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THE INFLUENCE OF IMPLANTATION ON THE BRIGHTNESS OF NITROGEN-VACANCY CENTERS

We investigate the properties of spin states in the electronic ground state of a single nitrogen-vacancy center (NV^-) in ^{13}C-enriched diamond. The analysis is based on application of a method that uses a complete set of commuting operators (CSCO). Each state is characterized by a single set of values of CSCO. The properties of the spin states change at the level anti-crossing (LAC). This change leads to an increase in the spin-lattice relaxation rate and to a change in the ODMR spectrum. The LAC can occur during implantation and thus influence the observed yield of NV^- centers of a certain type. We assume that during cascade transitions between the states of some NV^- centers obtained by implantation, an intense ^{13}C NMR signal can be observed. It is important to note that optical pumping of such NV^- centers can be carried out in an arbitrary magnetic field.

Исследованы свойства спиновых состояний в электронном основном состоянии единого азотно-вакансионного центра (NV^-) в алмазе, обогащенном ^{13}C. Анализ основан на применении метода, который использует полный набор коммутирующих операторов (CSCO). Каждое состояние характеризуется одним набором значений CSCO. Свойства спиновых состояний изменяются на уровне пересечения уровня (LAC). Это изменение приводит к увеличению скорости спин-решеточной релаксации и изменению спектра ODMR. LAC может возникать во время имплантации и, таким образом, влиять на наблюдаемый выход NV-центров определенного типа. Мы предполагаем, что при каскадных переходах между состояниями некоторых NV-центров, полученных имплантацией, может наблюдаться интенсивный сигнал ^{13}C ЯМР. Важно отметить, что оптическая накачка таких NV-центров может осуществляться в произвольном магнитном поле

Keywords: diamond, implantation, level anti-crossing.

Ключевые слова: алмаз, имплантация, антипереход уровня.

The controlled creation of single centers in solid state systems is an important step in the development of quantum devices. In particular, the negatively charged nitrogen-vacancy (*NV^-*) center in diamond has been considered as a suitable candidate for quantum information processing and magnetometry [1; 2]. The NV^- center is an atom-like impurity in diamond crystal. The optical transitions of the NV^- allow a high degree of spin polarization at room temperature via optical pumping. The electronic spin of the NV^- centers is polarized into the ground-state magnetic sublevel $m_s = 0$ under optical illumination and measured using optical detection techniques [3].

Typically, NV^- centers in diamond are mainly created by N^+ ion implantation or by nitrogen-doping during CVD growth [4]. Many factors may in-

fluence the probability of obtaining optically observable NV^- color centers. Amongst these factors there are proximity to the surface, the implantation and annealing temperature. In this article, we will consider an additional factor: the level anti-crossing (LAC). LAC may arise during implantation and may affect the output of NV^- centers. The NV^- center has a ground state triplet $|\pm1>$ and $|0>$. In a magnetic field B along the N-V axis at $B \sim 1024$ G there are a ground state level anti-crossing (GSLAC) between $m_s=-1$ and $m_s=0$ [5]. However, in the presence of magnetic field the NV^- experiences a complex LAC, due to hyperfine interaction of the NV^- electron spin with other spins. The properties of the spin states change at the LAC. This change leads to an increase in the spin-lattice relaxation rate and to a change in the ODMR spectrum. The LAC can occur during implantation and, thus, affect the observed output of certain types of NV^- centers. We hope that this factor can have a significant impact on the improvement of the observation methods of NV^- centers and the expansion of their application.

