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Cross-relaxation of nitrogen-related centers in diamond

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We studied the cross-relaxation processes between the centers of substitutional nitrogen (P1 center), nitrogen pairs and a negatively charged nitrogen vacancy (NV) center in synthetic diamond grown at high pressure and high temperature (using the HPHT method), as well as their angular dependences on the magnetic field. For the first time the cross-relaxation between nitrogen pairs and NV centers has been identified that based on detailed experimental angular dependencies and their calculations.

Keywords: diamond, NV center, level anti-crossing, optically detected magnetic resonance.

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1. Introduction

Diamond, due to its unique properties (high thermal conductivity, high refractive index and dispersion, chemical stability, transparency in a wide spectral range, low dielectric permittivity etc.) is promising for use as heat-release plates in microwave transistors, powerful multi-chip modules and series of semiconductor lasers. Besides, it is widely used to manufacture micro-electromechanical systems, acousto-electronic devices (filters on surface acoustic waves of gigahertz range) and ionising radiation detectors. But the main application, which attracts many researchers, is the use of diamonds in quantum spintronics [1].

Impurities in the diamond to a large extent define physical (electric and optic) properties of crystals. The main impurity in diamonds is nitrogen, which may be present in them as a separate impurity of substitution or in the form of a group of atoms.

The most interesting is the negatively charged nitrogen-vacancy (NV) center in the diamond, because of its unique physical properties. The NV-center is one of many point defects in the diamond, which is a damage to the structure of the crystalline lattice occurring when the carbon atom is removed from the lattice site, and the vacancy formed is bound to the nitrogen atom [2]. Spin states of a single localized electron are easily manipulated with light, magnetic, electric and microwave fields. Such manipulations are possible even at room temperature [3–6]. The NV-center has a long time of coherence reaching several milliseconds. Currently the NV-center may be seen as the basic element of the future quantum computer [7–9]. Besides, the diamond containing the NV-centers is a promising material for use as a source of single photons and a new generation of magnetometers with nanoscale resolution [10–14].

2. Samples and experimental procedure

Commercial single crystals of synthetic diamonds grown by HPHT (high-pressure high-temperature growth) method and having dimensions of $\sim 3 \times 3 \times 1\,\mathrm{mm}$ were studied. In the studied samples the initial concentration of nitrogen was approximately 10 ppm. Then the single crystals were irradiated with electrons in a reactor at a dose of $\sim 10^{18}\,\mathrm{cm}^{-2}$ and subsequently annealed ($\sim 2\,\mathrm{h}$) in vacuum at temperature of 900 °C.

The experiments were carried out using an electromagnet of a standard serial spectrometer of electron paramagnetic resonance (EPR) JEOL JES-PE. Spectra of integral photoluminescence (PL) dependence on the magnetic field were registered at room temperature. The magnetic field was modulated with low frequency 80 Hz and amplitude of 2 G. The experiment used a laser with wavelength of 532 nm and capacity of 50 mW, which provided for the continuous optical excitation. To focus the laser radiation on the sample, a lens was used with a tenfold zoom, focal distance of $f = 40\,\mathrm{mm}$ and aperture number 0.55. PL light in the range of $650-800\,\mathrm{nm}$ passed an OS13 glass filter and a dichroic mirror to cut off the laser radiation, and was focused with the lens onto a silicon semiconductor photodetector. Measurements were carried out using lock-in detection of the PL signal and the modulation of the magnetic field. When the orientation dependences of the spectra were studied, the samples were rotated in the crystallographic plane (110) to ensure the possibility to study the properties of the crystal in all main high-symmetry directions. The accuracy of sample orientation in the applied magnetic field along axis $\langle 111 \rangle$ was determined using a well-resolved spectrum of the ground state level anti-crossing (GSLAC) of the NV-center.

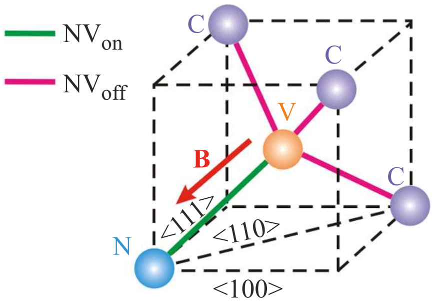

Figure 1. Structure of NV-center in diamond lattice.

