08

Nanosensor for Weak Magnetic Fields Based on a Kramers-Degenerate Spin System ^{14}N$V-^{13}$C

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A nanosensor for weak magnetic fields based on an individual ^{14}N$V-^{13}$C complex in diamond has been implemented, where the ^{13}C carbon atom is located in the third coordination shell of the ^{14}NV-center. Using this sensor, the background magnetic field in the laboratory was measured: the projection onto the quantization axis of the complex B_z was approximately 40 μT, which is close to the Earth's magnetic field strength. Comparative modeling of the optically detected magnetic resonance (ODMR) spectra of the ^{14}NV and ^{14}N$V-^{13}$C systems under various magnetic and electric fields was performed using their respective spin Hamiltonians. It was shown that employing the ^{14}N$V-^{13}$C complex mitigates the influence of internal crystal fields on the nanomagnetometer.

Keywords: Nitrogen–vacancy center, ^{13}C nuclear spin, magnetometry, Kramers degeneracy.

In the past decade, magnetometry with the use of single nitrogen–vacancy color centers (^{14}NV-centers) in diamond, which provides high sensitivity to magnetic fields with nanoscale spatial resolution, has become one of the frontiers of quantum sensorics [1–3]. The physical basis for application of an ^{14}NV-center as a sensor is the dependence of energies and eigen states of ground triplet state $^3A_2$ ^{14}NV-center on the magnetic field, which manifests itself in the modification of optically detected magnetic resonance (ODMR) spectra. The analysis of such spectra is one of the main methods for determining the characteristics of the magnetic field acting on a sensor. One of the challenges of magnetometry based on ^{14}NV-centers is the need to take into account the effect of intracrystalline deformation fields and associated electric fields E, which may reach significant magnitudes in actual diamond crystals [4]. In this context, the issue of separation of the contributions of magnetic and electric fields in the process of interpreting the ODMR spectra of an ^{14}NV-center used as a sensor becomes relevant. Kramers-degenerate spin systems with half-integer spin and double degeneracy of energy states, which may be removed by a magnetic field only, induced by an external electric or intracrystalline field have already been proposed as a means to solve this problem [5].

Specifically, an individual ^{14}N$V-^{13}$C complex, which is an ^{14}NV-center (electron spin $S = 1$) hyperfine-coupled to a single nuclear spin of isotope ^{13}C ($I = 1/2$), may be used a sensing spin system. In the present study, an individual complex of this kind was found experimentally in a sample that consisted of an epitaxial layer of CVD-grown diamond on an HPHT substrate 0.4×0.4 mm in size. The nitrogen content in the CVD layer was on the order of 1 ppb. ^{14}NV-centers were formed in it by electron irradiation and subsequent annealing. The density of ^{14}NV-centers was estimated from fluorescence maps. The majority of ^{14}NV-centers are located at a depth of approximately 5 μm. An average of four ^{14}NV-centers are found in a region 15×15 μm in size. The isolated nature of the detected object was verified by constructing a second-order autocorrelation function; the measured value of $g^{(2)}(0) < 0.5$ is indicative of the presence of a single-photon emitter.

The ODMR measurement setup included a confocal microscope and a system for photon counting system and microwave irradiation of the sample. Continuous-wave laser radiation with a wavelength of 532 nm was used for excitation. A copper wire positioned on the diamond plate surface served as an antenna. Microwave radiation was fed to the wire through an amplifier and had a power of approximately 100 mW.

According to the results of ODMR spectrum measurements in zero external field, the examined complex had a configuration in which the isotopic ^{13}C atom was located in the third coordination shell of the ^{14}NV-center. The splitting of ODMR resonance lines turned out to be close to 13 MHz and corresponded to exactly this type of positioning of ^{13}C relative to the ^{14}NV-center [6]. According to the data from [6], diamond with a natural ^{13}C content (1.1 %) has much more complexes of this kind than complexes with the ^{13}C isotope in the first coordination shell. According to [6], the probability of ^{13}C being located in the first and third coordination shells of an ^{14}NV-center is 3.3 % and 16.4 %, respectively. It should be noted that not all third neighbors have the same hyperfine coupling; however, it was easy to find experimentally such complexes where zero-field splitting is close to 13 MHz.

