption transition these authors observed spectra holes exhibiting lifetimes greater than 15 min at liquid-helium temperatures. Evidence was presented that a multiphoton mechanism may be responsible for the persistent hole burning within the GR1 center. However, the mechanism for the N–V center was not identified, and the presence of satellite features in the spectrum of this center was particularly puzzling in light of an earlier assignment of spin singlet characters to the ground and the excited states by Loubser and Van Wyk.[2] The presence of side holes in the N–V spectrum was conjectured to be due to a dynamic Jahn–Teller effect in the excited state.

Since the appearance of Ref. 1 evidence has accumulated that the ground and the excited states of the N–V center responsible for the 637-nm resonance are not singlet in character at all. In a series of papers Manson and co-workers[3–7] presented experimental measurements of magnetic circular dichroism, transient hole burning, and optically detected paramagnetic resonance, all of which are consistent with the existence of a triplet ground state. These authors therefore proposed a new electronic model of the center. To eliminate all doubt regarding spin assignments, Redman *et al.*[8] recently performed extensive paramagnetic resonance measurements versus temperature in complete darkness to provide independent evidence of triplet spin splitting in the ground state. Redman *et al.* also furnished accurate measurements of fundamental decay times and relaxation processes within the center through four-wave mixing[8] and two-beam coupling[9] experiments.

Here we reconsider the persistent hole-burning spectrum of the N–V center, confirm the presence of satellites, report previously unobserved lines, and discuss their origin. We examine the frequency dependence of the spectrum and the effect of applied electric fields. We remark on the prominence of satellites originating from excited-state spin transitions. We then present an interpretation of these new findings that is consistent with the reassigned electronic structure of the N–V center.[8]

We have also investigated a recent proposal for subnatural linewidth spectroscopy in solids that is based on the concept of separated fields, introduced originally by Ramsey[10] and extended to optical frequencies by several groups.[11–14] Ramsey's method furnishes resolving power in excess of the usual spectroscopic limit imposed by the natural linewidth, and fields separated in space or in time (pulses) have successfully been exploited in the past to improve line-center determinations in gas-phase spectroscopy. However, neither time nor space separation techniques have been applied previously to solid-state spectroscopy. This is undoubtedly because, first, cw rather than pulsed excitation is preferable for high resolution and, second, atoms in solids are not free to move between spatially separated fields.

Extension of separated-field methodology to the study of solids would be highly useful for subnatural linewidth spectroscopy of field-induced electronic splittings of optical centers. It would enable Stark and Zeeman spectroscopy to be performed in extremely small external fields by using hole-burning or four-wave mixing techniques, for example. In diamond it would greatly facilitate the determination of physical and electronic structures of defects. Hence the report by Saikin *et al.*[15] of Ramsey fringes in heterodyne-detected hole-burning spectra, obtained with intersecting cw beams differing only in path length to the sample, bears further investigation. These authors recognized that their experimental approach might permit high-resolution spectroscopy and increased storage density in frequency-domain optical memories.[16]

Here we report observations with a heterodyne-detection scheme employing phase-delayed cw laser beams, or phase-separated fields, similar to that of Ref. 15. With phase-separated fields and heterodyne detection, coherent oscillations are indeed shown to appear in the persistent hole-burning spectrum, with a period determined by the total phase difference between incident cw beams. Fringe spacings of much less than the homogeneous linewidth are readily achieved. We have carefully investigated whether phase-delay information is stored in the

0740-3224/92/050768-07$05.00

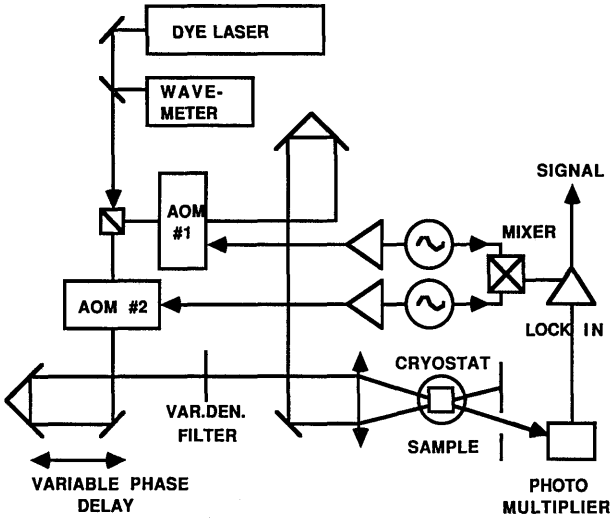

Fig. 1. Experimental apparatus for hole-burning spectroscopy. Conventional readout is obtained by blocking the beam from one acousto-optic modulator (AOM#1) during the read cycle, whereas for heterodyne detection both beams impinge upon the sample during readout.

persistent grating itself and whether the oscillations originate from the four-wave mixing interaction that is necessary for genuine Ramsey fringes.

