УДК 538.9

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PHOTOLUMINESCENCE OF THE $^{15}NV^-$-CENTER CREATED BY IMPLANTATION

We study the properties of the spin states in single diamond $^{15}NV^-$-center at the ground state level anti-crossing. Our approach uses a complete set of commuting operators. We have shown that under certain conditions in $^{15}NV^-$-center it is possible to obtain a 100 % transfer of polarization from the electron spin to the spin of the ^{15}N nucleus. We believe that these conditions can be satisfied for $^{15}NV^-$-centers obtained by implantation.

Мы изучаем свойства спиновых состояний в одиночном алмазном $^{15}NV^-$-центре на уровне пересечения основного состояния. Наш подход использует полный набор коммутирующих операторов. Мы показали, что при определенных условиях в $^{15}NV^-$-центре можно получить 100%-й перенос поляризации от спина электрона к спину ядра ^{15}N. Мы полагаем, что эти условия могут быть выполнены для $^{15}NV^-$-центров, полученных имплантацией.

Keywords: diamond, implantation, level anti-crossing.

Ключевые слова: алмаз, имплантация, антипереход уровня.

The negatively charged nitrogen-vacancy (NV^-) centers in diamond are used in a broad range of applications. They serve as qubits [1] or probes for various physical properties like magnetic field [2], electric field [3]. They can also be used to detect the properties of electronic and nuclear spins such as substitutional nitrogen (P_1) centers [4] or ^{13}C atoms [5]. For all these applications it is important to know in detail the hyperfine structure of the NV^--center.

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 [6]. The NV^--center has a ground state triplet $|\pm 1\rangle$ and $|0\rangle$ separated by zero-field splitting at $D \approx 2.87$ GHz. In a magnetic field B along the N-V axis, the Zeeman splitting $\gamma_e B$ with electronic gyromagnetic ratio $\gamma_e = 28.025$ GHz/T cancels the ground state zero-field splitting at a magnetic field at $B \sim 1024$ G, leading to a ground state level anti-crossing (LAC) between $m_s = |-1\rangle$ and $m_s = |0\rangle$ [7]. 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 diamond lattice consist also other spins i.e., electronic and nuclear spins that cannot be initialized or read out optically. A key challenge is to

transfer polarization controllably from bright NV spins to other spins. The authors of ref. [1] used the interaction of the electron spin NV^--center with nearest ^{13}C nuclear spin for the demonstration of quantum gate NOT and a conditional two-qubit gate. They used states of the form $|m_s\rangle|m_i\rangle$, where $m_s = \pm 1$, $m_i = \pm 1/2$. We will show that similar states can occur in a $^{15}NV^-$-center under appropriate conditions.

The basis of the presented approach of *NV* LAC investigation is a method based on a complete set of commuting operators (CSCO). 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 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 [8; 9]. The Hamiltonian in the presented approach is considered either a CSCO operator, or a function of CSCO. The properties of the spin states are uniquely determined by CSCO. Every eigenvector in this approach is determined by the unique value set of CSCO. Most of the resulting spin states are qualified as entangled spin states. The energy levels are found by solving a series of equations of less degree, than the ones found by diagonalizing the Hamiltonian using the numerical methods. It is also possible to obtain analytical expressions for some of the energy levels.

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 a ^{15}N nitrogen isotope having a nuclear spin $I=1/2$. The ground-state spin Hamiltonian of *NV*$^-$-center in the presence of magnetic field *B* reads as (as per [10], in frequency units):

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

where $D \approx 2870$ *MHz* is the fine structure splitting, $A_{||} = 3.03$ MHz and $A_{\perp} = 3.65$ MHz are the axial and non-axial magnetic hyperfine parameters, z-axis aligns with electronic spin quantization axis, $\gamma_e = 28.025\ \mathrm{GHz/T}$ is the electron gyromagnetic ratio and $\gamma_n = 4.316\ \mathrm{kHz/mT}$ is the ^{15}N gyromagnetic ratio.

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 $\hat{J}^2, \hat{J}_z, \hat{S}^2, \hat{I}^2$ form a complete set of commuting operators (CSCO). The eigenvectors $|J, M_z\rangle$ of this CSCO takes the form

$$|3/2,3/2\rangle = |1,1\rangle|1/2,1/2\rangle,$$

$$|3/2,1/2\rangle = \sqrt{\frac{2}{3}}|1,0\rangle|1/2,1/2\rangle + \frac{1}{\sqrt{3}}|1,1\rangle|1/2,-1/2\rangle,$$

$$|3/2,-1/2\rangle = \sqrt{\frac{2}{3}}|1,0\rangle|1/2,-1/2\rangle + \frac{1}{\sqrt{3}}|1,-1\rangle|1/2,1/2\rangle, \quad (2)$$

$$|3/2,-3/2\rangle = |1,-1\rangle|1/2,-1/2\rangle.$$

$$|1/2,1/2\rangle = \sqrt{\frac{2}{3}}|1,1\rangle|1/2,-1/2\rangle - \frac{1}{\sqrt{3}}|1,0\rangle|1/2,1/2\rangle,$$

$$|1/2,-1/2\rangle = \frac{1}{\sqrt{3}}|1,0\rangle|1/2,-1/2\rangle - \sqrt{\frac{2}{3}}|1,-1\rangle|1/2,1/2\rangle. \quad (3)$$

