Spectroscopy of Single N-V Centers in Diamond

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Abstract

Over the past few years, the detection of single N-V centers in diamond has attracted much interest, since it is expected to lead to innovative applications in various domains of quantum information. The N-V center in diamond is a defect consisting of a substitutional nitrogen atom adjacent to a carbon-atom vacancy. The optical transition between the $^3A$ ground state and the $^3E$ excited state has a very high quantum efficiency allowing single defect spectroscopy. Because of the paramagnetic nature of the ground electronic state, single N-V defects are believed to be promising candidates for solid state quantum computation. To date, however, the photophysics of the defect is not entirely understood. The existence of a singlet metastable state $^1A$ was challenged in a series of papers reporting hole-burning, optically detected magnetic resonance and single molecule experiments. We present here an overview of recent low and room temperature data, indicating the important role of a metastable state of the defect in single center experiments.

Introduction

Diamond and diamond-like materials are finding increasing use in various areas of modern technology because of their unique physical properties such as thermal conductivity, hardness, and high Debye temperature. Optical properties of diamond (which are mostly related to the presence of defects) are of great interest because of the proposed application of diamond as a laser source and high-efficiency photodetector for the UV [1]. More than 500 optical centers have been reported based on the absorption and luminescence spectra of diamond [2]. Half of them are believed to be impurity related. No other impurity exhibits in diamond such a variety of optical centers, as does nitrogen. Nitrogen-vacancy (N-V) defects show a particularly strong electronic transition, allowing to detect individual centers optically. Those defects show a remarkable photostability and they have been proposed as light sources for high-resolution scanning-probe microscopy and quantum cryptography [3,4,5]. The main goal of this paper is to give a short review on recent single-molecule studies on N-V centers in diamonds.

Nitrogen-Vacancy (N-V) Center in Diamond

The nitrogen-vacancy center in diamond is generated by irradiation damage and subsequent annealing of diamonds...
containing atomically dispersed nitrogen (type 1b crystals). Radiation damage creates vacancies in the diamond lattice. Annealing treatment leads to migration of vacancies towards nitrogen atoms creating the nitrogen-vacancy (NV) defect. Fig. 1a shows the structure of NV center. Mita and co-workers have reported, based on neutron irradiation experiments, that NV center is negatively charged [6].

Fig. 1. (a) Structure of the nitrogen-vacancy center in diamond. (b) Schematic representation of the energy level scheme of the center.

The excited state of the NV center is an orbital doublet and the ground state is an orbital singlet (see Fig. 1b). Optically detected magnetic resonance experiments demonstrated that the ground state is a spin triplet and the transition is \( ^3A \rightarrow ^3E \) [7,8]. The zero-phonon line associated with this transition is at 637 nm (1.945 eV) and exhibits a strong inhomogeneous broadening (30 cm\(^{-1}\)) attributed to a large strain variation in the excited \( ^3E \) state. The ground spin triplet is split into a singlet \( |0\rangle \) and a doublet \( |\pm\rangle \) separated by 2.88 GHz. Recent transient hole-burning studies [9] show that the excited state fine structure splitting is mostly dominated by spin-spin interactions. However, the detailed energetic structure of the excited \( ^3E \) state is still under debate. Ensemble site-selective methods, i.e. spectral hole burning and ODMR, allow selection of centers by the optical frequency of 0-0 transition. This may still select centers with a range of strain and, hence, the various centers can be affected differently by magnetic and electric fields. The single molecule approach, which is free of any ensemble averaging, is thus a suitable method to probe the fine structure of NV defects.

Single N-V Centers at Room Temperature

After a first report on the optical detection of single defect centers in diamond [10], this system caught attention because of the unique photostability. Detection of single N-V centers at room temperature can be achieved using confocal microscopy (for details of single molecule spectroscopy technique see ref. [11] and references therein). A suitable defect concentration can be reached by the control of diamond irradiation dose. N-V defects can be efficiently excited via the strong phonon sideband using the 514 nm line of an Ar laser. Fig. 2a shows a confocal image of a NV center containing diamond. The sample was irradiated with an electron dose 10\(^{12}\) e/cm\(^2\) and annealed for 2 hours at \( T= 800 \) °C. Average distance between N-V centers is larger than resolution of a confocal microscope allowing to address single defects optically. Some of untreated synthetic 1b-type diamonds show defect concentrations suitable for single center detection [3]. Fig. 2b shows a 30x30 \( \mu \)m area of untreated diamond (from Drukker International) containing a few N-V defects. Contrary to single molecules isolated in a matrix or immobilized on surfaces, no photobleaching of N-V defects was observed, even under excitation intensity close to the saturation conditions.