EXPERIMENTS

Our experiments were performed in a series of single synthetic diamond crystals from Sumitomo Electric Company with varying (relatively high) concentrations of N–V color centers. The N–V defect consists of a substitutional nitrogen atom with a nearest-neighbor vacancy in the carbon host crystal[17] and can be produced by using electron irradiation and subsequent annealing.[18] To ensure an optimum signal in the linear regime, we performed most of our observations using a single sample with an attenuation–length product close to but less than unity ($\alpha L = 0.3$ at 637 nm). This sample was prepared from a high-pressure-grown type Ib crystal (220 parts in 10^6 nitrogen) of dimensions 1.75 mm × 3.5 mm × 3.5 mm by irradiation at 1.7 MeV with a dose of 5×10^{17} cm^{-2} electrons. Subsequent annealing at 820°C for 4 h in argon was used to aggregate nitrogen impurities with vacancies created during the irradiation. This resulted in a density of N–V centers of 7.7×10^{18} cm^{-3}, a value determined directly from resolved electron paramagnetic resonance traces of N–V and substitutional nitrogen resonances. The sample was mounted with its 001 face perpendicular to the bisector of the incident light beams on the cold finger of an open-cycle liquid-helium cryostat.

Hole-burning spectroscopy of the N–V color center in diamond was performed by using a tunable, cw DCM ring dye laser, locked with 250-kHz rms linewidth to an external cavity. The optical setup is shown in Fig. 1. A beam splitter was used to produce two phase-correlated beams, and acousto-optic modulators driven by phase-locked synthesizers provided convenient control of writing and reading offset frequencies. In this way the relative frequency of the light beams was electronically programmable to within <1 Hz.[8] An optical delay line was inserted into one arm to permit relative phase delays of 0–250 cm for heterodyne experiments. The two incident beams were combined at an external angle of 3° at the sample.

Spectral holes were burned at liquid-helium temperatures at 637.2 nm, the wavelength of the zero-phonon transition of the N–V center. A typical single writing cycle consisted of exposure of the sample to incident beams of 10 μW each for 1 s. This exposure was sufficient to create single, satellite-free, homogeneously broadened holes exhibiting up to 40% reduction of the linear absorption at the laser frequency. Holes persisted in darkness with less than 10% erasure for an hour but could be erased rapidly by strong illumination with laser light scanned over a 30-GHz frequency interval about the hole or by heating to 80 K.

Detection of hole spectra was performed by two methods. In the first the intensity of one of the incident beams was reduced by a factor of 100 and its transmission (or induced fluorescence) was recorded as a function of frequency. In the second method probe light diffracted by the persistent grating was combined with light transmitted through the sample from the second beam, and their beat signal was recorded by a square-law detector. In the latter heterodyne mode a deliberate offset frequency of 20 kHz was imposed on one read beam to permit convenient detection of the beat signal with a low-frequency lock-in amplifier. In this way either conventional hole-burning or heterodyne-detected spectra could be recorded. All results were independent of the offset frequency.

The reference frequency for phase-sensitive detection during heterodyne experiments was furnished by combining the offset rf oscillator signals in a double-balanced mixer. The intensity of the probe heterodyne signal was then recorded versus the laser frequency over a 5-GHz spectral region centered on the writing-beam frequency. In general signal averaging was not effective for heterodyne experiments. Successive read operations exhibited systematic drifts of the recorded phase of the oscillation pattern, causing degradation with as few as five accumulated spectra. Hence all heterodyne spectra were recorded in a single pass.

For improved signal-to-noise ratios in satellite spectra, reading and writing cycles were repeated every 2 s in a refresh mode. In this approach holes written during an initial 1-s exposure and probed after a delay interval of 1 s (longer than the known relaxation times of the N–V center[8,9]) were reburned before each read cycle. This avoided excess broadening by long exposure times and erasure by multiple read operations while ensuring that transient hole-burning contributed negligibly to the measured spectrum.

