



## Minireview on Nuclear Spin Polarization in Optically-Pumped Diamond Nitrogen Vacancy Centers

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**Abstract** Nitrogen vacancy-centered diamond has recently emerged as a promising material for various applications due to its special optical and magnetic properties. In particular, its applications as a fluorescent biomarker with small toxicity, magnetic field and electric field sensors have been a topic of great interest. Recent review<sup>1</sup> (R. Schirhagl *et al* 2014) introduced those applications using single NV-center in nanodiamond. In this minireview, I introduce the rapidly emerging DNP (Dynamic Nuclear Polarization) field using optically-pumped NV center in diamonds. Additionally, the possibility of exploiting the optically-pumped NV center for polarization transfer source, which will produce a profound impact on room temperature DNP, will be discussed.

**Keywords** Nuclear Magnetic Resonance, Dynamic Nuclear Polarization, Nitrogen Vacancy Center

### Introduction

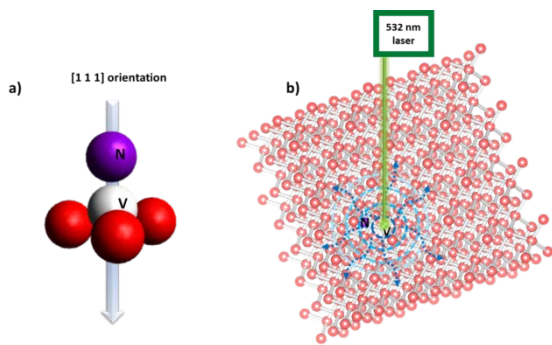
Nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) have been an essential technology for scientific research. Despite its

usefulness, its low signal-to-noise ratio arising from the Boltzmann distribution (population  $\propto e^{-\frac{\Delta E}{kT}} \propto e^{-\frac{\mu B}{kT}}$ , higher magnetic field (B) and lower temperature (T) produce more populations) has poses a great limitation in a typical NMR. Therefore, to obtain a higher sensitivity, lower temperature and higher magnetic field have been normally used.<sup>2</sup> Many other methods which drive much more polarization beyond equilibrium value have been widely studied: spin exchange optical pumping of noble gas,<sup>3-5</sup> parahydrogen induced polarization,<sup>6,7</sup> optical pumping in semiconductors,<sup>8,9</sup> chemically induced dynamic polarization,<sup>10</sup> and photo-excited triplet state.<sup>11</sup> Most of polarization transfer pathways in use are from electron polarization to neighboring nuclei, known as Dynamic Nuclear Polarization (DNP). Recently, refined high field DNP has been optimized in cryogenic temperature to hyperpolarize the electron spin and transfer to the nuclei. However, this polarization method loses a substantial extent of polarization during thawing the sample to the room temperature.<sup>12</sup> In this context, doped diamonds have been harnessed as an alternative polarization source with a long  $T_1$ .<sup>13</sup> Various diamond defects have been studied on those various physical properties, after doping with various atoms such as Nitrogen, Hydrogen, Boron, Silicon, Nickel, and Vacancy etc.<sup>14</sup>

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Their electronic properties were normally examined by Electron Paramagnetic Resonance (EPR) for using as hyperpolarization sources. Based on that, some NMR-related researches have been proved its DNP property with extraordinary long  $T_1$  (longitudinal relaxation time). Especially, many studies described that P1 center (diamond defect, carbon is substituted by nitrogen) and surface unpaired electrons are the useful sources for polarization transfer.<sup>13,15-19</sup>

This review will be focused only on one defect, Nitrogen Vacancy Center (NV center), since we can theoretically achieve ~100 % hyperpolarized electron spin in room temperature. Its detailed physics were introduced in a review by Doherty M. *et al.*<sup>20</sup> Some of its basic physics will be discussed here.



**Figure 1.** a) Single NV center structure showing nitrogen (purple) and vacancy (white) positions in carbon lattice (red). Blue arrow shows the [1 1 1] orientation with regard to the magnetic field. b) Schematic picture of polarization transfer from NV center to the bigger shells. The blue circles are indicating its first, second, and third shells of C atoms. Blue dotted arrow describes a spin diffusion, which is the main polarization transfer mechanism in a bulk diamond.