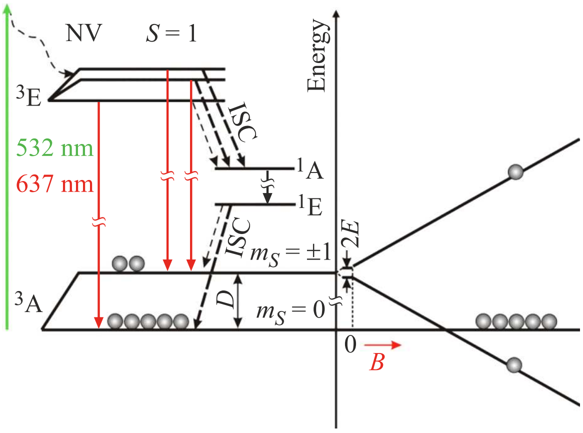

Figure 2. Scheme of NV-center levels.

3. Results and discussions

The studied synthetic diamonds had high concentration of nitrogen that may be located in the diamonds as single atoms that substitute carbon (P1-center), pairs of atoms or complexes consisting of substitutional nitrogen atom and adjacent carbon vacancy (NV-center, W15) etc. The spin Hamiltonian describing the spectra of the P1-center has the following form [15]:

$$H = g\mu_B \mathbf{B}\cdot\mathbf{S} + \mathbf{S}\cdot\mathbf{A}\cdot\mathbf{I},$$

where the first term describes Zeeman interaction in the magnetic field $\mathbf{B}$, μ_B — Bohr magneton, $S = 1/2$ — electron spin of the center $S = 1/2$, g — electron g-factor equal to 2.0024; the second term reflects hyperfine (HF) interaction in the form of a tensor $\mathbf{A}$ between an unpaired electron and one nitrogen nucleus ^{14}N (nuclear spin $I = 1$). HF structure parameters for the P1-center: $\mathbf{A}_\parallel = 114$ MHz, $\mathbf{A}_\perp = 82$ MHz.

High concentration of nitrogen in the synthetic diamonds leads to the formation of the centers consisting of the pairs of the nitrogen atoms. Series of EPR signals were observed in the synthetic diamonds enriched with nitrogen and grown in the solvent/catalyst system Fe–Ni–C at temperature of 1750 K and pressure of 5.5 GPa by the temperature gradient method in paper [16]. The observed signals were assigned