RESULTS AND DISCUSSION

The principal results of this work are presented in Figs. 2–6 below. Persistent spectral holes were written and probed at various positions within the zero-phonon line. Conventional readout techniques at 637.2 nm yielded single hole spectra with intensity- and electric-field-dependent linewidths. Heterodyne-detected scans of the same holes revealed oscillatory responses within the envelopes of spectral holes measured by the pump–probe method. A direct comparison between resolutions for

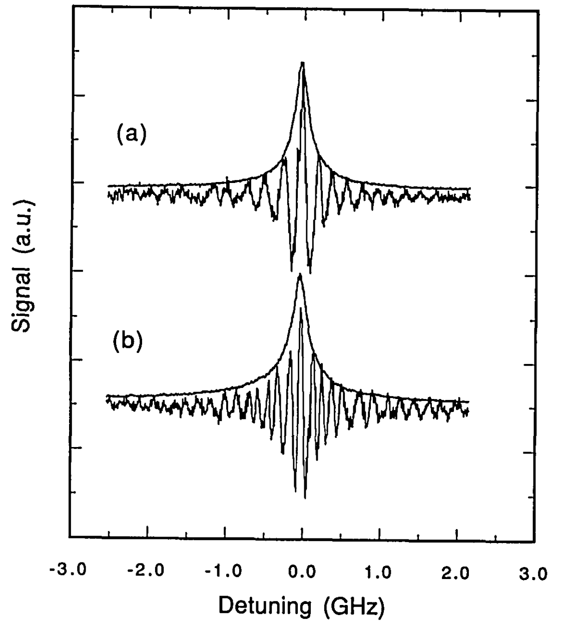

Fig. 2. Persistent hole spectra recorded at $T = 6.5$ K and $\lambda = 637.2$ nm by using conventional readout (smooth upper traces) and heterodyne detection of phase-separated fields. Phase delays are different in the two heterodyne scans, corresponding to pump–probe path-length differences of (a) $\Delta = 130$ cm and (b) $\Delta = 205$ cm.

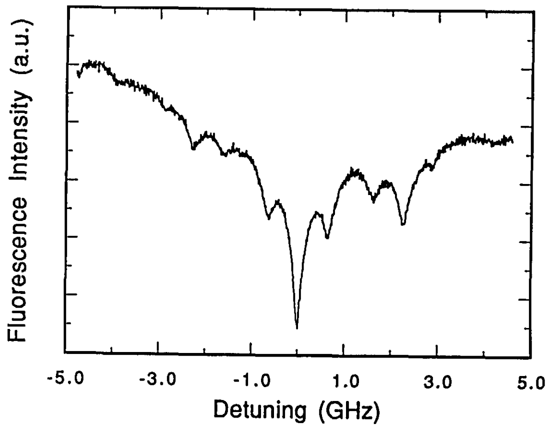

Fig. 3. Persistent hole spectrum recorded by using fluorescence detection at $T = 6.5$ K and $\lambda = 637.87$ nm.

conventional and heterodyne detections was therefore possible. At wavelengths longer than 637.2 nm a well-defined satellite structure was observed.

Conventional Hole-Burning

The smooth upper curves of Figs. 2(a) and 2(b) reveal single, persistent holes burned at a wavelength of 637.2 nm by using the conventional pump–probe method. At 6.5 K and microwatt power levels observed linewidths were typically in the range 0.1–0.5 GHz, several times that expected on the basis of the excited-state decay time[9,19] of 13.3 ns alone (FWHM = 48 MHz for holes). Below 8 K measured linewidths showed little variation with temperature. Linewidths attainable in this low-power, low-temperature limit were still intensity dependent. Also, they exhibited a curious minimum at 637.2 nm, near the center of the line. On the basis of this sensitivity to power, the unusual wavelength dependence, and observations of electric-field responses of spectral holes described below, this extra linewidth was ascribed to power broadening of a partly inhomogeneous distribution of burned centers.

Using the refreshing technique for repeated burning and reading of holes at a wavelength of 637.5 nm, we obtained the spectrum of Fig. 3. It shows satellite structure shifted from the laser burn frequency by a few gigahertz. This spectrum reproduces three pairs of peaks originally reported[1] at splittings of 0.63, 1.59, and 2.23 GHz. The temperature dependence of the spectrum is given in Fig. 4. Peak positions measured from our spectra are 0.65 ± 0.04, 1.61 ± 0.04, and 2.28 ± 0.01 GHz. New pairs of satellites are observed at 2.88 ± 0.01 GHz and (weakly, but reproducibly) at 3.94 ± 0.02 GHz. The 2.88-GHz splitting corresponds exactly to the zero-field spin splitting of the ^3A ground state.[3,8] Evidently this feature arises from centers that preserve spin orientation during excitation but relax from the excited state to the ground state by a spin-forbidden transition. Centers responsible for this feature effectively undergo a ground-state spin transition as the result of optical excitation.