Figure 1, *a* shows the model ODMR spectra of ^{14}N$V-^{13}$C and ^{14}NV constructed using the spin Hamiltonian method. As was demonstrated in our previous

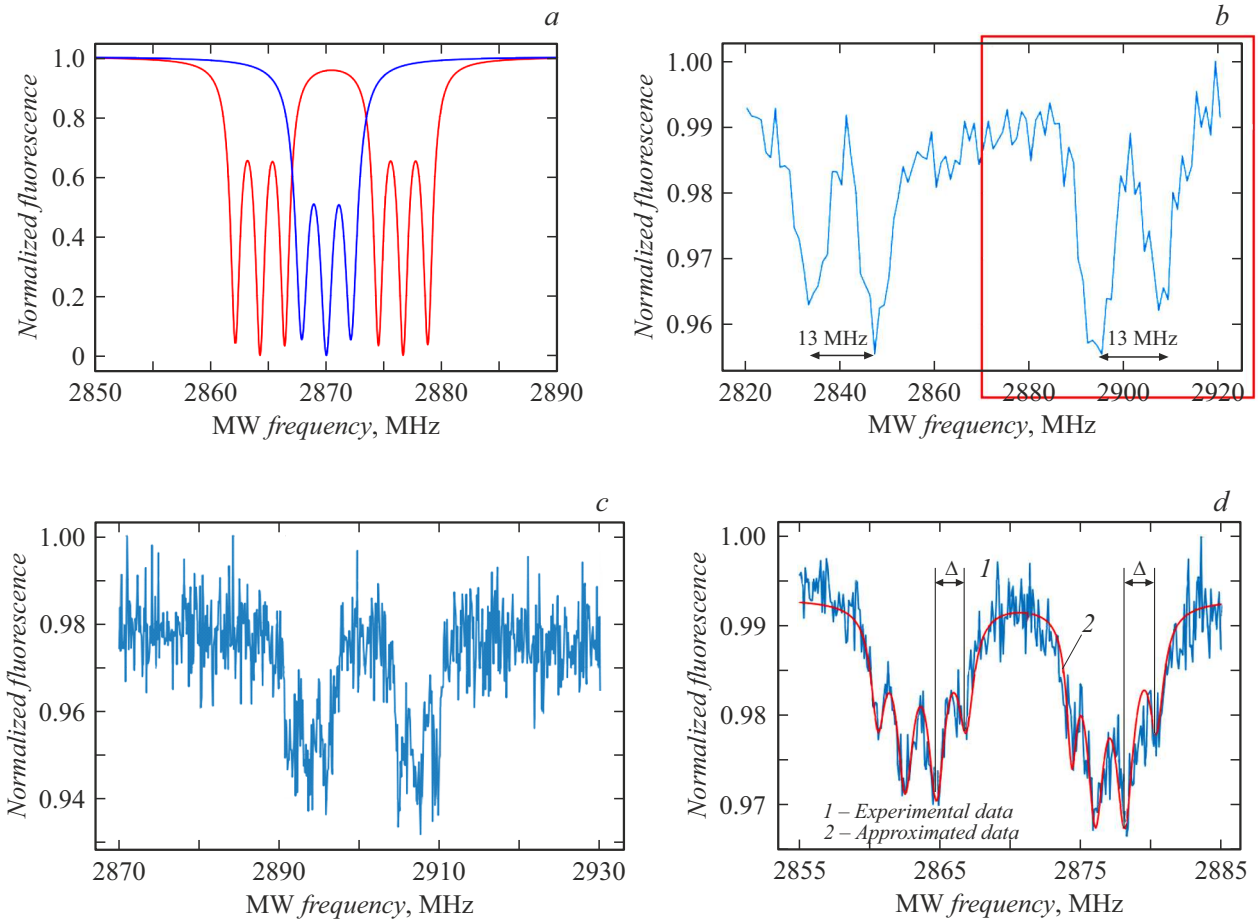

Figure 1. *a* — Model ODMR spectrum of $^{14}NV-^{13}C$ (red curve) and spectrum of ^{14}NV (blue curve); *b* — complete experimental ODMR spectrum in a 2 mT magnetic field; *c* — high-frequency part of the ODMR spectrum in high resolution (highlighted by the red frame in panel *b*); *d* — ODMR spectrum of the $^{14}NV-^{13}C$ complex in the laboratory background magnetic field. A color version of the figure is provided in the online version of the paper.