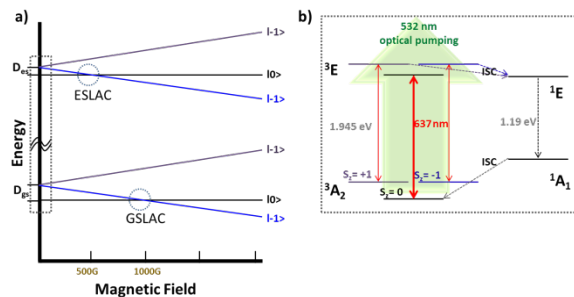
NV center in diamond is a color center containing a nitrogen atom and a vacancy, and they reside on neighboring lattice sites in the tetrahedral diamond structure (figure 1). This defect can be synthesized by Chemical Vapor Deposition (CVD) or High Pressure and High Temperature procedure (HPHT) followed by irradiation and annealation.<sup>20</sup> The color center has three charge states,  $NV^-$ ,  $NV^0$  and  $NV^+$ . Among them, the informative  $NV^-$  center (It will be simply called NV center) has two unpaired electrons with spin quantum number  $S=1$ . Its  $C_{3v}$  symmetry results in the

energy splitting in the confined crystal. The ground state is a triplet state, split between  $S_z=0$  and  $S_z=\pm 1$  by electron spin-spin interaction as much as 2.87 GHz ( $^3A_2$ ). The lowest excited state is split by 1.42 GHz ( $^3E$ ). Singlet states ( $^1A_1$ ,  $^1E$ ) are located between those two states by 1.19 eV. (figure 2)

The NV spin Hamiltonian is given by,<sup>20</sup>

$$H = D \cdot S_z^2 + E(S_x^2 - S_y^2) + \gamma_e B \cdot S + S \cdot A \cdot I - \gamma_c B \cdot I$$

Where the axial ( $D_{gs} = 2.87$  GHz,  $D_{es} = 1.42$  GHz) and transverse (Sample-dependent,  $E \sim 3.5$  MHz) zero field splitting energy,  $S$  ( $I$ ) is the electron (carbon nucleus) spin,  $B$  is the external magnetic field,  $A$  is the hyperfine-interaction tensor,  $\gamma$  is the gyromagnetic ratio ( $\gamma_e$  : electron,  $\gamma_c$  : carbon). Other than the zero field splitting term, the most influential term in the Hamiltonian is the electron Zeeman effect term. This is closely related to the polarization transfer mechanism that will be described later. This NV energy states with regard to magnetic field are

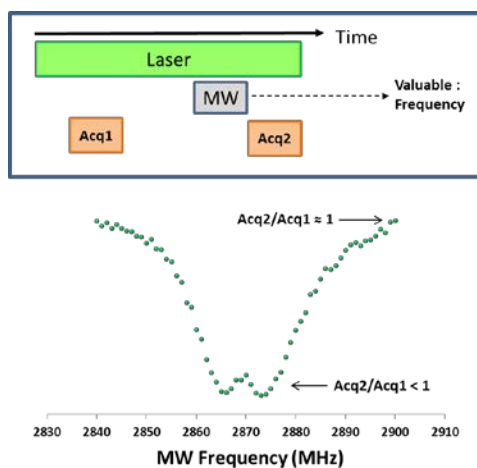


described in figure 2.

**Figure 2.** a) Energy diagram of ground/excited state triplet from the [1 1 1] oriented diamond with regard to the magnetic field. The excited state level anticrossing (ESLAC) is at ~ 500 G and ground state level anticrossing (GSLAC) occurs at ~ 1000 G. b) Electronic fine structure in 0 G (dotted square in a). Two states are separated by 1.945 eV and induce absorption and luminescence. Non-radiative transition (Inter systems crossing, ISC) happens between singlet and triplets. After several optical pumping cycles (typically 532 nm (2.32 eV) laser, which is off-resonance excitation), almost all transition occurs between  $S_z = 0$  and emit 637 nm fluorescence (the thin red arrows would disappear, which indicating transitions through  $S_z = \pm 1$  states).

