The Phenomenology of Optically Pumped ^{13}C NMR in Diamond at 7.05 T: Room Temperature Polarization, Orientation Dependence, and the Effect of Defect Concentration on Polarization Dynamics

Eric Scott^a, Melanie Drake^{b*}, Jeffrey A. Reimer^b

^a Department of Chemistry, University of California, Berkeley

^b Department of Chemical & Biomolecular Engineering, University of California, Berkeley Berkeley CA 94720

* Corresponding author: Department of Chemical & Biomolecular Engineering, B84 Hildebrand Hall, Berkeley, CA 94720, USA.

Phone: 510-643-2503

Email: drakem@berkeley.edu

Abstract

Room temperature optical illumination of NV- imbedded single crystal diamonds with a 532 nm laser produces ^{13}C polarization enhancements up to 200 times greater than that of the thermal equilibrium value at 7.05 T. We report high field NV- mediated ^{13}C polarization as a function of the number and type (NV- and P1) of defects in commercially available diamonds. Surprisingly, both positive and negative ^{13}C polarizations are observed depending on the orientation of the crystal with respect to the external magnetic field and the electric field vector of the optical illumination. The data reported herein cannot be explained by a previously proposed mechanism.

1. Introduction

The negatively charged nitrogen vacancy (NV-) defect in diamond has been the subject of much research [1]. A magnetically resonant triplet ground state [2-5] with a long coherence lifetime [6-8], optical spin state initialization and readout [9-13], as well as the ability to manipulate spin states of proximal nuclei via level anti-crossings or microwave control [14-16], have made NV- a fixture in the areas of quantum information [13, 15-18], magnetic field sensing [19-22], and nuclear spin control [23-25]. NV- also provides the opportunity to investigate a different type of solid state optically pumped NMR (OPNMR).

In the context of solid state NMR, optical pumping refers to the spontaneous dynamic polarization of nuclei from a reservoir of optically polarized electron spins [26, 27]. There have been substantive investigations of solid state OPNMR in semiconductors starting with Georges Lampel's original experiment with phosphorous-doped silicon [28]. Optically illuminating a zincblende semiconductor at cryogenic temperatures with circularly polarized laser light tuned to the material's band gap can yield highly athermal nuclear polarizations. The transfer of photonic angular momentum from the optical illumination results in a highly spin polarized collection of photoexcited electrons [26-33]. Subsequent hyperfine driven electron-nuclear flip-flop transitions provide a possible electronic spin lattice relaxation pathway allowing for athermal nuclear polarization.

The NV- defect in diamond provides an opportunity to explore optical pumping processes that do not rely on photonic angular momentum. The optically driven preferential population of the NV- $m_s = 0$ sublevel arises out of a fortuitous combination of intersystem crossing rates and selection rules [9-11]. Many studies have taken advantage of the mixing of electronic and nuclear states at the 50 mT NV- excited state level anti-crossing to perform room temperature ^{14}N , ^{15}N , and ^{13}C optical pumping [14, 23-25, 34]. However, comparatively little attention has been devoted to

OPNMR with NV- at high field [35]. We present herein a systematic investigation of the ^{13}C polarization at 7.05 T that derives from a series of diamond samples imbibed with varying amounts of NV- defects. The phenomenology presented herein are consistent with cross-relaxation from optically polarized electrons yet reveal some surprising subtleties.

Previously, ^{13}C optical pumping in diamond was reported in a 9.4 T field at cryogenic temperatures, yielding negative bulk ^{13}C polarizations of up to 5% [35]. It was surmised that nuclear spin transitions were driven by the exchange of energy between NV- dipolar and nuclear Zeeman reservoirs, with spin diffusion transporting polarization from nuclei near defect sites to the bulk crystal. The results reported herein show that this model is incomplete.

Here we study diamonds with varying concentrations of NV- and P1 defects and thereby assess the relationship between defect concentrations and nuclear polarization dynamics. We show that at room temperature we can prepare optically pumped NV- mediated ^{13}C polarization at 7.05 T. We find that the NV- mediated ^{13}C polarization changes sign and magnitude as a function of crystal orientation relative to the external magnetic field and the electric field vector of the optical illumination. These results proscribe the tools necessary to develop a quantitative model for this OPNMR process.