Note that the total spin *J* of the NV^--center is not preserved, as the Hamiltonian (1) does not commute with the operator $\hat{J}^2$. At the same time, the Hamiltonian commutes with the projection of the total spin, the square of the electron spin and nuclear spin square:

$$\left[\hat{H},\hat{J}_z\right] = \left[\hat{H},\hat{S}^2\right] = \left[\hat{H},\hat{I}^2\right] = 0. \quad (4)$$

Set of operators $\hat{H}$, $\hat{J}_z$, $\hat{S}^2$, $\hat{I}^2$ is also a CSCO. This set has the unique system of eigenvectors: each eigenvector is characterized by a single set of commuting observables values. Consequently, the spin states of the NV^--center are characterized by the energy *E*, the projection M_z of the total spin, the electron spin *S,* and the nuclear spin *I:* $|E,M_z,S,I\rangle$. Since for all of these states $S=1$, $I=1/2$, then the equation for the eigenvalues and eigenvectors of the Hamiltonian (1) can be written as

$$\hat{H}\left|E^{(i)}_{M_z}\right\rangle = E^{(i)}_{M_z}\left|E^{(i)}_{M_z}\right\rangle, \quad (5)$$

where the index (*i*) is introduced in order to distinguish the states with the even values of M_z and different values of energy *E*. Solving the equation (5) gives

$$E^{(\pm)}_{1/2} = \left[-D/3 - A_{||}/2 + \Gamma_e \pm \sqrt{\left(D - A_{||}/2 + \Gamma_e - \Gamma_n\right)^2 + 2A_\perp{}^2}\right]/2,$$

$$E^{(\pm)}_{-1/2} = \left[-D/3 - A_{||}/2 - \Gamma_e \pm \sqrt{\left(D - A_{||}/2 - \Gamma_e + \Gamma_n\right)^2 + 2A_\perp{}^2}\right]/2,$$

$$E_{\pm 3/2} = D/3 + A_{||}/2 \pm \Gamma_e \pm \Gamma_n/2, \quad (6)$$

$$\left|E_{3/2}\right\rangle = |1,1\rangle|1/2\,,1/2\rangle,$$

$$\left|E_{-3/2}\right\rangle = |1,-1\rangle|1/2\,,-1/2\rangle,$$

$$\left|E_{1/2}^{(\pm)}\right\rangle = C_1^{\pm}|3/2\,,1/2\rangle + C_2^{\pm}|1/2\,,1/2\rangle,$$

$$\left|E_{-1/2}^{(\pm)}\right\rangle = C_1^{\pm}|3/2\,,-1/2\rangle + C_2^{\pm}|1/2\,,-1/2\rangle,$$

where $\Gamma_e = \gamma_e B_z$, $\Gamma_n = \gamma_n B_z$. The states $\left|E_{1/2}^{(\pm)}\right\rangle$ and $\left|E_{-1/2}^{(\pm)}\right\rangle$ are entangled states.

The energy $E_{M_z}^{(i)}$ is a single-valued function of the total spin projection M_z. This means that if the projection M_z of the total spin in a certain state has a definite value, then the energy $E_{M_z}^{(i)}$ of this state also has a definite value. The opposite statement is also true: if the energy $E_{M_z}^{(i)}$ has a definite value, then the projection M_z also has a definite value. It is important to note that this function's uniqueness is violated, in particular, in a zero magnetic field. In this case the energy levels are pairwise equal and we have the complete level anti-crossing (CLAC):

$$E_{3/2} = E_{-3/2}, \qquad E_{1/2}^{(+)} = E_{-1/2}^{(+)}, \qquad E_{1/2}^{(-)} = E_{-1/2}^{(-)}. \tag{7}$$

When the equalities (7) are satisfied, all of these spin states do not have definite values for the total spin projection. The spin-lattice relaxation rates of all these states will increase, therefore, the ODMR spectrum of such an NV^--center will not have characteristic dips.

We further discuss the conditions under which one can observe the effective transfer of polarization from the electron spin to the nuclear spin in the $^{15}NV^-$-center. Assuming $A_\perp = 0$ in (1), the Hamiltonian $\hat{H}$ of the $^{15}NV^-$-center can be written in the following form:

$$\hat{H} = D\left(\hat{S}_z^2 - \hat{S}^2/3\right) + A_{||}\hat{S}_z\hat{I}_z + \gamma_e\hat{S}_z B_z + \gamma_n\hat{I}_z B_z. \tag{8}$$