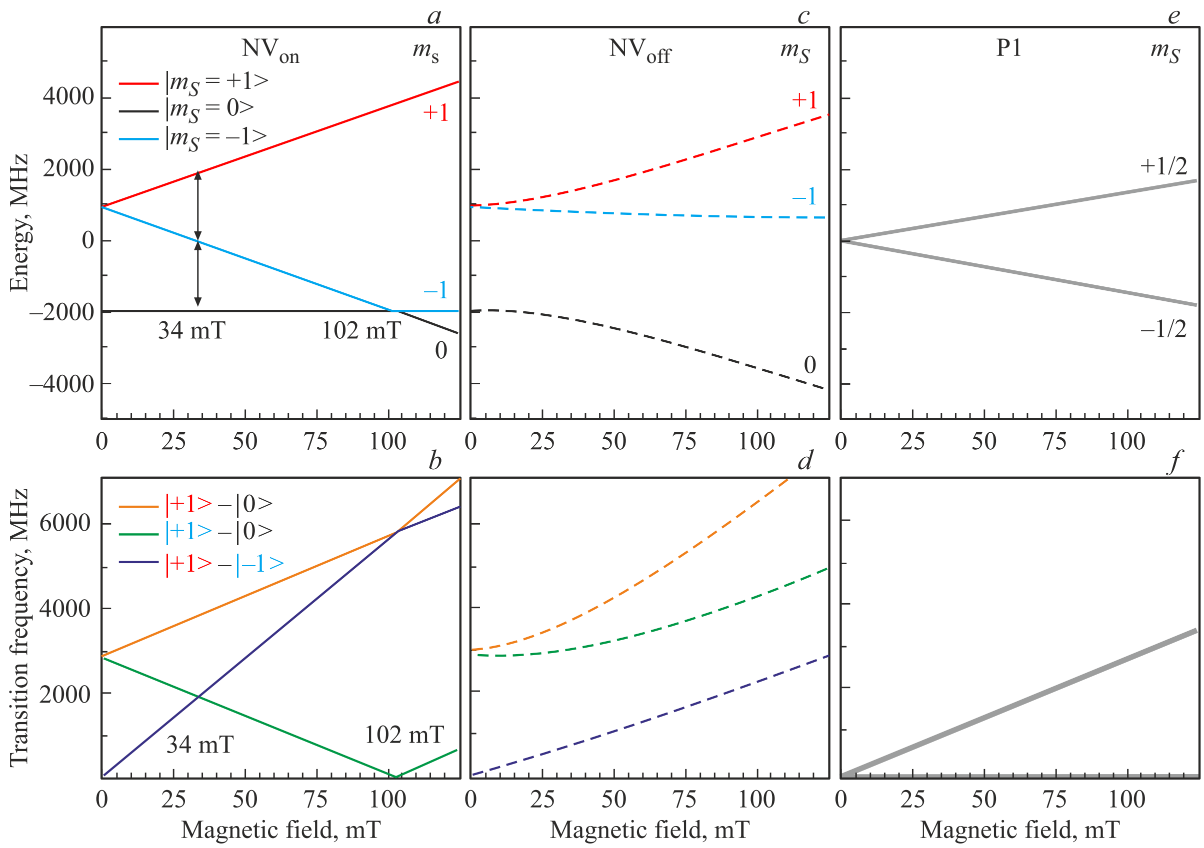

Figure 3. *a, c* and *e*) Dependence of energy levels on magnetic field at $\mathbf{B} \parallel \langle 111\rangle$ for NV- and P1-centers. *b, d* and *f*) Level transition energies of NV- and P1-centers as magnetic field functions at $\mathbf{B} \parallel \langle 111\rangle$.

to three centers related to the pairs of nitrogen atoms. One of them is the NOC4 center interpreted as the Novosibirsk Oxford Collaboration. It corresponds to the superposition of the variously oriented pairs of the nitrogen atoms with the distance between them of more than 0.7 nm. This center is described by the spin Hamiltonian of the following form:

$$H = g\mu_B \mathbf{B}\cdot\mathbf{S} + \mathbf{S}\cdot(\mathbf{A}_1\cdot\mathbf{I}_1 + \mathbf{A}_2\cdot\mathbf{I}_2),$$

where the second term reflects the HF interaction in the form of tensors $\mathbf{A}_1$ and $\mathbf{A}_2$, which are axially symmetrical to the main values $\mathbf{A}_{\parallel} = 114\,\mathrm{MHz}$, $\mathbf{A}_{\perp} = 82\,\mathrm{MHz}$, $\mathbf{I}_1 = \mathbf{I}_2 = 1$, $S = 1/2$ and $g = 4.0085$.

The electron irradiation and subsequent high-temperature annealing lead to the formation of the NV-centers in the synthetic diamonds. The schematic structure of the NV-center is presented in Figure 1, where the magnetic field is $\mathbf{B} \parallel \langle 111\rangle$. The NV-center in diamond consists of the pair of the nitrogen atom (shown in blue), substituting the carbon atom (purple), and the vacancy in neighboring lattice site (orange). The subscript in the designation $\mathrm{NV_{on}}$ means that the direction of the nitrogen—vacancy bond is collinear to the magnetic field, and all other possible directions — $\mathrm{NV_{off}}$.

The NV-center is described by the following spin Hamiltonian:

$$H = g\mu_B \mathbf{B}\cdot\mathbf{S} + D[\mathbf{S}_z^2 - \mathbf{S}(\mathbf{S}+1)/3] + E[\mathbf{S}_x^2 - \mathbf{S}_y^2],$$

where the second and the third terms correspond to the fine structure interaction, which induces the splitting of energy levels in zero magnetic field. The fine structure parameter D takes into account z-axial contribution of the crystalline field, and parameter E — of the non-axial part. The ground state of ($^3\mathrm{A}_2$) NV-center is the triplet ($S = 1$), and g-the factor of the nitrogen-vacancy center is 2.0028.

In absence of the external magnetic field the levels $m_S = 0$ and $m_S = \pm 1$ are split into $D = 2874\,\mathrm{MHz}$. The center has the axial local symmetry $\mathrm{C_{3v}}$, which results in the fact that the transverse parameter $E = 0\,\mathrm{MHz}$ and levels $m_S = \pm 1$ remain degenerated [2,17].