2. Methods

Sample #	Source	Dimensions (mm)	Out of plane orientation	[NV-] (ppm)	[P1] (ppm)	T_{rise} at 20 K (min)	T_{decay} at 20 K (min)	NV- 2Γ (MHz)
1	Element 6	0.311 x 3.239 x 3.238	{100}	1.4 ± 0.2	17 ± 2	17.47 ± 0.21	136.1 ± 9.8	0.72 ± 0.04
2	Element 6	0.311 x 3.238 x 3.232	{100}	1.9 ± 0.2	24 ± 3	45.26 ± 3.43	77.65 ± 3.64	1.15 ± 0.09
3	Sumitomo	0.327 x 2.001 x 2.000	{100}	7.8 ± 1.0	71 ± 9	2.61 ± 0.28	4.80 ± 0.35	1.54 ± 0.11
4	Sumitomo	0.350 x 2.018 x 2.014	{100}	6.9 ± 0.8	48 ± 6	7.35 ± 0.51	10.39 ± 0.65	1.05 ± 0.12
5	Sumitomo	0.295 x 2.015 x 2.015	{110}	7.3 ± 0.9	52 ± 6	4.59 ± 0.41	9.58 ± 0.83	1.27 ± 0.13
6	Sumitomo	0.279 x 2.006 x 2.010	{110}	8.7 ± 1.1	101 ± 12	0.84 ± 0.04	3.01 ± 0.21	1.58 ± 0.17
7	Sumitomo	0.337 x 2.056 x 2.056	{111}	4.2 ± 0.5	22 ± 3	6.46 ± 0.60	11.37 ± 0.65	0.73 ± 0.06
8	Sumitomo	0.339 x 2.053 x 2.053	{111}	6.7 ± 0.8	40 ± 5	6.75 ± 0.36	11.85 ± 1.85	1.16 ± 0.07

Table 1. Diamond sample properties including manufacturer, size, orientation, and defect concentration. Characteristic ^{13}C polarization rise and decay time constants (T_{rise} and T_{decay}) experimentally measured under conditions described in the text. X-band NV- EPR linewidth 2Γ is given in column 9.

Diamond samples

Commercially available high-pressure high-temperature (HPHT) type Ib diamond plates with a quoted substitutional nitrogen content in the range of 5 – 200 ppm were purchased from Element 6 and Sumitomo. The samples were sent to Prism Gem LLC for 1 MeV of electron irradiation and were subsequently annealed at 800 °C. Sample #1 was annealed for 1 hour and samples #2 – #8 were annealed for 2 hours. Sample characteristics are summarized in Table 1 and pictures of the samples post-irradiation and annealing are shown in Figure 1.

Figure 1. Pictures of diamond samples post-electron irradiation and annealing. Top row: samples 1 – 4. Bottom row: 5 – 8. Photographs are not to scale. The origin of discoloration within samples is unknown, but was present before electron irradiation.

Equipment

NMR experiments were conducted using a homebuilt non-resonant transmission line probe [36] and goniometer, an Oxford 7.05 T magnet, a single channel Tecmag LapNMR spectrometer, and an ENI LPI-10 RF amplifier. Details of the goniometer are included in Appendix A. Sample temperature was maintained with an Oxford Spectrostat^{NMR} helium cryostat and a two channel Lakeshore 332S temperature controller capable of simultaneously monitoring the cryostat's built-in temperature sensor as well as a sensor attached to the probe (both sensors are Lakeshore CX-1050-CU-HT). Spectrosil B windows allow optical access through the bottom of the cryostat. The 532 nm output of a commercial (Viasho 3.7 W) frequency doubled Nd:YAG laser was used for optical illumination (5mm circular beam diameter).

¹³C polarization rise and decay experiments

The time constants characterizing the rise of ¹³C polarization under optical illumination (T_{rise}) and the decay back to thermal polarization after illumination ceases (T_{decay}) were measured using the pulse sequences shown in Figure 2. In both cases, thermal ¹³C polarization was first eliminated by saturating the nuclear transitions with a series of fifty 90° pulses separated by 10 ms of dephasing time. For the case of T_{rise} , the sample was then subjected to a varying period of optical illumination (τ_{Light}) followed by a 90° pulse and acquisition. For T_{decay} experiments, the sample was subjected to a fixed τ_{Light} followed by a variable period of dark time (τ_{Dark}) before acquiring the NMR spectrum. The dark time was controlled by means of a TTL signal from the spectrometer to either a mechanical shutter or directly to the laser power supply. A 90° pulse width of 17 μ s with an RF power of 550 W was used in all experiments. The integrated intensity of the resulting single crystal ¹³C NMR spectrum was converted to a percent polarization by comparison with the integrated spectrum of a thermally polarized monocrystalline diamond powder (Microdiamant MSY 0-0.1) standard

containing a known number of ^{13}C spins. The diamond powder spectra were recorded with the same pulse sequence and spectrometer settings used in recording the OPNMR spectra. The resulting plots of percent ^{13}C polarization vs. τ_{Light} and of percent ^{13}C polarization vs. τ_{Dark} were fit to single exponentials to extract T_{rise} and T_{decay} .

To investigate how defect content influences the ^{13}C polarization dynamics, the T_{rise} and T_{decay} of each sample were measured at 20 K using 50.9 mW/mm² of circularly polarized 532 nm laser light. As discussed later and shown in Figure 7, T_{decay} is independent of the initial ^{13}C polarization. Therefore, the selection of τ_{Light} in decay experiments was simply a compromise between adequate signal-to-noise and experiment time. The values of τ_{Light} for the 20 K T_{decay} experiments were 25 minutes for samples #1 and #2, 12 minutes for sample #4, 10 minutes for sample #8, 8 minutes for samples #3, #5, and #7, and 4 minutes for sample #6.