Additional features of the persistent hole spectrum in Fig. 3 can be similarly explained on the basis of an assigned spin sublevel splitting of 0.65 GHz in the excited state. Spectral holes at frequency shifts of $A = 2.88$ GHz, $B = 0.65$ GHz, and $A - B = 2.28$ GHz match within experimental error those expected from a system with ground- and excited-state level splittings of $A = 2.88$ GHz and $B = 0.65$ GHz, respectively, assuming finite branching ratios on all transitions. This model is shown explicitly in Fig. 5, where optical pumping is presumed to have resulted in persistent depletion of the populations of four basic types of center, all resonant with the original burn frequency. During subsequent probing the absorptive transitions of these centers should show persistent holes at all their absorption frequencies: ω_0, $\omega_0 \pm A$, $\omega_0 \pm B$, $\omega_0 \pm (A - B)$, and $\omega_0 \pm (A + B)$. Holes appear at all these frequencies in Fig. 3 except $\omega_0 \pm (A + B)$. Holes at these splittings were presumably too weak to be observed.

The weak features at ±1.61 GHz and ±3.94 GHz are also consistent with these level splittings. They correspond to frequency shifts of $\pm(A - 2B)$ and $\pm(A + 2B)$, respectively. While shifts at these combination frequen-

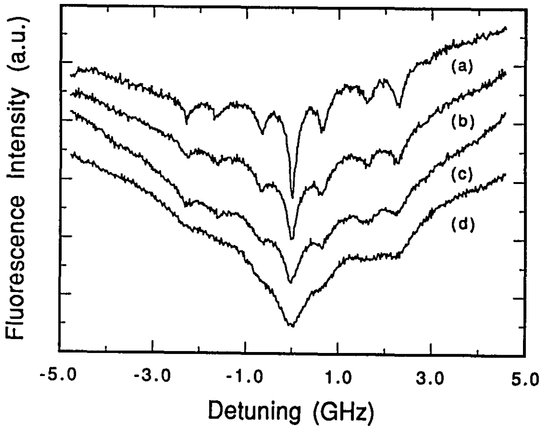

Fig. 4. Persistent hole spectra recorded at various temperatures by using fluorescence detection: (a) 6.4 K, (b) 9.8 K, (c) 12.2 K, (d) 15.4 K.

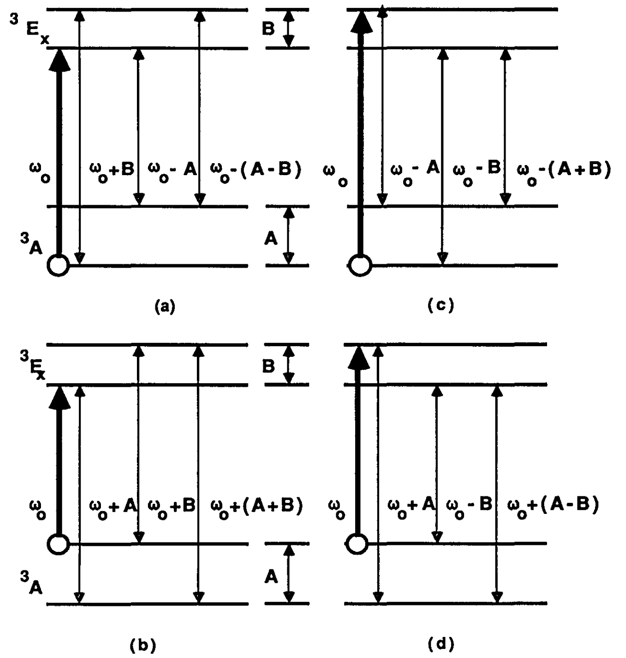

Fig. 5. Origin of satellite holes in the persistent hole-burning spectrum. In (a) the thick arrow indicates resonant excitation during the burn cycle between the lowest sublevels of the ^3A and ^3E states for one group of centers within the inhomogeneous distribution of the N–V center. The open circle represents the consequent population depletion of centers of this type. (b)–(d) show similar excitation of the three remaining classes of center that are simultaneously resonant with the laser frequency ω_0 during burning. The lighter arrows are labeled to show all possible absorption transitions of depleted centers in the vicinity of the central hole at ω_0.

cies can be explained without an appeal to additional level splittings, holes at these transition frequencies are not expected from the simple picture of depleted absorption given in Fig. 5. Consequently their origin is not completely understood.