We note also that the set of the operators $\hat{S}_z, \hat{I}_z, \hat{S}^2, \hat{I}^2$ is a CSCO. The Hamiltonian (8) commutes with all operators of this set. Consequently, the operator $\hat{H}$ is a function of this operator set. The eigenvalues and eigenvectors of Hamiltonian (8) are:

$$E_{3/2} = D/3 + A_{||}/2 + \Gamma_e + \Gamma_n/2,\ E_{-1/2}^{(+)} = D/3 - A_{||}/2 - \Gamma_e + \Gamma_n/2,$$

$$E_{-3/2} = D/3 + A_{||}/2 - \Gamma_e - \Gamma_n/2,\ E_{1/2}^{(-)} = -2D/3 + \Gamma_n/2,$$

$$E_{1/2}^{(+)} = D/3 - A_{||}/2 + \Gamma_e - \Gamma_n/2,\ E_{-1/2}^{(-)} = -2D/3 - \Gamma_n/2, \tag{9}$$

$$\left|E_{3/2}\right\rangle = |1,1\rangle|1/2\,,1/2\rangle, \qquad \left|E^{(+)}_{-1/2}\right\rangle = |1,-1\rangle|1/2\,,1/2\rangle,$$

$$\left|E_{-3/2}\right\rangle = |1,-1\rangle|1/2\,,-1/2\rangle, \quad \left|E^{(-)}_{1/2}\right\rangle = |1,0\rangle|1/2\,,1/2\rangle,$$

$$\left|E^{(+)}_{1/2}\right\rangle = |1,1\rangle|1/2\,,-1/2\rangle, \quad \left|E^{(-)}_{-1/2}\right\rangle = |1,0\rangle|1/2\,,-1/2\rangle.$$

We see that in such a $^{15}NV^-$-center there is a 100 % transfer of polarization from the electron spin to the spin of the ^{15}N nucleus: all states are completely polarized and have the form $|m_s\rangle|m_i\rangle$. States $\left|E^{(-)}_{1/2}\right\rangle$ and $\left|E^{(-)}_{-1/2}\right\rangle$ under optically pumped are effectively populated. The energies of these states do not depend on the parameter $A_{||}$. We note that in a zero magnetic field these energies are equal $E^{(-)}_{1/2} = E^{(-)}_{-1/2}$ (LAC). Therefore, the observable I_z in zero magnetic field is not a function of the observable E [11]. This means that the quantum number m_i in a zero magnetic field for the states $\left|E^{(-)}_{-1/2}\right\rangle$ and $\left|E^{(-)}_{1/2}\right\rangle$ is not has a definite value. We note that in a weak magnetic field (for example, in the field of the Earth) these energies are close to each other: $E^{(-)}_{1/2} \approx E^{(-)}_{-1/2}$ (LAC). The energy splitting $\delta = E^{(-)}_{1/2} - E^{(-)}_{-1/2}$ at $B = 0.5$ *G* (Earth's magnetic field at its surface) is only 200 Hz, therefore, the two peaks of the ODMR spectrum of such a $^{15}NV^-$-center will overlap. This means that the quantum number m_i in a weak magnetic field also is not a good quantum number. In contrast, the quantum number m_s is a good quantum number. For states $\left|E^{(-)}_{-1/2}\right\rangle$ and $\left|E^{(-)}_{1/2}\right\rangle$, the value of m_s is 0 and, therefore, such a $^{15}NV^-$-center is a bright center. The quantum number m_i for these states will be a good quantum number in a sufficiently strong magnetic field.

Typically, NV^--centers in diamond are mainly created by N^+ ion implantation [12—14] or by nitrogen-doping during CVD growth [15]. Diamond substrates already contain NV^--centers. To distinguish between native and artificial NV^--centers, ^{15}N isotopes are often used for the implantation. The different nuclear spins of I=1 for ^{14}N and I=1/2 for ^{15}N result in hyperfine triplet or doublet splittings in $^{14}NV^-$ and $^{15}NV^-$-centers, respectively. In ref. [12] $^{14}NV^-$-centers in diamond have been generated via ^{14}N ions implantation and ODMR was used to measure the hyperfine splitting. The analysis of a number of NV^--color centers leads to the conclusion, that on average two nitrogen ions need to be implanted per $^{14}NV^-$-center. $^{15}NV^-$-centers were created in ref. [13] by implantation of the $^{15}N^+$ ions. The analysis indicates that 1 in 40 implanted $^{15}N^+$ ions give rise to an optically observable $^{15}NV^-$-center. Many factors may influence the yields for $^{15}NV^-$-centers. We consider an additional factor that can affect the yield of observable $^{15}NV^-$-centers: LAC. The ^{15}N ion beam used in the implantation process has strong anisotropy, therefore, it can be assumed that the isotropic contribution to the energy of the $^{15}NV^-$ center produced by implantation will be small.

We investigated the properties of the spin states in single diamond $^{15}NV^-$-center at the LAC. Our approach uses a complete set of commuting operators. Each state is characterized by a single set of the values of CSCO. The uniqueness of this set of values is violated, in particular, in a zero magnetic field. In this case the energy levels are pairwise equal and can be considered a special case of a level anti-crossing. We have shown that under certain conditions in $^{15}NV^-$-center it is possible to obtain a 100 % transfer of polarization from the electron spin to the spin of the ^{15}N nucleus. We believe that these conditions can be satisfied for $^{15}NV^-$-centers obtained by implantation.

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