The basis of the presented approach of NV^- LAC investigation is the calculation of NV^- energy levels in magnetic field. To find an eigenvalues for a NV^- spin Hamiltonian, it is necessary to choose the spin basis functions. Usually, simple products of one-particle spin functions are used as approximations for a many-particle basis functions. To obtain eigenvectors and eigenvalues of the spin Hamiltonian we introduce a method based on a complete set of commuting operators (CSCO). This method is well known in quantum mechanics for a long time, but has never been implemented in spectroscopy up until recently [6—8]. The Hamiltonian in the presented approach is considered either a CSCO operator, or a function of CSCO. Most of eigenvectors are qualified as entangled spin states. In our approach, energy levels can be found by solving a series of equations of a lesser degree than those that need to be solved when the Hamiltonian is diagonalized using numerical methods. It is also possible to obtain analytical expressions for certain energy levels. The properties of spin states are uniquely determined by CSCO and each spin eigenvector is determined by a unique set of CSCO values.

The NV^- center in diamond consists of a nitrogen atom, which substitutes for a carbon atom, and a lattice vacancy. Its ground state is triplet state ($S=1$) with an spin quantization axis provided by the NV^- center axis of symmetry. We consider a single NV^- center with three of ^{13}C atoms in the first shell. The spin of ^{13}C nucleus is $I=1/2$. The hyperfine coupling of nearest neighbor carbons is around 130 MHz [8]. Hyperfine coupling of the electron spin to ^{14}N at the NV^- center around 3 MHz. The ground-state spin Hamiltonian of NV^- center in the presence of magnetic field B reads as (in frequency units):

$$\hat{H} = D\left(\hat{S}_z^2 - \hat{S}^2/3\right) - \gamma_e \hat{S}_z B_z + A_\perp (\hat{S}_x \hat{I}_x + \hat{S}_y \hat{I}_y) + A_{||} \hat{S}_z \hat{I}_z - \gamma_n \hat{I}_z B_z, \qquad (1)$$

where $\vec{\hat{S}}$ is electron spin operator, $\vec{\hat{I}}_i$ is spin operator of ^{13}C nucleus (i=1, 2, 3), $\vec{\hat{I}} = \vec{I}_1 + \vec{I}_2 + \vec{I}_3$, $D \approx 2870\ MHz$ is the fine structure splitting, $A_{||} = -121\ MHz$ and $A_\perp = 166$ MHz are the axial and non-axial magnetic hy-

perfine parameters, z-axis aligns with electronic spin quantization axis, γ_e is the electron gyromagnetic ratio and $\gamma_n = 10.705 kHz/mT$ is the nuclear gyromagnetic ratio of ^{13}C.

To calculate the energy spectrum for the Hamiltonian we first determine the total spin operator:

$$\hat{\vec{J}} = \hat{\vec{S}} + \hat{\vec{I}}.$$

The operators

$$\hat{J}^2, \hat{J}_z, \hat{I}_{12}^2, \hat{I}^2, \hat{\vec{S}}^2, \hat{I}_1^2, \hat{I}_2^2, \hat{I}_3^2$$

form a complete set of commuting operators. Note that the Hamiltonian (1) does not commute with the operator $\hat{J}^2$. The operators

$$\hat{H}, \hat{J}_z, \hat{I}_{12}^2, \hat{I}^2, \hat{\vec{S}}^2, \hat{\vec{I}}_1^2, \hat{\vec{I}}_2^2, \hat{\vec{I}}_3^2$$

also form a complete set of commuting operators (CSCO). The properties of the eigenvectors of this set are uniquely determined by CSCO and every spin eigenvector is determined by the unique value set of CSCO: $\left|E_n, M_j, I_{12}, I, S, I_1, I_2, I_3\right\rangle$. Since for all of these states $S=1$, $I_1 = I_2 = I_3 = 1/2$, then the equation for the eigenvalues and eigenvectors of the Hamiltonian (1) can be written as

$$\hat{H}\left|E_n, M_j, I_{12}, I\right\rangle = E_n\left|E_n, M_j, I_{12}, I\right\rangle, \quad (2)$$

where the index n is introduced in order to distinguish the states with different values of energy E. Having solved equation (2), we found all energy levels and the corresponding eigenvectors of the NV^- center in a magnetic field.

Thus, all the energy levels of the NV^- center in a magnetic field were calculated. Radiation transitions between these states are subject to selection rule $\Delta M_j = \pm 1$.