In spectra recorded at wavelengths longer than 637.2 nm all satellites appeared as holes rather than as a mixture of holes and antiholes as in transient hole burning.[3] The satellite features are somewhat asymmetric in intensity about zero detuning, indicating a preference in relaxation to the lower ^3A ground-state component, just as for transient hole burning. The satellite features are not equally prominent. Lines occurring at ±0.65 GHz and ±2.28 GHz are dominant. These lines correspond to transitions involving a single excited-state transition, whereas the position of the weaker line at 1.61 GHz may be explained as the result of a ground-state transition in combination with two excited-state spin transitions. The hole at 2.88 GHz is quite weak, in sharp contrast to the case of transient hole burning, and was not observed at all in earlier experiments.[1] While its shift is consistent with a single ground-state transition, its low intensity suggests that it too may arise instead from a process involving two excited spin transitions, one down and one up.

The visibility of satellites depended strongly on wavelength. This result is shown in Fig. 6 by a sequence of spectra recorded at different positions within the zero-phonon line of the N–V center. It can be seen that the most prominent satellite data was obtained at wavelengths to the red side of the line center. No satellites were observed at all on the blue side, and satellite splittings were nearly independent of wavelength. The largest observed variation of a splitting was a 9% increase for the ±0.65 GHz holes between the wavelengths 638.23 and 637.54 nm. This last result seems difficult to reconcile with the picture presented by Reddy *et al.*[3] of strain-dependent excited-state splittings. Variations in the shift of the lowest-frequency satellite features between 0.6 and 30 GHz as a function of wavelength under the inhomogeneous line are expected. We have no entirely adequate explanation for their constancy at the present time.

At wavelengths close to 637.2 nm, where satellites are not normally observed, unusual behavior occurs during prolonged or intense burning cycles, as can be seen from Fig. 7. Persistent antihole burning begins to compete with the usual hole-burning process. At first this competition results in the appearance of superimposed holes and antiholes, as in Fig. 7(a). Eventually, however, it leads to purely antihole spectra showing several weak satellites at the usual positions, as in Fig. 7(b). In antihole spectra the intensity asymmetry between features at negative and positive detunings was found to be reversed compared with those in hole spectra.

The effect of an external electric field is illustrated in Fig. 8. Since the N–V center lacks inversion symmetry, both a linear Stark effect and pseudo-Stark splittings of orientationally distinguishable centers are expected in nonzero fields.[20,21] Persistent holes burned in zero field should split on application of an external electric field in any direction. In the data of Fig. 8, however, the hole merely broadens and diminishes in amplitude with increasing field strength. This effect may be attributed to the presence of a distribution of homogeneous groups in the power-broadened hole initially created in zero field.

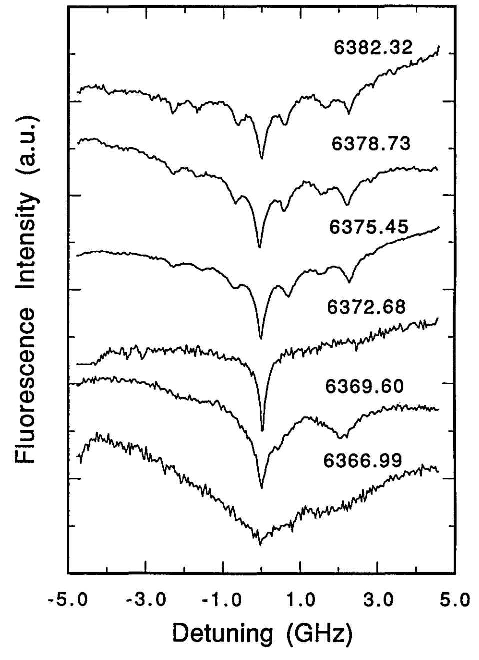

Fig. 6. Persistent hole spectra of the N–V center recorded at various wavelengths within the inhomogeneously broadened zero-phonon line ($T = 6.5$ K). Conventional fluorescence detection was used, and experimental conditions were comparable for all spectra except that at 637.2 nm, which required a longer writing time.

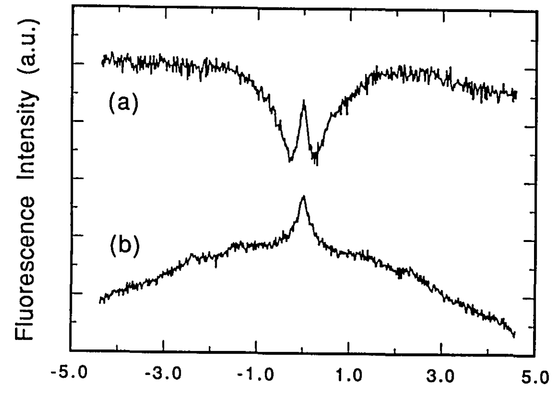

Fig. 7. Persistent antihole spectra at 637.2 nm ($T = 6.5$ K). In (a) an antihole appears at line center following intense burning at the frequency of a previously low-intensity burn. More prolonged, intense burning results in the emergence of the spectrum shown in (b), which is entirely antihole in nature with weak satellites not ordinarily seen at this wavelength.