study [7], spectra constructed this way agree closely with experimental ones. When a magnetic field is applied, the double Kramers degeneracy of the system states is lifted, and six lines in the ODMR spectrum are split additionally. Thus, the ODMR spectrum in a magnetic field should feature 12 lines. Figure 1, *b* shows the ODMR spectrum in a magnetic field, where resonance lines shift due to the Zeeman effect and two pairs of lines split by 13 MHz are visible. Figure 1, *c* reveals the presence of a substructure, which is the result of hyperfine interaction of the ^{14}NV-center with the nuclear spin of nitrogen ^{14}N ($I = 1$). In addition, mechanical deformations of diamond induce a local electric field in the region of the ^{14}NV-center, which leads to Stark splitting and shifting of its energy levels by Δ. The magnitude of the induced electric field may be estimated from the ODMR spectrum based on the transverse dipole moment of the ^{14}NV-center ($d_\perp = 17.3$ Hz·cm/V). The intracrystalline electric field of the examined sample was estimated as $E = \Delta/d_\perp$ at 6 kV/cm. According to the data from [8], the magnitude of splitting in zero external field for bulk diamond is 100 kHz.

Figure 1, *d* shows the ODMR spectrum measured in the laboratory background magnetic field (i. e., without any intentionally applied magnetic field). This spectrum reveals eight out of twelve lines, since four pairs of lines overlap. As a result, two pairs of lines appear to be more intense. Resonance peaks are approximated by Lorentz curves. Figure 1, *d* illustrates the lifting of Kramers degeneracy. The approximate splitting magnitude Δ in this experiment was 2.25 MHz. The projection of the magnetic field onto the quantization axis of the complex may be estimated using the following formula: $\Delta = 2g_e\beta_e B_z$ [5], where $g_e = 2.008$ is the nearly isotropic electronic g-factor of the ^{14}NV-center and $\beta_e = 1.4 \cdot 10^4$ MHz/T is the Bohr magneton. The calculation showed that $B_z \approx 40\,\mu$T. Since this value is close to the magnitude of the terrestrial magnetic field in Moscow (53 μT, which was obtained using the magnetic field calculator on the NOAA National Geophysical Data Center website), the sensor under study may be used to estimate it.

To compare the obtained data with the results of conventional ^{14}NV-center magnetometry, the effect of deformations