Figure 1 shows a comparison between theoretical (vertical) and experimental [9; 10] NV^- ODMR spectra.

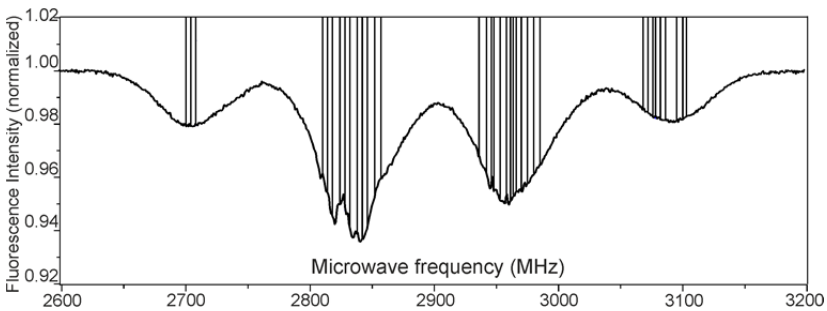

Fig. 1. Theoretical (vertical lines) and experimental [9; 10] NV^- ODMR spectra

The ODMR spectrum consists of four irregularly shaped overlapping peaks with a substructure of features observed on the two central peaks. These features are due to the LAC. Indeed, the energy levels are pairwise equal ($E_{11(12)} = E_{13(14)}$, $E_{15(16)} = E_{17(18)}$) and we have the special case of the LAC, which is not removed by magnetic field. Therefore, in the states $\left|E_{11(12)}, 1/2, 1, 1/2\right\rangle$, $\left|E_{13(14)}, 1/2, 0, 1\right\rangle$, $\left|E_{15(16)}, -1/2, 1, 1/2\right\rangle$, $\left|E_{17(18)}, -1/2, 0, 1\right\rangle$ the observed I_{12} and I are not a functions of the observed E [11]. This means that if the observed E has the definite value ($E_{11(12)} = E_{13(14)}$, $E_{15(16)} = E_{17(18)}$), then in these states observed I_{12} and I do not have automatically definite values. The uncertainty of the values of I_{12} and I leads to an increase in the relaxation rate of these states. Taking into account intersystem crossing, we can assume that these states do not contribute to photoluminescence, and their microwave excitation will lead to a substructure in the ODMR spectrum.

Let $A_{\perp} = 0$, then the Hamiltonian (1) takes the form

$$\hat{H} = D\left(\hat{S}_z^2 - \hat{S}^2/3\right) - \gamma_e \hat{S}_z B_z + A_{||} \hat{S}_z \hat{I}_z - \gamma_n \hat{I}_z B_z . \quad (3)$$

The operators

$$\hat{I}_z, \hat{S}_z, \hat{I}_{12}^2, \hat{I}^2, \hat{\vec{S}}^2, \hat{I}_1^2, \hat{I}_2^2, \hat{I}_3^2$$

also form a CSCO and eigenvectors are $\left|\mathrm{M_I}, \mathrm{m_s}, \mathrm{I_{12}}, \mathrm{I}\right\rangle$. Hamiltonian (3) commute with this set. Moreover, the Hamiltonian (3) is a function of this operator set. The energy levels and the corresponding eigenvectors of the NV- center in a magnetic field are listed in the Supplementary materials. In particular, when $A_{\perp} = 0$, we get

$$E_8 = -2D/3 - 3\gamma_n B_z/2 , \; E_{10} = -2D/3 + 3\gamma_n B_z/2 , \quad (4)$$

$$E_{12} = E_{14} = E_{21} = -2D/3 - \gamma_n B_z/2 , \quad (5)$$

$$E_{16} = E_{18} = E_{24} = -2D/3 + \gamma_n B_z/2 . \quad (6)$$

When the equalities (4—6) are satisfied, the spin states

$$\left|E_8, 3/2, 1, 3/2,\right\rangle \; \left|E_{10}, -3/2, 1, 3/2,\right\rangle,$$