Room temperature ^{13}C polarization

The T_{rise} of samples #1 and #2 was measured at 290 K using 127.3 mW/mm² of linearly polarized 532 nm laser light. It was necessary to use the cryostat to maintain a 290 K sample temperature in the presence of laser heating. The T_{decay} of sample #2 was measured near room temperature using a τ_{Light} of 20 minutes with 127.3 mW/mm² of linearly polarized laser light. Near room temperature, the temperature equilibration time exceeds τ_{Dark} and thus the temperature dropped by as much as 20K in the absence of laser heating during τ_{Dark} (270-280K).

Influence of orientation on ^{13}C polarization

The orientation experiments presented in this work were conducted with sample #2 at 20 K using 50.9 mW/mm² of 532 nm laser intensity with a 25 minute τ_{Light} . The orientation of the sample was set by adjusting the rotation angle ϕ of the sample about its out-of-plane crystal axis with respect to the sample holder followed by a rotation about the sample holder axis by a tilt angle θ (Figure 3a). For samples with a $\{100\}$ out-of-plane orientation, $\phi = 0^\circ$ is defined such that the tilt angle θ will be about one of the crystal's in-plane $\langle 100 \rangle$ axes. For $\phi = 45^\circ$, θ is about one of the in-plane $\langle 110 \rangle$ axes (Figure 3b). For a given set of experiments, the sample is mounted to the sample holder at a fixed ϕ using GE varnish and spectra are acquired for a set of θ values adjusted ex-situ using a rotary feedthrough (Appendix A). The quadrupole splitting of the ^{27}Al NMR signal from the sapphire sample holder was used to determine θ . Because the electric field vector of the laser light must be orthogonal to the NV- defect axis in order to be absorbed [37], circularly polarized laser light was used in all orientation experiments. This ensured that sequential experiments at the same sample orientation with respect to the 7.05 T magnetic field did not also have to be oriented relative to a laser polarization axis.

Figure 2. OPNMR pulse sequences for T_{rise} (top) and T_{decay} (bottom) experiments. Solid green shading indicates optical illumination. Grey shading indicates a lack of illumination. Fifty 90° pulses followed by 10 milliseconds of dephasing time constitute the saturation sequence.

Electron Paramagnetic Resonance

EPR experiments were performed at room temperature with a modified Active Spectrum extended range benchtop EPR system operating at 9.7 GHz with an average Q of ~ 1300 . Optical access to the sample was added perpendicular to the magnetic field direction by mounting a 45-degree mirror underneath a hole in the bottom of the microwave cavity. Samples were varnished to the end of fiberglass rods and subsequently positioned in the cavity.

NV- spin counting spectra were recorded with a fixed sweep range of 270.5 – 422.5 mT, 100 data points per mT, a sweep rate of 0.1 mT/s, and a modulation frequency of 43 kHz with an amplitude of 0.2 mT. Low signal-to-noise made it necessary to signal average for 40 scans. P1 spin counting spectra were recorded with a fixed sweep range of 302.5 – 392 mT, a sweep rate of 0.1 mT/s, and a modulation frequency of 43 kHz with an amplitude of 0.1 mT. P1 spectra were signal averaged for 5 scans. To avoid saturating the EPR transitions, power saturation tests were performed on each sample. A microwave (MW) power of 0.00079 mW was subsequently selected and used for all spin counting experiments. To avoid baseline problems and for more accurate results [38] double integration was carried out on line fits of the derivative spectra. The best fits were achieved using the first derivative of a Tsallian [39] lineshape. Defect concentrations were determined by comparison with a solid cupric sulfate pentahydrate intensity standard [40].

NV- EPR linewidths of the optically polarized $|1,0\rangle \rightarrow |1,+1\rangle$ transition of defects oriented parallel to B_0 were measured over a range of modulation amplitudes. Single shot spectra were recorded during continuous illumination with 25.5 mW/mm² of linearly polarized 532 nm laser light using an incident microwave power of 0.00158 mW, a sweep rate of 0.02 mT/s with 283 points per mT, and 43 kHz field modulation with an amplitude range of 0.006 mT – 0.2 mT. The spectra recorded with the modulation amplitude of 0.006 mT were fit to a sum of three first derivative Tsallian lineshapes. The three values of the half-width at half-height (Γ) extracted from the fits were used to calculate the average linewidths reported in Table 1. Representative EPR spectra for all samples are shown in the supplemental material.

3. Results & Discussion

¹³C polarization rise and decay experiments

The ¹³C polarization was found to increase exponentially with τ_{Light} , consistent with earlier results [35]. The ¹³C polarization dependence on laser intensity was also consistent with earlier results [35]. These polarization rise experiments were performed at 20 K on all samples and the data fit to extract characteristic time constants (T_{rise} , Table 1). Figure 4a shows these values plotted as a function of NV- concentration, as determined by EPR spin counting experiments. In the originally proposed

Figure 3. Illustration of diamond lattice (ball and stick model) on top of diamond sample (purple square) mounted on sapphire platform (grey rectangle). Orientation of the lattice with respect to the face and edges of the sample is representative of Sample #2. (a) Illustration of rotation angle ϕ and tilt angle θ . (b) Definition of rotation angle ϕ as it relates to the tilt axis for a sample with a $\{100\}$ out-of-plane orientation. For a given crystal orientation there are four possible defect orientations.