The reported saturation signal of about 5000 photocounts per second [3] is more than an order of magnitude lower that one can expect from two-level system with a lifetime corresponding to the NV center radiative decay rate (11.6 ns [12]). Weak saturation fluorescence intensity can be explained in terms of presence of the metastable singlet state (See Fig. 1b). Surprisingly, ensemble experiments give only a few indications of the presence of this state. Nearly degenerate four-wave mixing shows a relaxation time of 0.6 s, which has been attributed to the decay of a metastable state [13]. In single center experiments, evidence for the population of the metastable state comes from the bunching observed in fluorescence autocorrelation function \( g^{(2)}(\tau) \). At low excitation power the
decay time of the $g^{(1)}(\tau)$ approach to $1/k_{31}$, whereas at excitation close to the saturation the decay rate is given by $2/k_{23}$. Table 1 shows the population and depopulation rates of a metastable state obtained in single-center and ensemble experiments. Note that the back rate is only 4.11 times slower than forward rate indicating the presence of thermally or optically activated deshielding occurring at room temperature.

**Table 1.**

<table>
<thead>
<tr>
<th>Rate Work</th>
<th>$k_{31}$</th>
<th>$k_{32}$</th>
<th>$k_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence autocorrelation [18]</td>
<td>2 MHz</td>
<td>2 KHz</td>
<td></td>
</tr>
<tr>
<td>Excitation – 514 nm Room temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fluorescence autocorrelation [3]</td>
<td>4 MHz</td>
<td>1 MHz</td>
<td></td>
</tr>
<tr>
<td>Excitation – 532 nm Room temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transient hole-burning [31]</td>
<td>87 kHz</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Four-wave mixing [13]</td>
<td></td>
<td>1.7 Hz</td>
<td></td>
</tr>
<tr>
<td>$T=80$ K</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Spectroscopy of Single N-V Defects at Low Temperature.

Numerous ensemble experiments like non-degenerated four-wave mixing [13], photon echo [14], and spectral hole-burning [15,16,9] have been directed to unravel the energy level scheme of the N-V center. Under selective excitation of the pure electronic transition (637 nm) at low temperature N-V centers show a remarkable nonselective bleaching of the luminescence with two characteristic time constants of 1 ms and 40 s [17]. The fast (1ms) component can be attributed to relaxation between spin sublevels. The slow (40s) rate is possibly related to the decay of the metastable singlet state. This state becomes an efficient energy trap at low temperatures because of blocking of a thermally activated depopulation channel. Such trapping of energy is
an important obstacle to detect single N-V centers at low temperature, because of a strong decrease of saturation fluorescence intensity. The excited state population $p$ for the system with a metastable state can be obtained by calculation of the excited-state population for a two-level system $p_2$, and the result can be corrected by including an additional factor:

$$p = \frac{p_2}{(p_2 + k_{32} \tau_{31})}$$

where $k_{32}$ and $\tau_{31}$ are the population rate and lifetime of a metastable singlet state, respectively. The correction factor $k_{32} \tau_{31}$ plays an important role at low temperature, when depopulation rate of a singlet slows down to its spontaneous decay rate (seconds).

This shelving explains the decrease of the single N-V center luminescence beyond a detectable level at temperatures below 80 K. Based on the temperature dependence of the single center fluorescence intensity, it was found that the metastable $^1A$ state lies 300 cm$^{-1}$ below the excited $^3E$ state [18]. Ab initio cluster calculations reported by Goss et al. [19] predict $^3E-^1A$ splitting of 866 cm$^{-1}$, which is in a reasonable agreement with experimentally determined values. Single centers, however, can be detected also at low temperature, using the so-called "deshelving technique." The idea of the method is to apply an additional laser, which repumps the population back towards short living excited triplet $^3E$ state. With the aid of desheling, it was possible to detect fluorescence excitation spectra of the $^3A-^3E$ transition at $T = 4K$ [20].