$$\left|E_{12}, 1/2, 1, 1/2\right\rangle, \; \left|E_{14}, 1/2, 0, 1/2\right\rangle, \; \left|E_{21}, 1/2, 1, 3/2\right\rangle, \quad (7)$$

$$\left|E_{16}, -1/2, 1, 1/2\right\rangle, \; \left|E_{18}, -1/2, 0, 1/2\right\rangle, \; \left|E_{24}, -1/2, 1, 3/2\right\rangle$$

change and take the following form:

$$|E_8, 3/2, 1, 3/2\rangle \to |3/2, 0, 1, 3/2\rangle = \alpha_1\alpha_2\alpha_3|0\rangle,$$

$$|E_{10}, -3/2, 1, 3/2\rangle \to |-3/2, 0, 1, 3/2\rangle = \beta_1\beta_2\beta_3|0\rangle,$$

$$|E_{12}, 1/2, 1, 1/2\rangle \to |1/2, 0, 1, 1/2\rangle = \frac{1}{\sqrt{6}}(2\alpha_1\alpha_2\beta_3 - \alpha_1\beta_2\alpha_3 - \beta_1\alpha_2\alpha_3)|0>,$$

$$|E_{14}, 1/2, 0, 1/2\rangle \to |1/2, 0, 0, 1/2\rangle = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\alpha_3|0>,$$

$$|E_{21}, 1/2, 1, 3/2\rangle \to |1/2, 0, 1, 3/2\rangle = \frac{1}{\sqrt{3}}(\alpha_1\alpha_2\beta_3 + \alpha_1\beta_2\alpha_3 + \beta_1\alpha_2\alpha_3)|0>, \quad (8)$$

$$|E_{16}, -1/2, 1, 1/2\rangle \to |-1/2, 0, 1, 1/2\rangle = \frac{1}{\sqrt{6}}(2\beta_1\beta_2\alpha_3 - \alpha_1\beta_2\beta_3 - \beta_1\alpha_2\beta_3)|0>,$$

$$|E_{18}, -1/2, 0, 1/2\rangle \to |-1/2, 0, 0, 1/2\rangle = \frac{1}{\sqrt{2}}(\alpha_1\beta_2 - \beta_1\alpha_2)\beta_3|0>,$$

$$|E_{24}, -1/2, 1, 3/2\rangle \to |-1/2, 0, 1, 3/2\rangle = \frac{1}{\sqrt{3}}(\alpha_1\beta_2\beta_3 + \beta_1\alpha_2\beta_3 + \beta_1\beta_2\alpha_3)|0>,$$

where $|0\rangle$ is eigenvector of operator $\hat{S}_z$, α_i and β_i are eigenvectors of operator $\hat{I}_{iz}$ with eigenvalues 1/2 and –1/2, respectively. The states (8) are spin-polarized states of ^{13}C nuclei and electron spin. The electron spin in these states is not entangled with nuclear spins. Moreover, since in the states (8) the quantum number m_s is a good quantum number ($m_s = 0$), then under optical pumping these states are effectively populated. It is seen from equalities (5) that LAC takes place for the states $|1/2,0,1,1/2\rangle$, $|1/2,0,0,1/2\rangle$ and $|1/2,0,1,3/2\rangle$. Therefore, in these states, the observed I_{12} and I are not a functions of the observed E [11]. This means that if the observed E has the definite value ($E = -2D/3 - \gamma_n B_z/2$), then in these states observed I_{12} and I do not have automatically definite values. The uncertainty of the values of I_{12} and I leads to an increase in the relaxation rate of these states. Taking into account intersystem crossing, we can assume that these states do not contribute to photoluminescence. A similar conclusion holds for the states $|-1/2,0,1,1/2\rangle$, $|-1/2,0,0,1/2\rangle$ and $|-1/2,0,1,3/2\rangle$ at $E = -2D/3 + \gamma_n B_z/2$.