Figure 4. (a) T_{rise} values plotted vs. NV^- concentration. (b) Rescaled plot of T_{rise} vs. NV^- concentration. (c) T_{decay} values plotted vs. the total $P1 + NV^-$ concentration. (d) Rescaled plot of T_{decay} vs. the total $P1 + NV^-$ concentration.

mechanism for high-field NV^- mediated ^{13}C polarization, dipolar coupled pairs of NV^- defects drive local ^{13}C polarization, which then spin diffuses to the bulk [35]. The T_{rise} values of several minutes reported herein are consistent with a spin-diffusion-limited model ($D=6.7 \times 10^{-15} \text{ cm}^2/\text{s}$ [41]) for bulk polarization. The decrease in T_{rise} with increasing NV^- concentration is also consistent with this model as more NV^- centers presumably lead to increased $NV^- NV^-$ dipolar coupling and a stronger interaction with the ^{13}C nuclear Zeeman bath.

We determined the time constants associated with the return of the ^{13}C polarization to thermal equilibrium after turning off the laser and found them to behave exponentially. The values of T_{decay} are listed in Table 1. Because the ^{13}C NMR signal intensity in the absence of optical pumping is negligible, we could not ascertain whether or not T_{decay} is the same as the ^{13}C T_1 . Because the T_{decay} values are both independent of initial ^{13}C polarization (Figure 7) and have magnitudes comparable to T_1 values given in the literature [41], we surmise that fluctuating magnetic fields associated with all unpaired electron spins would contribute to the return of the ^{13}C polarization to thermal equilibrium. We therefore plotted T_{decay} as a function of the sum of NV^- and $P1$ defect concentrations (Figure 4b). The shortening of T_{decay} values with increasing defect concentrations is consistent with our assumption that all paramagnetic defects contribute to T_{decay} (plots as a function of the concentration of various defects are given in the supplemental material).

Figure 5. (a) T_{rise} curve of sample #1 at 290 K. (b) T_{rise} curve of sample #2 at 290 K. (c) T_{decay} curve of sample #2 taken at ~270K-280K. (d) Single shot optically pumped spectrum of sample #2 taken at 290 K (blue) compared to an 85 scan thermal equilibrium spectrum taken at 80 K (black).

In both T_{rise} and T_{decay} experiments there are substantive differences between the time constants for samples #1 and #2 (from Element 6) and samples #3 – #8 (from Sumitomo). Because these differences correlate to differences in color and apparent inhomogeneity (Figure 1), these effects need to be further explored using a larger sample pool with better-controlled defect concentrations. Figures 4a and 4b also show plots isolating the data of Sumitomo manufactured diamonds, but there are still differences in sample homogeneities within this set (Figure 1). These effects highlight the importance of overcoming the current materials science challenges in preparing HPHT diamonds in which all sample variables are well controlled.

The ^{13}C polarization was observed at 290 K in samples #1 and #2 using 127.3 mW/mm^2 of linearly polarized 532 nm light. ^{13}C polarization increased exponentially with τ_{Light} with a T_{rise} of 13.36 ± 1.85 min for sample #1 and 9.88 ± 0.43 min for sample #2 as shown in Figure 5a and b. The maximum observed ^{13}C polarization at 290 K was 0.125%, seen in a single acquisition after a τ_{Light} of 36 minutes using sample #2 (Figure 5d). For comparison, an 85 scan thermal equilibrium spectrum at 80 K (corresponding to a ^{13}C polarization of 0.00226%) is plotted in Figure 5d as well. As discussed later, sample orientation with respect to the magnetic field and laser propagation axis was found to influence ^{13}C polarization magnitude. We therefore surmise that greater room temperature

Figure 6. (a) Percent ^{13}C polarization of sample #2 oriented with rotation angle $\phi = 25^\circ, 30^\circ, 35^\circ$, and 40° plotted as a function of tilt angle θ adjusted in 0.5° increments. (b) Example ^{13}C NMR spectra corresponding to data points for $\phi = 30^\circ, \theta = 3^\circ - 20^\circ$ in (a).

polarizations may be attainable. This is also the reason for the discrepancy in maximum polarization between the polarization rise experiment shown in Figure 5b and the maximum polarization shown in Figure 5d, which was obtained after re-mounting the sample. The ^{13}C polarization in sample #2 persisted with a $T_{\text{decay}} = 26.8 \pm 2.9$ min (Figure 5c). All room temperature experiments were performed with the large $\{100\}$ face of the samples oriented normal to the applied magnetic field axis.

Influence of orientation on ^{13}C polarization

The percent ^{13}C polarization was measured in sample #2 at 20 K under 50.9 mW/mm^2 of circularly polarized 532 nm laser illumination with the crystal mounted at different orientations relative to the parallel applied magnetic field and laser propagation axis. Figure 6a shows data obtained at four different fixed ϕ angles and varying θ angles in 0.5° increments. Figure 6b shows the raw ^{13}C NMR spectra for a subset of the ^{13}C polarization data shown in Figure 6a. This figure demonstrates that small changes in crystal orientation can drastically affect both the magnitude and sign of the ^{13}C polarization. However, as seen in the $\phi = 25^\circ$ data set, there are also large sets of sample orientations that result in little or no ^{13}C polarization. These results represent new phenomena for NV-mediated ^{13}C polarization at high field. Only negative ^{13}C polarizations were observed in the original high field study [35].