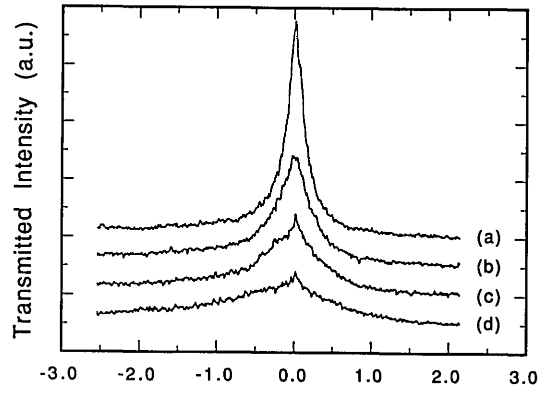

Fig. 8. Effect of an electric field applied to a narrow persistent hole at 637.2 nm. Voltages applied across the 3.5-mm width of the sample in the [100] direction in (a)–(d) were 0, 100, 200, and 400 V dc.

A broad distribution of Stark and pseudo-Stark coefficients would result in the superposition of many splitting patterns at each applied field strength and a consequent smearing of the spectrum. The initial distribution shows residual inhomogeneity because of saturation during the burning process. The presence of an inhomogeneous distribution of centers contributing to the power-broadened linewidth of persistent holes is unfortunate because it prevents the application of Stark splitting spectroscopy in this system as a convenient, independent check of the physical model of the N–V center. However, we remark that the observation that no centers remain unshifted in the presence of an electric field is in accord with expectations based on the nitrogen–vacancy model and C_{3v} symmetry of the center.

The strong satellite features in our spectra all have splittings that invoke an excited-state spin transition. This observation suggests a link between spin transitions in the excited state and persistent optical storage in this system. The persistence mechanism does not appear to be photochemical, since hole erasure occurs when the laser frequency is simply scanned over a few gigahertz, and since holes burned at one frequency tend to fill neighboring holes. We have no evidence of photoproducts at significantly different energies. Also, there is no evidence for nonphotochemical hole burning that involves multiphoton processes, as is pointed out by Harley *et al.*[1] Hence we are led to a conjecture about single-photon, nonphotochemical processes that may be responsible for persistent hole burning in this system.

One possible mechanism takes account of the fact that ^3E orbitals place active, unpaired electrons of the center close to dangling bond orbitals on adjacent carbon atoms. Excited-state spin transitions may occur by exchange between one of the unpaired electrons and a dangling bond electron in the opposite spin state. Direct exchange would be equivalent to a spin flip in the excited state and would result in a change of the quasi-static environment of the center if dangling bond orbitals were strongly oriented as a frozen cage at low temperatures. It is known from hyperfine spin resonance observations that neither the carbon electrons nor their nuclei significantly affect the electronic structure of the N–V center in its ground state. However, it is possible that in the extended excited state the situation could be quite different.

Memory of excited-state spin exchange interactions in such a model could be preserved as an altered, quasi-static cage of oriented spins on the neighboring carbons. Modification of their collective field at the vacancy would shift the electronic resonance of the center and could result in persistent depletion of population among centers resonant with the laser burn frequency. Memory of as many as three such exchange interactions could in principle be stored in this way, since there are three equivalent carbon neighbors, although the short lifetime of the excited state would render the probability of successive exchanges progressively less likely.

An exchange model of this type could account for other qualitative features of our observations. The intensity of satellites at ±1.61 GHz and ±3.94 GHz that appear to require two excited-state transitions is low. This would be understandable in view of the reduced probability for two spin exchanges to occur in a time less than the excited-state lifetime. The similarly low intensity of the 2.88-GHz line may be caused by this feature's arising not from a ground-state transition alone but from a ground-state transition in combination with two excited-state spin transitions of opposite sign. Further experiments are clearly necessary, however, to investigate the mechanism of persistent hole burning of the N–V center in detail.