Surprisingly, the linewidth of the excitation line was more than 4 orders of magnitude broader than expected lifetime-limited value (12 MHz). The origin of the strong line broadening can not be attributed only to dephasing because single center lines are 100 times broader than observed hole width (0.5 GHz). One of the possible interpretations could be an influence of a matrix. It must be taken into account that atomic nitrogen is always present in a high (500 ppm and more) concentration in 1b type diamond matrix. The single substitutional nitrogen is a donor with ionization energy of 1.7 eV (note, that the action of nitrogen as a donor can explain the fact, that the negative charge state is typical for defect centers in type 1b diamond). Single molecule experiments are always carried out using strong excitation intensities leading to effective nitrogen ionization in the local environment of the N-V defect. Resulting local field fluctuations may lead to a broadening of the spectral line. On the other hand, the read-out process in hole-burning experiments requires moderate laser intensities, allowing to observe narrow holes (the holewidth, however, still broader than a lifetime-limited value). It was found, that the spectral diffusion rate is particularly sensitive to desheling laser illumination (488 nm) [21].

Summarizing single center data available so far, one can conclude that low-temperature excitation spectra are strongly influenced by the effect of a metastable state population. This bottleneck can be overcome by using repumping laser, but desheling procedure leads to the strong broadening of spectral lines. A metastable singlet state lies close to excited triplet state of N-V center, and a possible solution of the problem would be to find a system where a strain in the diamond lattice would lead to an inverse energetic order of the $^3E$ and $^1A$ states. Diamond nanocrystals showing strongly increased inhomogeneous broadening of the spectral lines can be a suitable candidate for high-resolution low-temperature spectroscopy on single N-V centers.

**Fluorescence Spectroscopy on Single N-V Centers in Diamond Nanocrystals**

The so-called "explosion diamonds" – diamond nanocrystals obtained by detonation [22], – have been of great interest in last decade. X-ray crystallography and Raman spectroscopy show that even nanometer-size crystals show a diamond-type crystal lattice [23]. Material properties of ultradisperse diamond differ from natural and synthetic diamond because a considerable part of its atoms are located close to the grain surface and feel strongly its influence.

**Fig. 3.** Fluorescence emission spectra of individual N-V centers in a bulk diamond (black) and in a diamond nanocrystal (blue) at $T= 1.6 K$. Excitation was at 514 nm.
As a consequence, the crystal and band structures are distorted within an important part of the volume and differ from those of a bulk diamond [24]. Photoluminescence properties of N3 defects (three nitrogen atoms replacing carbons in a lattice) are found to have distinguishing features compared with a spectrum in a bulk diamond: short-wavelength spectral shift and the change in the shape of the spectral line [25]. Recently detection of single N-V centers in diamond nanocrystals has been reported [26,27,28,29]. Grangier and co-workers [28] observed a radiative decay rate modification, related to modification of the surrounding refraction index.

Low temperature emission spectra of N-V center in ultradisperse diamond differ from those in a bulk crystal by higher inhomogeneous broadening of their pure electronic transition lines. Fig. 3 shows the fluorescence emission spectrum of the single nanocrystalite at T = 1.6 K compared with the spectrum of the single defect in a bulk crystal. Note that well-resolved zero-phonon lines corresponding to emission of four N-V centers present in the nanocrystal are visible. A spread in the line position is about 5 nm indicating a large inhomogeneity of the local field in the vicinity of the center. The phonon sideband structure of the defect in a nanocrystal is different compared to bulk diamond. Spectral lines of N-V centers in ultra-disperse diamond are narrower than in type 1b bulk samples. This effect can be related to the suppression of the dephasing processes, because of the quantization of phonon states in nanocrystals. Quantization of acoustic phonon modes leading to unusual temperature dependence of homogeneous linewidth was recently observed in single quantum dots [30].

Conclusion

In conclusion, we briefly highlighted the state of the art of single molecule spectroscopy on color centers in diamond. Optical access to single defect centers at low temperature opens the door to unravelling of their electronic structure. Two limitations of low-temperature technique are discussed. The first is related to the existence of a metastable singlet state, irreversibly capturing excitation energy at cryogenic temperatures. A second bottleneck is the broadening of single central lines because of the influence of the matrix. The paramagnetic nature of a triplet ground state makes the system suitable for single-spin nuclear magnetic resonance experiments. Efficient desheving of a trapping state at room temperature makes individual color centers a good candidate for production of single photons on demand.

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References