The most important property of NV center in the NMR field is that we can hyperpolarize the electron

spin after multiple optical excitations. Some portion of excited centers undergoes the intersystem crossing into the singlet state by spin-orbit coupling between triplet and singlet state. After relaxation in the singlet states, another intersystem crossing populates the triplet  $S_z=0$  state. These multiple optical pumping produces more and more electron populations on the  $S_z=0$  state. Therefore, eventually, almost all of fluorescence is from  $S_z=0$  in ground state because each optical pumping yields more population contrast between  $S_z = \pm 1$  and  $S_z = 0$  (figure 2). The extent of spin polarization and fluorescence intensity can be controlled by the microwave (MW, radiofrequency: RF) irradiation which is matched with the ground state (excited state) energy differences between  $S_z=0$  and  $S_z= \pm 1$ . That fluorescence intensity vs MW (RF) can be used for reading out the ground state (excited state) energy difference between spin projected states ( $S_z=\pm 1$  and  $S_z=0$ ). This technique is called Optically Detected Magnetic Resonance (ODMR) (figure 3). This precise measurement on the optically polarized electron energy state makes it possible to analyze all energy states split by spin active nuclei (e.g.  $^{13}\text{C}$ ,  $^{14}\text{N}$ , or  $^{15}\text{N}$ ) or unpaired electrons (e.g. P1 center or other NV center), and manipulate energy state populations by internal/external perturbations.



**Figure 3.** ODMR protocol and ODMR spectrum of NV ensemble at magnetic field ( $B_z \approx 0$  G). Microwave (MW) is irradiated in each MW frequency (x-axis, described as a valuable in a square) and acquired fluorescence signals (Acq 1 and Acq 2) are compared in each loop (Acq2/Acq1), which make each data point (green dot) in ODMR

spectrum. The center of the ODMR spectrum is 2.87 GHz, which is perfectly matched with the ground state zero field splitting,  $D_{gs}$  (figure 2a).

The ODMR technique and manipulating electron state populations in various environments (mainly in selected magnetic fields) with external perturbations (mainly with microwave/radiofrequency irradiations) have been used for polarization transfer in various situations (figure 1b). Herein, I introduce the main polarization transfer studies with brief descriptions.

### Polarization transfer mechanism:

#### Internal perturbation

J. King *et al* obtained  $^{13}\text{C}$  nuclei spin polarization by using dipolar field fluctuations including electron-electron dipole interactions in neighboring defects.<sup>21</sup> This system is introduced at a low temperature (5 K) and its polarization can be up to 5.2% after spin diffusion from the area of strong laser irradiation (5 W). This system is based on the direct laser irradiation on the single crystal sample in the high magnetic field (8.7 T). The following experiments were performed in the same group (Reimer group). E. Scott *et al* investigated polarization mechanism of  $^{13}\text{C}$  in various NV center - concentrated diamonds by using natural abundance  $^{13}\text{C}$  samples (1.1%).<sup>22</sup> They observed the orientation dependent  $^{13}\text{C}$  polarization both in magnetic field and in electric field stemmed from the optical pumping vector. The amount of polarization in their sample was greater by the factor of 200 compared to room temperature. Those oriented samples in different magnetic/electric fields symmetry create many electron-electron interactions to consider, which may be the reason that this polarization transfer mechanism is not solely estimated by dipolar field fluctuations. They measured  $T_1$  time and showed that it is closely related to the NV center and P1 concentrations, which explained well by nuclear relaxation enhancement by unpaired electrons.

V. Jacques *et al* obtained 98% polarization on  $^{15}\text{N}$  which is in a NV center, in the level anticrossing in excited state condition (ESLAC, around 500 G, See

figure 2a).<sup>23</sup> In the low or high magnetic field, hyperfine term between electron and nucleus is truncated with respect to the zero field splitting and/or electron Zeeman effect terms, whereas hyperfine interaction in the LAC (GSLAC, ESLAC) could not be ignored any more. This indicates energy state is mixed by off-diagonal term of Hamiltonian, resulting in the hyperfine mixing. Additionally, one of the nuclear spins is only possible to be flipped by the hyperfine interaction with the polarized electron ( $S_z = 0$  state), which induces polarization transfer into nuclear spin (dominant isotropic hyperfine term is considered). With this mechanism, they observed the  $^{13}\text{C}$  polarization to be in the first shell by using the ODMR (figure 4a). Another closely related research has been done by R. Fischer *et al* with  $^{14}\text{N}$  nuclear spin in NV center.<sup>24</sup> Around 90 % polarization on  $^{14}\text{N}$  and 70% polarization on  $^{13}\text{C}$  in the first shell were observed by using ODMR in ESLAC at low temperature ( $< 50$  K). This polarization transfer mechanism is same as the previous work with  $^{15}\text{N}$ , which can be explained in the other way that almost degenerated electronic sub-states with nucleus ( $^{14}\text{N}$ ) can be mixed by the hyperfine interactions in ESLAC.