Heterodyne Detection

Heterodyne-detected hole-burning signals exhibited sinusoidal behavior within the envelope of the homogeneously broadened hole, as shown by the oscillatory curves in Fig. 2. The spacing of the interference fringes depended sensitively on the path difference between beams incident upon the sample, as can be seen by a comparison of Figs. 2(a) and 2(b). In Fig. 2 both the read and the write operations were performed with the same phase delay, and the average fringe spacing agreed within 5% with the value calculated by using the expression of Saikan *et al.*[15]:

$$\phi = (\omega_r - \omega_w)t_{21} - \tan^{-1}(\omega_r - \omega_w)T_2/2\,. \qquad (1)$$

Here ω_r and ω_w are the read and the write frequencies,

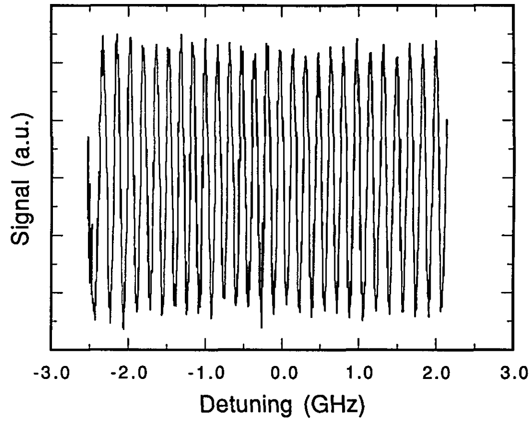

Fig. 9. Intensity of the heterodyne beat signal recorded at the sample input plane for a phase delay of $\Delta = 205$ cm, as the laser detuning is scanned over a 5-GHz range.

t_{21} is the phase-delay time between beams, and T_2 is the homogeneous dephasing time.

When persistent gratings were written with one phase delay and read with a different one, the observed spacing always corresponded to the read-beam delay. For example, experiments performed with zero delay during the write cycle and a delay of 100 cm for the read cycle resulted in an observed pattern corresponding to 100 cm. Similarly, with a 100-cm delay during the write cycle but zero delay during the read, no fringes were observed. This result indicates that phase-delay information is not stored in the persistent grating and that oscillations are completely determined by relative phasing of the read beams.

Indeed, it is clear that net phases accumulated by two intersecting read beams in the interferometric leg of the experiment are $\phi_1 = \omega t_1$ and $\phi_2 = \omega t_2$, for a path difference $\phi = \phi_2 - \phi_1$. The net phase with respect to the writing frequency therefore depends on the read frequency according to

$$\phi = \int_{\omega_w}^{\omega_r} \frac{d\phi}{d\omega} d\omega = (\omega_r - \omega_w) t_{21}. \qquad (2)$$

Notice that the dependence on detuning of the signal phase in Eq. (2) is identical to that in the first term of Eq. (1). Furthermore, for $T_2/2$ small compared with $(\omega_r - \omega_w)$, as is required for subnatural linewidth resolution, Eq. (1) reduces to Eq. (2). Hence the oscillatory phase calculated from Eq. (1) is identical to that from Eq. (2) in this limit, although the physical origins of the signal phases are quite different. To distinguish two cw beams on the basis of phase alone, the phase delay must be nonzero ($t_{21} \neq 0$). Hence phase oscillations that are non-Ramsey in origin but that exhibit a period close to the Ramsey fringe period given by Eq. (1) are unavoidable in a phase-separated-field method.

First-order fringing between phase-delayed cw beams give rise to oscillations with a period equal to the phase delay whenever the read laser frequency is tuned. These oscillations can be expected to mask completely any small contributions from Ramsey interference. Further confirmation of this is provided in Fig. 9, where coherent oscillations with a period given by Eq. (2) were obtained by removing the sample altogether and placing a detector at the read-beam intersection beam.

CONCLUSION

In summary, we have observed new satellite holes and antiholes in the persistent hole-burning spectrum of the N–V center. The Stark field response, together with the wavelength and the power dependences of hole linewidths, suggest that even at extremely low incident laser powers persistent holewidths in this system are dominated by power broadening of a slightly inhomogeneous distribution of centers. This effect may be related to the extremely broad inhomogeneous linewidth (~1000 GHz) of the zero-phonon line itself. The origin of satellites can be explained on the basis of multiple spin transitions within the center by making use of the known spin splitting of the ^3A ground state (2.88 GHz) and an assigned value of 0.65 GHz for the ^3E electronic state. Surprisingly, the excited-state splitting does not show a large variation within the strain-induced inhomogeneous profile of the zero-phonon line.