For each crystal orientation there are four equally probable defect orientations. If each individual NV- defect can be dipolar coupled to contribute to the resulting ^{13}C polarization [35], then the bulk ^{13}C magnetization is governed by spin diffusion from sixteen pairwise combinations of dipolar-coupled defects with differing electron spin polarizations [42] owing to each defect's differing

orientation relative to the applied magnetic field and incoming electric field vector of the optical illumination. Because we know the lattice bond angles relative to the faces and edges of each sample, the relative absorption and polarization of each NV- defect can be calculated for each sample orientation through absorption rules [37] and field alignment effects [42]. However, neither of these orientation dependences account for the extreme sensitivity of the bulk ^{13}C polarization to sample orientation seen in Figure 6. Further experiments are required in which the applied magnetic field and laser propagation axes are decoupled.

As a result of the orientation effects seen in Figure 6, the absolute maximum ^{13}C polarization cannot be determined with certainty. The polarization rise and decay time constants T_{rise} and T_{decay} however, were found to be independent of sample orientation. As an example, Figure 7a shows the ^{13}C polarization rise curves, exponential fits, and resulting T_{rise} values for sample #3 at two separate crystal orientations relative to the parallel applied magnetic field and laser propagation axis. Figure 7b shows the same information for a ^{13}C polarization decay experiment with sample #3 at two different crystal orientations from those in Figure 7a.

Figure 7. (a) T_{rise} and (b) T_{decay} curves of sample #3. The differences in polarization are the result of the orientation of the crystal. Note: (a) and (b) were obtained with differing sample orientations.

The maximum ^{13}C polarization observed thus far at 20 K in samples #1 and #2 is 2.5% and 2.2%, and the maximum observed in samples #3 – #8 is $\sim 1\%$. Because the magnitude of the ^{13}C polarization is so sensitive to the orientation of the crystal these values may not necessarily be the ultimate ^{13}C polarizations. The values of T_{rise} are nonetheless independent of the ultimate polarization and the values of T_{decay} are independent of the initial polarization. This is consistent with a picture in which the time constants for polarization rise and decay only depend on nuclear spin diffusion and the concentration of polarization sources and sinks.

Constraints on the Polarization Mechanism

The mechanism behind this high-field OPNMR process is not yet quantitatively understood, though qualitatively formulated as a result of an exchange of energy between the NV- dipolar and nuclear Zeeman energy reservoirs. A quantitative model [35] was given in terms of a three spin process wherein a 10 MHz dipolar coupling between NV- defect pairs provides for an energy exchange between an NV- pair and a nuclear spin, yielding a spin-temperature equilibration during the optical pumping process. While this model accounts for the previously observed negative ^{13}C polarization and polarization dynamics, it does not account for both positive and negative ^{13}C polarizations that depend on the orientation of the crystal. Furthermore, the model was based on the assumption that the apparent peak-to-peak NV- EPR linewidth (ΔB_{pp}) of approximately 0.2 mT (which corresponds to a full-width at half-height (2Γ) of ~ 10 MHz) reported in [43] was an accurate measure of the NV- dipolar coupling. As summarized in Table 1 and demonstrated in Figure 8, the actual NV- linewidth is much narrower. The reported 0.2 mT ΔB_{pp} is not due to dipolar coupling, but is instead a result of the gross overmodulation of B_0 . The relatively small number of NV- defects in any given sample in

conjunction with the low MW power levels needed to avoid saturating the NV- transitions makes such overmodulation necessary in order to detect a thermal equilibrium signal. The large signal enhancement resulting from optically polarizing the NV- defects makes it possible to record a lineshape in a single shot even after reducing the modulation amplitude (B_{mod}) nearly two orders of magnitude. Figure 8a shows the optically polarized EPR spectra from sample #1 recorded using B_{mod} values from 0.2 to 0.012 mT in which the observed ΔB_{pp} decreases from 0.27 mT to 0.026 mT. As seen in Figure 8, the NV- lineshape can be resolved into three ^{14}N hyperfine lines. Similar plots for the remaining samples are included in the supplemental material. The actual NV- linewidths are likely narrower than the values listed in Table 1 as these are broadened by convolution with ^{13}C hyperfine transitions.

4. Conclusion

We have presented a phenomenological study of high-field OPNMR of ^{13}C through optically polarized NV- defects in diamond. The polarization rise and fall kinetics indicate that higher NV- concentrations shorten T_{rise} . The methodology for varying defect concentration (electron irradiations and subsequent high temperature annealing) results in a lack of independent control of P1 and NV defect concentrations. Thus samples with more NV- defects also have more P1 defects; the latter of which contribute to nuclear relaxation [41] such that rapidly rising ^{13}C polarization comes at the expense a lower polarization magnitude and faster decay. On the other hand, lower NV- concentrations give rise to a longer T_{rise} with larger ^{13}C polarizations and longer lifetimes. The defect concentrations in samples #1 and #2 allow for room temperature ^{13}C polarizations up to 200 times that of the thermal equilibrium value. These results suggest that it may be possible to tailor the defect content to optimize polarization kinetics to a desired regime.