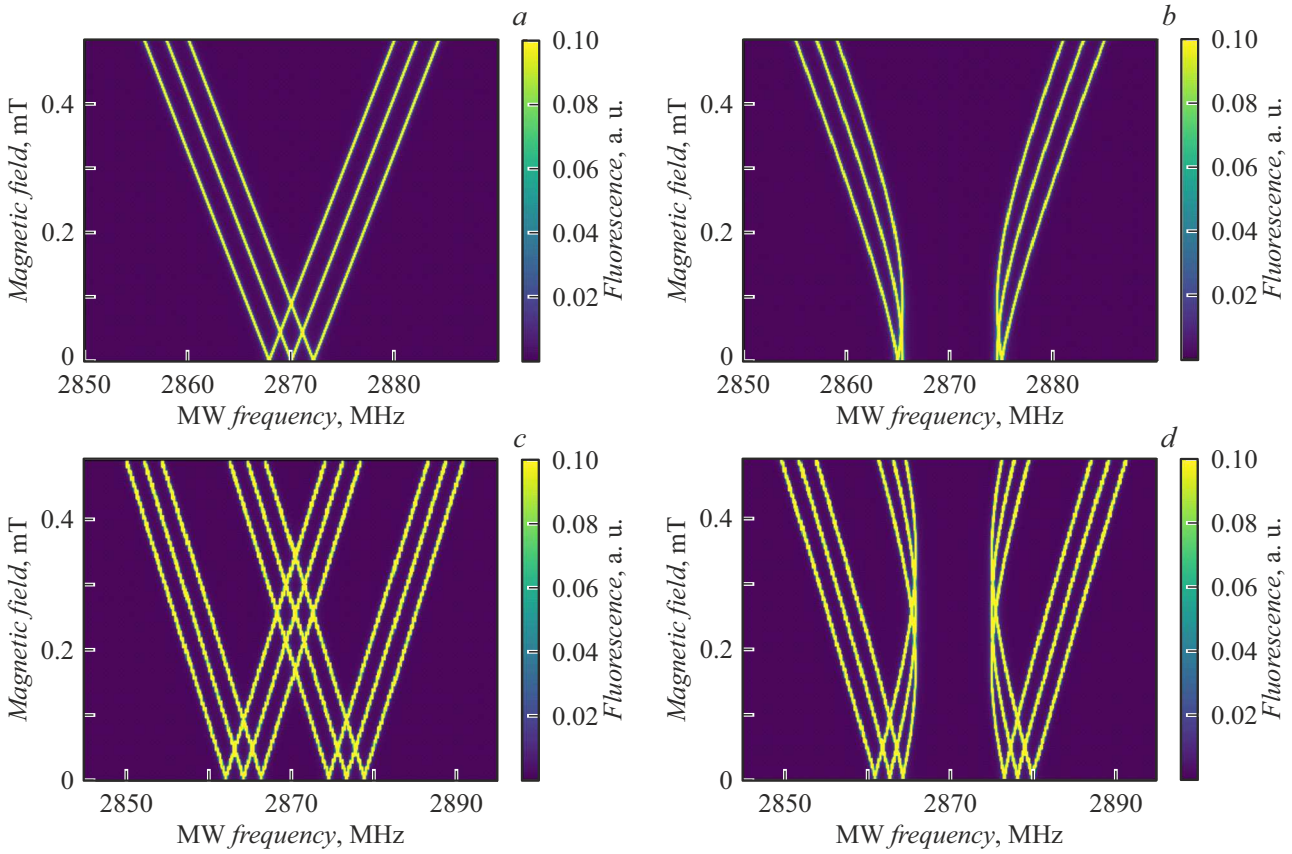

Figure 2. *a* — ODMR spectra of an NV-enter at $E_\perp = 0$; *b* — ODMR spectrum of an ^{14}NV-center at $E_\perp = 300$ kV/cm; *c* — ODMR spectra of ^{14}N$V-^{13}$C at $E_\perp = 0$; and *d* — ODMR spectrum of ^{14}N$V-^{13}$C in various magnetic fields at $E_\perp = 300$ kV/cm.

on ODMR spectra was calculated in different magnetic fields both for the ^{14}NV-center without ^{13}C and for the ^{14}N$V-^{13}$C complex. This calculation was performed using a model based on the spin Hamiltonian. According to the data from [9], the splitting of ODMR resonance lines in zero external field may be as large as 5 MHz, which corresponds to a local electric field on the order of 300 kV/cm. This field magnitude may be used in the model to compare the effect of deformations on ^{14}NV and ^{14}N$V-^{13}$C. The calculation results are presented in Fig. 2 in the form of heat maps. Figure 2, *a* shows the ODMR spectra of the ^{14}NV-center (without ^{13}C) in different magnetic fields and without an applied effective electric field, while the spectra in Fig. 2, *b* were calculated with a transverse electric field of 300 kV/cm applied in the model. It is evident that the resonance lines are split in zero magnetic field, thus reducing the sensitivity of magnetometry.

Figures 2, *c* and *d* present similar distributions for the ^{14}N$V-^{13}$C complex. It can be seen that the degeneracy of states is lifted by a magnetic field only and does not depend on intracrystalline electric fields, which is a characteristic feature of Kramers-degenerate systems. Thus, the ^{14}N$V-^{13}$C complex allows one to separate the effects of intracrystalline and external (measured) magnetic fields. Specifically, a ^{14}N$V-^{13}$C sensor may be used to measure a known magnetic field, interpret the results theoretically, and determine the components of intracrystalline fields acting on this center (i. e., perform calibration) that will then be applied in theoretical interpretation of the ODMR spectra of the complex exposed to an unknown measured magnetic field. This is infeasible in the case of an individual ^{14}NV-center, since the effects of electric and magnetic fields are mixed.

Note that the stationary method of ODMR spectra measurement was used in the present study: the examined center was exposed to laser and microwave radiation acting simultaneously, which translates into broadening of resonance lines (FWHM $\approx$ 1 MHz in Fig. 1, *d*) and a reduction in sensitivity of magnetometry. A pulsed ODMR spectra measurement design [10] may be used to enhance the spectral resolution. This measurement arrangement is more technically complex, but will raise the sensitivity of the proposed magnetometry technique utilizing the Kramers-degenerate ^{14}N$V-^{13}$C system. Theoretically, the sensitivity of the ^{14}N$V-^{13}$C complex to a constant magnetic field corresponds to the sensitivity of the ^{14}NV-center with zero deformations or complete compensation of their influence (i. e., less than 50 nT/$\sqrt{\text{Hz}}$ [9]).

The obtained results highlight the application potential of the ^{14}N$V-^{13}$C quantum system in nanomagnetometry

and open up new horizons in the development of quantum sensors.

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Conflict of interest

The authors declare that they have no conflict of interest.

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