Figure 2 shows a cycle of optical excitation and radiation of NV-center, where ^{3}A and ^{3}E are ground and excited triplet states, and ^{1}A and ^{1}E are metastable states. The intersystem transitions in these states are marked as ISC (inter-system crossing). The resolved optical transitions between the ground and excited states are shown with solid lines, and nonradiative transitions are shown with dotted ones. The thickness of arrows conventionally shows the rate of transition between various states. Depending on the rate of transition, the system relaxes either with light radiation or nonradiatively by means of the ISC transition to the metastable state. Due to different transition rates, immediately (less than in $1\,\mu$s) after optical excitation, the distribution of spin population results in the fact that the level $m_S = 0$ is populated, and $m_S = \pm 1$ levels are empty. In Figure 2 the resulting distribution is conventionally shown by the number of balls [18].

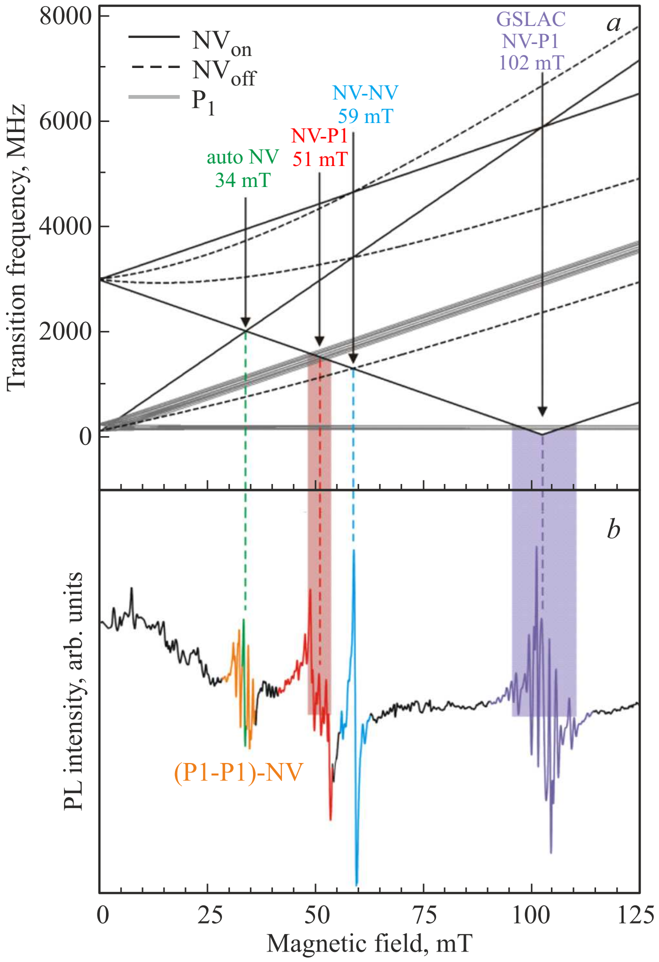

Figure 4. *a*) Transition energies of magnetic levels of NV- and P1-centers; *b*) photoluminescence spectrum as function of magnetic field at $\mathbf{B} \parallel \langle 111\rangle$.

Optical initialization and readout allow to use NV-centers as an effective tool to study the adjacent paramagnetic centers and their interactions.

Under the influence of continuous optical excitation of NV-centers in diamond, the spins of the ground triplet state of the NV center align. If a certain external magnetic field is applied along one of the crystallographic $\langle 111\rangle$ directions, these spins will interact with centers having a different spin temperature, and a resonant change in the PL intensity of the NV-centers will be observed. This allows the registration of cross-relaxation (CR) lines, which are caused by resonant energy exchange between NV-centers and other centers [19].