The results of the orientation experiments hinder simple attempts to model the ^{13}C polarization process as a coupling between NV dipolar and nuclear Zeeman reservoirs. Because of the symmetry of the tetrahedral diamond lattice, a pairwise calculation of NV- dipolar interactions, for example,

Figure 8. Effect of B_{mod} on the NV- EPR lineshape. (a) Optically polarized $|1,0\rangle \rightarrow |1,+1\rangle$ transition of sample #1 recorded with different modulation amplitudes. (b) The first and last spectrum from (a) overlapped. (c) Overlapped EasySpin [44] simulations that include the $A_{\perp}^N = -2.7$, $A_{\parallel}^N = -2.14$ and $A_{\perp}^C = 13.26$, $A_{\parallel}^C = 18.5$ MHz interactions reported in [45] as well as the 12.75, -8.6, -6.46, 4.15, and 2.6 MHz ^{13}C hyperfine splittings reported in [46].

results in sixteen different inter-electron vectors whose orientations relative to the applied magnetic field and the electric field vector of the laser light must be taken into account to begin a quantitative model. Such an effort should, in the view of the present authors, be preceded by experimental data that vary independently the two orientation effects. Nevertheless, the ease of generating large ^{13}C polarizations at high field by merely using a green laser beam portends more detailed studies as well as investigation of polarization transfer to targets within or near the diamond crystal.

This material is work supported in part by the National Science Foundation under contract/Grant no. NSF-DMR 1106288.

References

- [1] M.W. Doherty, N.B. Manson, P. Delaney, F. Jelezko, J. Wrachtrup, L.C. L. Hollenberg, The nitrogen-vacancy colour center in diamond, *Phys. Rep.* 528 (2013) 1
- [2] J.H.N. Loubser, J.A. van Wyk, Electron spin resonance in the study of diamond, *Rep. Prog. Phys.* 41 (1978) 1202
- [3] N.R.S. Reddy, N.B. Manson, E.R. Krausz, Two-laser spectral hole burning in a colour centre in diamond, *J. Lumin.* 38 (1987) 46
- [4] E. van Oort, N. B. Manson, M. Glasbeek, Optically detected spin coherence of the diamond N-V centre in its triplet ground state, *J. Phys. C: Solid State Phys.* 21 (1988) 4385
- [5] D. A. Redman, S. Brown, R. H. Sands, 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 (1991) 3420
- [6] T. A. Kennedy, J. S. Colton, J. E. Butler, R. C. Linares, P. J. Doering, Long coherence times at 300 K for nitrogen-vacancy center spins in diamond grown by chemical vapor deposition, *Appl. Phys. Lett.* 83 (2003) 4190
- [7] Torsten Gaebel, Michael Domhan, Iulian Popa, Christoffer Wittmann, Philipp Neumann, Fedor Jelezko, James R. Rabeau, Nikolas Stavrias, Andrew D. Greentree, Steven Prawer, Jan Meijer, Jason Twamley, Philip R. Hemmer, Jörg Wrachtrup, Room-temperature coherent coupling of single spins in diamond, *Nat. Phys.* 2 (2006) 408
- [8] G. Balasubramanian, P. Neumann, D. Twitchen, M. Markham, R. Kolesov, N. Mizusochi, J. Isoya, J. Achard, J. Beck, J. Tissler, V. Jacques, P.R. Hemmer, F. Jelezko, J. Wrachtrup, Ultralong spin coherence time in isotopically engineered diamond, *Nat. Mat.* 8 (2009) 383
- [9] J. Harrison, M.J. Sellars, N.B. Manson, Optical spin polarisation of the N-V centre in diamond, *J. Lumin.* 107 (2004) 245-248