The Same group (Budker lab) with Frydman group unveiled advanced research results. R. Fischer *et al* also used ESLAC regime to transfer polarization from polarized electron spin to  $^{13}\text{C}$ .<sup>25</sup> However, they used the shuttling system: they aligned the single crystal around 500 G (ESLAC) and transferred to higher magnetic field to detect the polarized NMR

signal. They obtained  $\sim 0.5$  % nuclear polarization on a bulk diamond at room temperature. To my knowledge, this was the first result of *in situ* detecting polarized nuclei signal from optical pumped NV center. However, polarization decays during shuttling time, which gives less polarization number in detecting the signal.

Polarization transfer in GSLAC was studied in Pines group. H. Wang *et al* used the level anticrossing in the ground state (GSLAC,  $\sim 1000$  G, see figure 2a).<sup>26</sup> Basic ideas are same with the ESLAC researches. They proved the magnetic field dependent polarization transfer mechanism from NV center to the first shell  $^{13}\text{C}$  by flip-flop hyperfine elements. They successfully described its polarization mechanism with detailed simulations and proved that  $^{13}\text{C}$  polarization reached up to  $\sim 100$  % by using the ODMR.

### Polarization transfer mechanism:

#### External perturbation

Polarization transfer mechanisms introduced so far are based on the internal quantum transitions in the selected magnetic fields and orientations, which this can be called as ‘the internal perturbations’. Now I will discuss polarization transfers by ‘the external perturbations’ using microwave and/or radiofrequency, which are used as forces to change populations among selected states through the allowed/slightly allowed transitions, after optical pumping in NV

**Table 1.** Summary of the studies on polarization transfer to nuclei from diamond NV center.

Reference Number	21	22	23	24	25	26	27	28	29
Mechanism <sup>a)</sup>	Dipole field fluctuations	-	ESLAC	ESLAC	ESLAC	GSLAC	MW/RF <sup>b)</sup>	MW	MW
Nuclei <sup>c)</sup>	$^{13}\text{C}$	$^{13}\text{C}$	$^{15}\text{N}$ , $^{13}\text{C}$	$^{14}\text{N}$ , $^{13}\text{C}$	$^{13}\text{C}$	$^{13}\text{C}$	$^{14}\text{N}$	$^{13}\text{C}$	$^{13}\text{C}$
Detection method	High Field	High Field	ODMR	ODMR	High Field	ODMR	ODMR	High Field	Middle Field
Single/bulk <sup>d)</sup>	Bulk	Bulk	Single	Single	Bulk	Single	Single	Bulk	Bulk
Temperature	Low	Low/RT	RT <sup>e)</sup>	Low	RT	RT	RT	RT	RT
Sample	Natural <sup>f)</sup>	Natural	$^{15}\text{N}$ doped	Natural	Natural	100 % $^{13}\text{C}$	Natural	10 % $^{13}\text{C}$	Natural

<sup>a)</sup>Mechanism is the polarization transfer mechanism from NV center to nuclei. <sup>b)</sup>MW is microwave irradiation and RF is the radiofrequency irradiation. <sup>c)</sup>Nuclei is the polarized/measured nuclei. <sup>d)</sup>Single/bulk is the detected nuclei state. <sup>e)</sup>RT is the room temperature. <sup>f)</sup>Natural is the diamond sample containing natural abundance of  $^{13}\text{C}$ .)

center (figure 4b).

D. Pagliero *et al* succeeded in polarizing  $^{14}\text{N}$  nuclear spin in NV center as much as  $\sim 80\%$ .<sup>27</sup> Magnetic field independent quadrupolar coupling and hyperfine interaction between  $^{14}\text{N}$  and NV center were used for the split energy states that are polarized and result in the polarization on the specific nucleus spin state. By applying sequential microwave and radiofrequency irradiations, which are matched with the energy state differences, they polarized selected nuclear spin state (spin swapping) and its polarization was measured by the ODMR (optical pumping, continuous wave microwave irradiation, and reading out).

G. Alvarez *et al* used shuttling system for polarization transfer (in low magnetic field) and detection (in high magnetic field) at room temperature.<sup>28</sup> They used the asymmetric hyperfine interaction-mediated polarization transfer system in low magnetic field by addressing different powers of microwave irradiations, which induce different microwave fields. In a low magnetic field, optically-pumped NV center transfers its polarization to the adjacent  $^{13}\text{C}$  and its polarization was transferred to the outer nuclei by spin diffusion (nuclear – nuclear dipole coupling). This result is very interesting since the bulk  $^{13}\text{C}$  polarization means that the polarization transfer overcame the detuned energy, more than 60 MHz, which is from the electron hyperfine coupling with first shell  $^{13}\text{C}$ . Furthermore, this low magnetic field polarization transfer is very powerful because its dependence on orientations could be somewhat overcome, depending on the magnetic field (the higher magnetic fields broaden asymmetric hyperfine splitting energies from different orientations).