Figure 3, *a, c* and *e* show the energy diagrams for $\mathrm{NV_{on}}$-, $\mathrm{NV_{off}}$- and P1-centers at $\mathbf{B} \parallel \langle 111\rangle$, calculated with Grachev's software [20], which is based on diagonalization of the spin Hamiltonian's matrix. Red lines indicate the energy levels for NV-centers with $|m_S = +1\rangle$, blue lines indicate with $|m_S = -1\rangle$, and black lines indicate with $|m_S = 0\rangle$. Solid lines correspond to NV-centers with the axis of symmetry coinciding with the direction of the magnetic field $\mathbf{B} \parallel \langle 111\rangle$ ($\mathrm{NV_{on}}$), dotted lines correspond to three

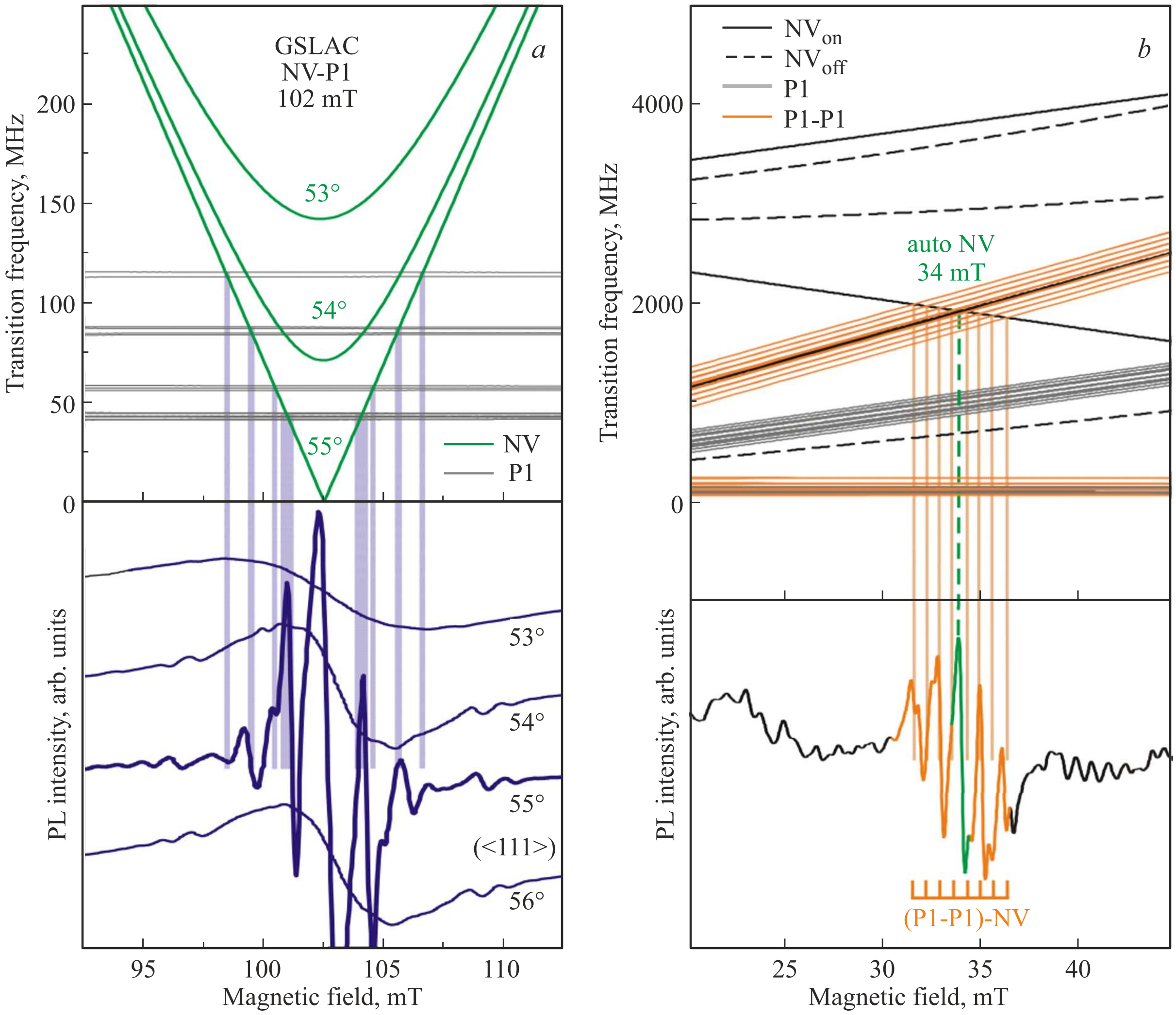

Figure 5. a) The occurance of a well resolved GSLAC structure. *b*) Calculation of CR energy levels for nitrogen atom pairs (orange lines), NV- (black lines) and P1- (grey lines) centers at $\mathbf{B} \parallel \langle 111\rangle$.

other NV-centers that deviate at the angle of 109° (NV_{off}). Figure 3, *e* shows energy levels of the P1-center with grey lines. It should be noted that each of the lines with $|m_S = 1/2\rangle$ is split into several lines due to HF interaction of nitrogen atom with ^{14}N nuclei.