- [10] N. B. Manson, J. P. Harrison, M. J. Sellars, Nitrogen–vacancy center in diamond: model of the electronic structure and associated dynamics Phys. Rev. B 74 (2006) 104303
- [11] J.P. Tetienne, L. Rondin, P. Spinicelli, M. Chipaux, T. Debuisschert, J.F. Roch, V. Jacques, Magnetic-field-dependent photodynamics of single NV defects in diamond: an application to qualitative all-optical magnetic imaging, New J. Phys. 14 (2012) 103033
- [12] F. Jelezko, J. Wrachtrup, Read-out of single spins by optical spectroscopy, J. Phys. Condens. Mat. 16 (2004) R1089-R1104
- [13] L. Robledo, L. Childress, H. Bernien, B. Hensen, P. F. A. Alkemade, R. Hanson, High-fidelity projective read-out of a solid-state spin quantum register, Nature 477 (2011) 574-578
- [14] B. Smeltzer, J. McIntyre, L. Childress, Robust control of individual nuclear spins in diamond, Phys. Rev. A 80 (2009) 050302(R)
- [15] F. Jelezko, T. Gaebel, I. Popa, M. Domhan, A. Gruber, J. Wrachtrup, Observation of Coherent Oscillation of a Single Nuclear Spin and Realization of a Two-Qubit Conditional Quantum Gate, Phys. Rev. Lett. 93 (2004) 130501
- [16] P. Cappellaro, L. Jiang, J. S. Hodges, M. D. Lukin, Coherence and Control of Quantum Registers Based on Electronic Spin in a Nuclear Spin Bath, Phys. Rev. Lett. 102 (2009) 210502
- [17] M. V. Gurudev Dutt, L. Childress, L. Jiang, E. Togan, J. Maze, F. Jelezko, A. S. Zibrov, P. R. Hemmer, M. D. Lukin, Quantum Register Based on Individual Electronic and Nuclear Spin Qubits in Diamond, Science 316 (2007) 1312
- [18] J. R. Weber, W. F. Koehl, J. B. Varley, A. Janotti, B. B. Buckley, C. G. Van de Walle, D. D. Awschalom, Quantum computing with defects, Proc. Natl. Acad. Sci. 107 (2010) 8513-8518
- [19] J.M. Taylor, P. Cappellaro, L. Childress, L. Jiang, D. Budker, P. R. Hemmer, A. Yacoby, R. Walsworth, M. D. Lukin, High-sensitivity diamond magnetometer with nanoscale resolution, Nat. Phys. 4 (2008) 810-816
- [20] V. M. Acosta, E. Bauch, M. P. Ledbetter, C. Santori, K.-M. C. Fu, P. E. Barclay, R. G. Beausoleil, H. Linet, J. F. Roch, F. Treussart, S. Chemerisov, W. Gawlik, D. Budker, Diamonds with a high density of nitrogen-vacancy centers for magnetometry applications, Phys. Rev. B 80 (2009) 115202
- [21] A. Laraoui, J.S. Hodges, C.A. Meriles, Nitrogen-Vacancy-assisted magnetometry of paramagnetic centers in an individual diamond nanocrystals, Nano Lett. 12 (2012) 3477

- [22] K. Jensen, N. Leefer, A. Jarmola, Y. Dumeige, V. M. Acosta, P. Kehayias, B. Patton, D. Budker, Cavity-enhanced room-temperature magnetometry using absorption by nitrogen-vacancy centers in diamond, *Phys. Rev. Lett.* 112 (2014) 160802
- [23] V. Jacques, P. Neumann, J. Beck, M. Markham, D. Twitchen, J. Meijer, F. Kaiser, G. Balasubramanian, F. Jelezko, J. Wrachtrup, Dynamic Polarization of Single Nuclear Spins by Optical Pumping of Nitrogen-Vacancy Color Centers in Diamond at Room Temperature, *Phys. Rev. Lett.* 102 (2009) 057403
- [24] R. Fischer, A. Jarmola, P. Kehayias, D. Budker, Optical polarization of nuclear ensembles in diamond, *Phys. Rev. B* 87 (2013) 125207
- [25] H. J. Wang, C. Shin, C. Avalos, S. Seltzer, D. Budker, A. Pines, V. Bajaj, Sensitive Magnetic Control of Ensemble Nuclear Spin polarization in Diamond, *Nat. Commun.* 4 (2013) 1940
- [26] R. Tycko, J. A. Reimer, Optical Pumping in Solid State Nuclear Magnetic Resonance, *J. Phys. Chem.* 100 (1996) 13240-13250
- [27] J. A. Reimer, Nuclear hyperpolarization in solids and the prospects for nuclear spintronics, *Solid State Nucl. Magn. Reson.* 37 (2010) 3-12
- [28] G. Lampel, Nuclear dynamic polarization by optical electronic saturation and optical pumping in semiconductors, *Phys. Rev. Lett.* 20 (1968) 491
- [29] R. Tycko, Optical pumping in indium phosphide: ^{31}P NMR measurements and potential of signal enhancements in biological solid state NMR, *Solid State Nucl. Magn. Reson.* 11 (1998) 1
- [30] K. Hashia, A. Goto, R. Miyabec, T. Shimizua, G. Kidoa, S. Ohkia, S. Machida, Optically pumped NMR in semiconductor InP *Physica B* 329-333 (2003) 1235-1236
- [31] I. J. H. Leung, C. A. Michal, Optical enhancement of NMR signals in CdTe, *Phys. Rev. B* 70 (2004) 035213
- [32] A. K. Paravastu, S. E. Hayes, B. E. Schwickert, L. N. Dinh, M. Balooch, J. A. Reimer, Optical polarization of nuclear spins in GaAs, *Phys. Rev. B* 69 (2004) 075203
- [33] S. Hayes, S. Mui, K. Ramaswamy, "Optically pumped nuclear magnetic resonance of semiconductors", *J. Chem. Phys.* 128 (2008) 052203
- [34] R. Fischer, C.O. Bretschneider, P. London, D. Budker, D. Gershoni, L. Frydman, Bulk Nuclear Polarization Enhanced at Room Temperature by Optical Pumping, *Phys. Rev. Lett.* 111 (2013) 057601