J. King *et al* produced notable experimental polarization transfer results on  $^{13}\text{C}$  in NV center by using external strong microwave after realizing the solid effect and/or thermal mixing.<sup>29</sup> They observed the *in situ* polarized signal in  $\sim 420$  mT by harnessing strong microwave sources available. Measured polarization number of  $^{13}\text{C}$  in 1.1%  $^{13}\text{C}$  concentrated single crystal diamond was around 6% in room temperature. This astonishing polarization number

provides another strong expectation on using NV center as a source for hyperpolarizing various nuclei outside the NV center diamond. If this is realized, we can anticipate great advancements to on organic/inorganic materials in NMR, but also for the MRI field, for hyperpolarization on informative materials by detecting specific functional groups in body.

### **Polarization transfer mechanism:**

#### **Outside of diamond**

To accomplish that wonderful concept, we need to think of 1) feasible spin interaction mechanisms and 2) physical surface area of diamond for effective polarization transfer from diamond to the outside materials. To overcome the physical surface area problem, we need to use nanodiamonds with NV centers, which provide several orders of magnitude of more surface area. Several closely related studies were performed. M. Drake *et al* compared the polarization of NV center in different alignments relative to NV axis.<sup>30</sup> It shows that the polarization in the different electronic spin state is same and its polarization is independent to the orientations. This study suggests that any randomly oriented NV centers in diamond may be used for polarization transfer source. It also suggests that the diamond with higher concentration of NV center and lower concentration of P1 center is better for the optical polarization. J. Scheuer *et al* provided some possible methods for  $^{13}\text{C}$  polarization in a wide range of NV orientations.<sup>31</sup> Based on polarization transfer experiment by Nuclear Spin Orientation Via Electron Spin Locking (NOVEL), they proposed and proved the protocol, integrated solid effect, which sweeps the quasi-adiabatic electron spin resonance frequencies covering some orientations in a selected magnetic field (we can also sweep magnetic field to accomplish ISE). These two recent studies suggest that we can polarize the NV center and  $^{13}\text{C}$  in nanodiamond.

Now, More ideas about the polarization transfer mechanisms are suggested (figure 4c). Recently, E.

Rej *et al* presented the polarization transfer from the electron spins on the nanodiamond surface to the absorbed water at room temperature.<sup>19</sup> They obtained the polarized signal of proton in water using strong microwave irradiation and they proved that the mechanism is from solid effect, not from Overhauser effect, which explains on the state of the water and its correlation time. Even though optical electron polarization was not used for this case and its polarization number is quite small, this result shows a great promise for NV center as a polarization transfer source. Because we may polarize P1 center by NV center, in which the unpaired electrons are strongly coupled with NV center,<sup>32,33</sup> surface electron spins could be polarized by optical pumped NV center, which will be utilized for polarization source, too. Furthermore, we might be able to transfer polarization from polarized <sup>13</sup>C (<sup>14</sup>N, <sup>15</sup>N) in NV diamond to the outside material by using the Hartmann-Hahn condition or the SPINOE (Spin Polarization-Induced Nuclear Overhauser Effect). Because <sup>13</sup>C enriched diamond could be

hyperpolarized, we might be able to use the diamond sample of more concentrations of <sup>13</sup>C spins in the diamond surface. (Shortened T<sub>1</sub> by dipole-dipole interaction would be a trade-off.) We might be able to transfer polarization from the surface NV centers to the outside material directly (figure 4c). While extensive researches have been focused on developing ways of shortening the length of NV center depth from diamond surface, it has been shortened only as much as 2 nm so far.<sup>34</sup> That distance induces a less than several kHz of hyperfine interaction. Therefore, we need to shorten the distance. This should be possible by ongoing material science researches on the diamond NV center in near future. Then, we might be able to transfer polarization by direct solid effect, thermal mixing, or cross effect. Or, we can use Hartmann-Hahn condition which is less affected by distance (1/r<sup>3</sup>). Also, freeze-thaw system with fast heat exchange could provide more efficiency in polarization transfer by lengthening the T<sub>1</sub>.<sup>35</sup>

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