Thus, for the ODMR spectrum of such an NV center, two peaks are characteristic: one peak is due to transitions to the state $|3/2,0,1,3/2\rangle$ with energy $E_8 = -2D/3 - 3\gamma_n B_z/2$, the other peak is due to transitions to the state $|-3/2,0,1,3/2\rangle$ with energy $E_{10} = -2D/3 + 3\gamma_n B_z/2$. The energy levels (4—6) do not depend on the parameter $A_{||}$ of the hyperfine interaction and, therefore, in a weak magnetic field difference between peaks is small. For example, in the Earth's magnetic field this difference ≤ 1.5 *kHz*. Thus, the ODMR

spectrum of such an NV^- center in a weak magnetic field coincides with the ODMR spectrum of a single NV^- center that does not interact with neighboring spins.

We assume that during cascade transitions between states (7) one can observe an intense ^{13}C NMR signal. It is important to note that in this NMR experiment, unlike [12; 13], the optical pumping of NV^- centers can be carried out in an arbitrary magnetic field.

We note that parameter $A_\perp$ represent an isotropic contribution to the energy. This contribution has small value for the implantation, since the ion beam has strong anisotropy. This conclusion is consistent with the results of ref. [4]. Indeed, in [4], a diamond layer of nanometer thickness with ^{13}C carbon atoms on two substrates, called samples I and II, was manufactured by chemical vapour deposition (CVD). In sample I the ^{13}C layer was additionally doped with nitrogen and sample II was implanted with nitrogen ions, in order to create NV^- centers in the vicinity of the ^{13}C layer. Three implantation energies were used — 5, 2.5 and 1 keV. ODMR spectra of over 483 NV^- centers (sample I) and 584 NV^- centers (sample II) at zero magnetic field showed strong coupling of the NV-s to ^{13}C. The spectra were divided into four groups, distinguished by the number of ^{13}C next to the vacancy: NVs (A) lacking a first-shell ^{13}C spin, (B) interacting with a single first-shell ^{13}C spin, (C) interacting with two first-shell ^{13}C spins and (D) interacting with three first-shell ^{13}C spins. It were obtained the probability p_A, p_B, p_C, p_D of finding an NV^- center of group A, B, C, D (see Table).

Probability of finding the four groups of NV-centers in samples I and II (from ref. [4])

Probability in %	Sample I	Sample II		
		E_{impl} = 5 keV	E_{impl} = 2.5 keV	E_{impl} = 1keV
p_A	73.4	88.1	84.5	88.5
p_B	13.7	11.9	14.6	11.5
p_C	7.2	0	1.0	0
p_D	5.7	0	0	0

From the results presented in Table I, it can be seen that the probability p_D for sample II is zero. Therefore, it is natural to assume that the NV^- centers of group D are not formed in sample II, obtained by implantation. However, based on our results, it can also be assumed that the implantation of nitrogen ions also leads to the formation of NV^- centers of group D, but their ODMR spectra coincide with ODMR spectra of group A in a weak magnetic field.

From the results presented in Table I, it can also be seen that the output of type A NV^- centers increases with implantation. This is an indirect confirmation of the validity of our assumption. In order to detect the NV^- centers of group D obtained by implantation, it is necessary to change the experimental conditions.

We investigated the properties of the spin states in single diamond NV^- center in the electronic ground state. The used approach is based on the us-

ing a complete set of commuting operators (CSCO). Each state is characterized by a single set of values of CSCO. The uniqueness of this set of values is sometimes violated. In this case the energy levels are pairwise equal and can be considered a special case of a LAC. The properties of the spin states change at the LAC. This change leads to an increase in the spin-lattice relaxation rate and to a change in the ODMR spectrum. The LAC can occur during implantation and thus influence the observed yield of NV^- centers of a certain type. We assume that during cascade transitions between the states of some NV^- centers obtained by implantation, an intense ^{13}C NMR signal can be observed. It is important to note that optical pumping of such NV^- centers can be carried out in an arbitrary magnetic field.

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