A tentative mechanism accounting for the persistence of hole burning at liquid-helium temperatures has also been outlined, based on the concept of excited-state spin exchange between the unpaired N–V electrons and dangling bond spins on carbon neighbors of the center. Finally, a direct comparison of the resolution attainable with conventional and heterodyne-detected, persistent hole-burning spectroscopy with phase-delayed, cw lasers was made. It was concluded that the nonzero phase delay between incident beams in the phase-separated field method and its unavoidable imposition on the signal of first-order fringing at the predicted Ramsey period renders the method inapplicable to subnatural linewidth spectroscopy of solids or to storage enhancement in optical memories.

ACKNOWLEDGMENTS

This research was sponsored by the U.S. Air Force Office of Scientific Research, Itami Research Division of Sumitomo Electric Company, and a Phoenix Memorial Laboratory grant. We acknowledge technical support and useful discussions with S. Yazu, K. Tsuji, and S. Satoh of Sumitomo, L. E. Haliburton of Oklahoma State University, N. B. Manson of the Australian National University, R. N. Schwartz of Hughes Laboratories, and R. H. Sands of the University of Michigan. D. Redman is also grateful for the support of an AT&T fellowship.

*Current address, Sandia National Laboratories, Albuquerque, New Mexico 87185.

REFERENCES

1. R. T. Harley, M. J. Henderson, and R. M. Macfarlane, J. Phys. C Phys. **17**, L233–L236 (1984).
2. J. H. N. Loubser and J. A. Van Wyk, Diamond Res. (1977), pp. 11–14.
3. N. R. S. Reddy, N. B. Manson, and E. R. Krausz, J. Lumin. **38**, 46–47 (1987).
4. E. van Oort, N. B. Manson, and M. Glasbeek, J. Phys. C **21**, 4385–4391 (1988).
5. K. Holliday, N. B. Manson, M. Glasbeek, and E. van Oort, J. Phys. Condensed Matter Phys. **1**, 7093–7102 (1989).
6. K. Holliday, X.-F. He, P. T. H. Fisk, and N. B. Manson, Opt. Lett. **15**, 983–985 (1990).
7. N. B. Manson, X.-F. He, and P. T. H. Fisk, Opt. Lett. **15**, 1094–1096 (1990).

8. D. Redman, S. Brown, R. H. Sands, and S. C. Rand, "Spin dynamics and electronic states of N–V centers in diamond by EPR and four-wave mixing spectroscopy," Phys. Rev. Lett. **67,** 3420 (1991).
9. D. Redman, Q. Shu, A. Lenef, S. Brown, and S. C. Rand, "Two-beam coupling due to N–V color centers in diamond," Opt. Lett. **17,** 175 (1992).
10. N. F. Ramsey, *Molecular Beams* (Oxford U. Press, New York, 1956), p. 124.
11. Ye. V. Baklanov, B. Ya. Dubetskii, and V. P. Chebotayev, Appl. Phys. **9**, 171 (1976); **11,** 201 (1976).
12. M. M. Salour and C. Cohen-Tannoudji, Phys. Rev. Lett. **38,** 757 (1977).
13. J. C. Bergquist, S. A. Lee, and J. L. Hall, Phys. Rev. Lett. **38,** 159 (1977).
14. R. Teets, J. Eckstein, and T. W. Hänsch, Phys. Rev. Lett. **38,** 760 (1977).
15. S. Saikan, A. Imaoka, and T. Kishida, "Optical Ramsey fringes in photochemical hole-burning," Phys. Rev. B **39,** 11207–11209 (1989).
16. W. E. Moerner, ed., *Persistent Spectral Hole-Burning: Science and Applications* (Springer-Verlag, Berlin, 1988).
17. G. Davies and M. F. Hammer, "Optical studies of the 1.945 eV vibronic band in diamond," Proc. R. Soc. London A **348,** 285–298 (1976).
18. L. du Preez, Ph.D. dissertation (University of Witwatersrand, Johannesburg, 1965).
19. A. T. Collins, M. F. Thomaz, and M. I. B. Jorge, "Luminescence decay time of the 1.945 eV centre in type Ib diamond," J. Phys. C **16,** 2177–2181 (1983).
20. G. Johannson, W. von der Osten, R. Piehl, and W. Widelich, "Linear Stark and pseudo-Stark effect of the F_3^+ centre in LiF and NaF," Phys. Status Solidi **34,** 699–709 (1969).
21. R. M. Shelby and R. M. Macfarlane, "Measurement of the pseudo-Stark effect in Pr:LaF_3 using population hole-burning and optical free induction decay," Opt. Commun. **27,** 399–402 (1978).