- [35] J. P. King, P. J. Coles, J. A. Reimer, Optical polarization of ^{13}C nuclei in diamond through nitrogen vacancy centers, *Phys. Rev. B* 81 (2010) 073201
- [36] E. Scott, J. Stettler, J. A. Reimer, Utility of a tuneless plug and play transmission line probe, *J. Magn. Reson.* 221 (2012) 117-119
- [37] R. J. Epstein, F. M. Mendoza, Y. K. Kato, D. Awschalom, Anisotropic interactions of a single spin and dark-spin spectroscopy in diamond, *Nat. Phys.* (2005) 1 94-98
- [38] M. Tseitlin, S. S. Eaton, G. R. Eaton, Uncertainty Analysis for Absorption and First Derivative Electron Paramagnetic Resonance Spectra, *Concepts in Magnetic Resonance Part A* 40 (2012) 295-305
- [39] D. F. Howarth, J. A. Weil, Z. Zimpel, Generalization of the lineshape useful in magnetic resonance spectroscopy, *J. Magn. Reson.* 161 (2003) 215-221
- [40] R. M. Chrenko, H. M. Strong, R. E. Tuft, Dispersed paramagnetic nitrogen content of large laboratory diamonds, *Phil. Mag.* 23 (1971) 313-318
- [41] C. J. Terblanche, E. C. Reynhardt, and J. A. van Wyk, ^{13}C spin-lattice relaxation in natural diamond: Zeeman relaxation at 4.7 T and 300 K due to fixed paramagnetic nitrogen defects, *Solid State Nucl. Magn. Reson.* 20 (2001) 1
- [42] M. Drake, E. Scott, J. Reimer, Influence of magnetic field alignment and defect concentration on nitrogen-vacancy polarization in diamond, *New. Jour. Physics* (2015), in press
- [43] S. Takahashi, R. Hanson, J. van Tol, M. S. Sherwin, D. Awschalom, Quenching Spin Decoherence in Diamond through Spin Bath Polarization, *Phys. Rev. Lett.* 101 (2008) 047601
- [44] S. Stoll, A. Schweiger, EasySpin, a comprehensive software package for spectral simulation and analysis in EPR, *J. Magn. Reson.* 178 (2006) 42-55
- [45] S. Felton, A. M. Edmonds, M. E. Newton, P. M. Martineau, D. Fisher, D. J. Twitchen, J. M. Baker, Hyperfine interaction in the ground state of the negatively charged nitrogen vacancy center in diamond, *Phys. Rev. B* 79 (2009) 075203
- [46] B. Smeltzer, L. Childress, A. Gali, ^{13}C hyperfine interactions in the nitrogen-vacancy centre in diamond, *New J. Phys.* 13 (2011) 025021

Appendix A – Construction of Homebuilt Equipment

NMR probe and probe body construction

NMR transitions are excited and detected with a non-resonant transmission line probe. Details of probe construction are found in reference (36). The split solenoid design allows optical access (Figure A1). The probe is positioned in the cryostat with a simple and lightweight coaxial cable assembly (Figure A2). An appropriate length of 0.25" OD semi-rigid coaxial cable (Micro-Coax UT-250A-TP-M17) and two 0.25" OD/0.180" ID aluminum tubes are held together with three 2.41" OD radiation baffles and two support brackets cut from 0.021" thick copper sheets. The aluminum tubes provide structural support and also serve as guide-pipes for wiring. The baffles and brackets are soldered directly to the coaxial cable and are attached to the aluminum tubes with Eccobond 286 epoxy. The coaxial cable is fed through a 0.25" quick-disconnect vacuum coupling which is welded off-center to a type 316 stainless steel flange designed to seal the sample tube of the cryostat.

Figure A1. Top: Non-resonant probes. Bottom: Goniometer components. (a) Gear assembly retaining ring (b) retaining ring washer (c) gear sleeve (d) sample holder platform (e) miter gear (f) sapphire sample holder (g) freely rotating fiberglass sample holder platform (h) goniometer base (i) control rod sleeve (j) control rod washer.

Figure A2. (a) Complete probe assembly (b) temperature sensor (c) sample on sample holder (d) fiberglass control rod. (e) SMA plug (f) 0.25" OD aluminum tubes (g) copper radiation baffle (h) rotary feedthrough (i) electrical feedthrough (j) aluminum control rod sleeve.

Goniometer assembly

Sample orientation is adjusted ex-situ with a home built goniometer constructed of aluminum, fiberglass, and PTFE. The goniometer employs a pair of commercially available miter gears (W.M. Berg M96P-1A). Aluminum socket head screws are used to secure the probe to the goniometer base. The end of a sapphire sample holder is secured to an aluminum platform that is attached to the gear

assembly via brass set screws. The opposite end of the sample holder is screwed onto a freely rotating fiberglass platform resting in a cavity on the opposite side. The goniometer is controlled by means of a fiberglass rod screwed to the gear assembly. The opposite end of the rod is square shaped and slides into a fitted aluminum sleeve which is coupled via two set screws to the shaft of a vacuum rotary feedthrough equipped with a fine-adjust worm drive (Thermionics FPRM-133-25). The sleeve allows the rod to contract and expand without interfering with goniometer control. Sample holders were machined from a ~1.2" square block of sapphire purchased from Precision Sapphire.