Figure 3, *b, d* and *f* shows transition energies (the figure indicates „transition frequency") as magnetic field function of NV-centers (collinear and noncollinear **B**), and also impurities with the spin $S = 1/2$ (P1-center), which are produced by subtraction of the corresponding levels from each other ($|mS = -1\rangle - |m_S = 0\rangle$, $|m_S = +1\rangle - |m_S = -1\rangle$, $|m_S = +1\rangle - |m_S = 0\rangle$, $|m_S = +1/2$, $m_I = -1, 0, +1\rangle - |m_S = -1/2, m_I = -1, 0, +1\rangle$).

CR occurs when the transition energies of NV-center and other spin systems coincide. At magnetic field of 34 mT the energies of transitions inside the center NV_{on} $|m_S = -1\rangle - |m_S = 0\rangle$ and $|m_S = +1\rangle - |m_S = 0\rangle$ coincide, as shown in Figure 3, *a* with black arrows, and in Figure 3, *b* as the crossing point of transition energy lines.

At magnetic field 102 mT the anti-crossing of $|m_S = 0\rangle$ and $|m_S = -1\rangle$ levels was observed for NV_{on} center.

Figure 4, *b* shows the dependence of the total photoluminescence on the magnetic field, recorded at room temperature, with a magnetic field modulation of 2 G, a magnetic field sweep rate of 60 G/min, and laser excitation with $\lambda = 532$ nm and a magnetic field oriented along one of the four equivalent ($\langle 111\rangle$) axes of the NV-center. A series of signals were observed in low magnetic fields. Some of them can be explained well by crossings of the transition energies (Figure 3, *b, d* and *f*), simultaneously depicted in Figure 4, *a*.

The group of lines around 51 mT marked with red in Figure 4, *b* occurs due to CR processes between NV-centers whose axes are parallel to the magnetic field **B**, and P1-center. At magnetic field of 59 mT the transition energies of differently oriented NV-centers (collinear and noncollinear to the magnetic field) coincide, and the CR occurs (in Figure 4, *b* the signal is marked with blue) [21].

The group of signals (in Figure 4, *b* marked purple) located near the magnetic field of 102 mT is related to the anti-crossing of the ground state levels of NV-centers [22,23]. According to [24,25], the resolved structure of the GSLAC spectrum is caused by cross-relaxation processes between NV- and P1-centers.

Figure 5, *a* presents the angular dependence of GSLAC with a step of $\Delta\theta = 1°$. It should be noted that the resolution of the anticrossing spectrum of ground state levels of NV-center depends on diamond orientation. From the figure, it is clearly seen that at orientation $\theta = 53°$ there is no crossing of the transition energies between NV- and P1-centers. At $\theta = 54°$, the transition energies start crossing, and the maximum crossing occurs when $\mathbf{B} \parallel \langle 111 \rangle$. At this point, the GSLAC spectra are resolved most clearly. The accuracy of determining the sample orientation was precisely established based on the well-resolved structure of the ground state level anticrossing (GSLAC) spectrum of the NV-center.

The series of CR signals in the magnetic field of around 34 mT at the magnetic field orientation along the crystallographic direction $\langle 111 \rangle$ were observed previously in the diamonds with high initial concentration of P1-centers grown by HPHT method [26]. The authors of this paper attributed the entire group of signals to autocrossing of NV-centers (autoNV) which is caused by the interaction with neighboring ^{13}C spins. However, our calculations, presented below, have shown that in addition to autoNV (green line), there is a number of additional signals associated with nitrogen atom pairs (orange lines), the detailed energy scheme of which is presented in Figure 5, *b*. It should be noted that we also performed calculations of the levels taking into account the interaction with ^{13}C, which explained all the low-intensity lines in Figure 5, *a*. However, we did not include them in the figures to avoid complicating the diagrams.

Further evidence that, in addition to autocrossing of NV-centers, CR occurs between NOC4 and NV is provided by the angular dependence of the CR signals recorded via photoluminescence at room temperature, modulations of the magnetic field of 2 G, given in Figure 6, *a*.

In Figure 6, *b* the points indicate the experimental positions of CR signals, and the lines show the calculated angular dependences of CR, which were obtained by comparing the transition energies of differently oriented NV-centers, P1 and pairs of nitrogen atoms using the above listed spin Hamiltonian parameters for each of these centers. Blue and green lines show the calculated angular dependences of two differently oriented NV-centers. The lower right insert of Figure 6, *a* shows the detailed experimental angular dependences of CR on the magnetic field and estimated CR lines between P1- and NV-centers (red lines). Orange lines are the calculated angular dependences of CR NOC4-NV-centers. To simplify the estimation of CR between NOC4- and NV-centers, we did not take into account the HF-structure of nitrogen atom pairs (wide orange strip in the figure conventionally shows some lines related to CR of NOC4-NV-center taken into account the HF interaction). These angular dependences clearly show three series of CR lines related to the nitrogen atom pairs, which are in good agreement with our calculations. Therefore, our experimental and calculated dependences of CR show that there are two types of signals at 34 mT, related to autoNV (green line) and CR of NV with pairs of nitrogen atoms NOC4 (orange lines), which have different angular dependences.

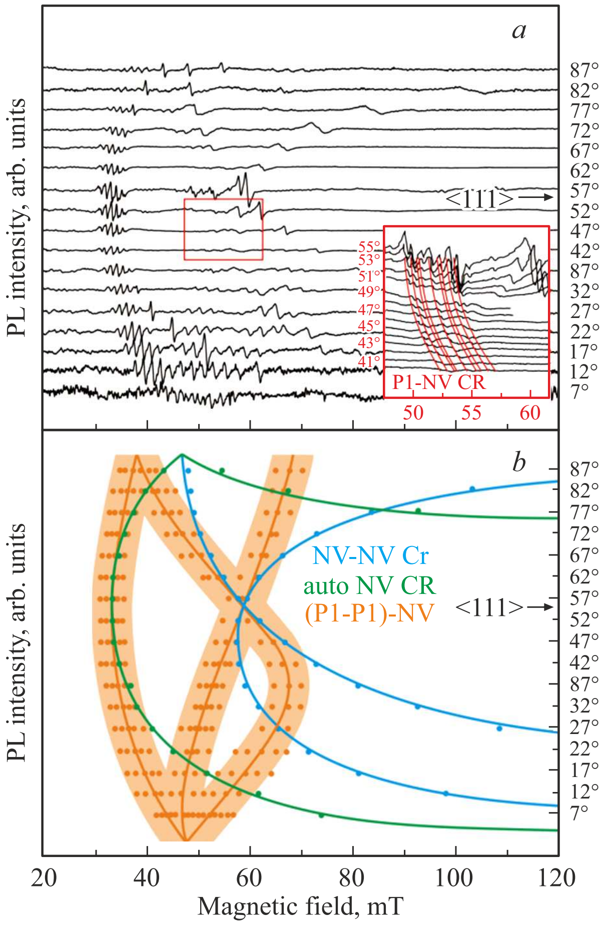

Figure 6. *a*) Angular dependences of nitrogen-related centers in the crystallographic plane of rotation (110). *b*) Experimental data is shown for autocrossing of NV-centers (green lines), CR between NV–NV-center (lines marked with blue), NV and P1 (red) and between NV- and NOC4-centers (orange). Here the points are experimental positions of cross relaxation signals, and lines are estimated angular dependences.

4. Conclusion

The cross-relaxation spectra in synthetic diamonds associated with nitrogen centers, as well as their angular dependencies, are presented. It has been established that in the magnetic field region of 34 mT, in addition to the previously interpreted CR signals associated with autoNV, there is CR between the nitrogen atom pairs

(NOC4) and NV-centers. It should be noted that there have been no such detailed angular dependences so far in the literature between cross-resonances of NV−P1- and NV−NV-centers recorded in such wide range of angles; besides, angular dependences of cross relaxation between NOC4−NV-centers were presented for the first time.

Registration of the nitrogen atom pairs by cross-resonance method may be used in quantum magnetometry. A significant advantage compared to magnetometers operating on optically detected magnetic resonance is the absence of the need to apply microwave radiation and precisely align the magnetic field, as well as the use of weaker magnetic fields.

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Conflict of interest

The authors declare that they have no conflict of interest.

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