Low-field feature in the magnetic spectra of NV⁻ centers in diamond

S V Anishchik¹, V G Vins², A P Yelisseyev³, N N Lukzen⁴,⁵, N I Lavrik¹ and V A Bagryansky¹

¹ Voevodsky Institute of Chemical Kinetics and Combustion SB RAS, 630090, Novosibirsk, Russia
² VinsDiam Ltd., Russkaya Str., 45, 630058, Novosibirsk, Russia
³ V. S. Sobolev Institute of Geology and Mineralogy SB RAS, 630090, Novosibirsk, Russia
⁴ International Tomography Center SB RAS, 630090, Novosibirsk, Russia
⁵ Novosibirsk State University, 630090, Novosibirsk, Russia

E-mail: svan@kinetics.nsc.ru

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Abstract

The low-magnetic-field feature in the magnetic field dependence of the luminescence of negatively charged nitrogen-vacancy (NV⁻) centers in diamond has been experimentally observed for the first time. This feature, centered at the zero magnetic field—henceforth the zero field line—and observed with a magnetic field sweep of NV⁻ center luminescence (magnetic spectrum), is quite narrow. The properties of this line are considerably different from those of other narrow NV⁻ magnetic spectrum lines. Its amplitude is weakly dependent on the orientation of the single-crystal sample with respect to the external magnetic field. This line is also observed in a powdered sample. The shape of the line changes drastically with a change in the polarization of excitation light. The amplitude of the line non-linearly depends on excitation light intensity. For low intensities this dependence is close to the square law. We attribute the occurrence of this line to the dipole–dipole interaction between different NV⁻ centers.

1. Introduction

Negatively charged nitrogen-vacancy centers (NV⁻ centers) are of great interest to researchers due to their unique properties [1]. They are promising systems for numerous applications, especially in quantum information processing [1–16] and nanoscale magnetometry [17–34].

The ground state of NV⁻ centers is a triplet state and is split depending on the spin projection on the symmetry axis. The ground energy term is the term with zero spin projection. The splitting between this term and the ones with projections +1 and −1 in the zero magnetic field is ∼2.87 GHz.

In an NV⁻ center, a spin projection–selective intersystem crossing takes place from the excited triplet state to the excited singlet one, as well as from the ground singlet state to the ground triplet state. First, this crossing leads to a much higher quantum yield of luminescence when light excitation occurs from the zero spin projection state rather than from the states with projections +1 or −1 on the center’s symmetry axis. Second, it gives rise to a non-equilibrium state of the NV⁻ center after multiple cycles of light absorption and emission, with a population of the zero spin projection state much higher than those of the states with spin projections +1 or −1. The latter effect is commonly referred to as optically induced spin polarization [35–37], despite the fact that in this state the spin projection in any direction is zero. It is spin polarization, combined with a long spin relaxation time, exceeding, under certain conditions, 1 s at room temperature [11], that provides the possibility for various applications of NV⁻ centers.

One of the methods for studying NV⁻ centers is to analyze the dependence of their luminescence intensity on an applied external magnetic field (magnetic spectrum) [38–44]. A magnetic field modifies the degree of optically induced spin polarization of NV⁻ centers. Since luminescence intensity increases with increasing spin polarization [36], a decrease in polarization due to the Zeeman interaction of NV⁻ centers with an external magnetic field reduces photoluminescence intensity. In addition to a smooth magnetic field dependence of the luminescence intensity, sharp lines can be observed in the spectrum [38, 39, 41]. However, these lines are
detectable only if the magnetic field is parallel to axis \(\langle 111\rangle\) of the diamond crystal lattice. Even a slight misalignment strongly broadens the lines and suppresses their magnitude. The lines are attributed to either an anticrossing of terms in the NV\(^-\) center or a resonance interaction of the NV\(^-\) center with other paramagnetic defects in the diamond. However, a comprehensive theoretical description of the processes giving rise to these lines still remains to be developed.

It is known that in weak magnetic fields there are effects resulting from the coherence of quantum states, e.g., the Hanle effect [45]. Another example is the so-called zero field line in magnetically affected reaction yield (MARY) spectroscopy [46–48]. We took this as a hint to study NV\(^-\) center magnetic field behavior in weak magnetic fields. As a primary result of this study we observed a low-field feature in the magnetic spectrum of NV\(^-\) centers. To our knowledge this feature has been observed for the first time.

2. Experimental

2.1. Samples

The experiments were performed using five samples of an irregularly shaped synthetic diamond (see figure 1(a)) grown at high temperature and pressure in an Fe–Ni–C system. As-grown crystals were then irradiated by electrons with energy of 3 MeV. The dose was \(10^{18}\) e cm\(^{-2}\). Then the samples were annealed for 2 h in a vacuum at 800 °C. The state of impurity defects was monitored through the measurement of absorption spectra in the UV, VIS, and IR bands. The absorption spectra in the shortwave band were measured at 300 and 77 K and in the middle IR band at 300 K. The IR absorption spectra were normalized using an internal 12.3 cm\(^{-1}\) absorption standard at 1995 cm\(^{-1}\) [49]. The single-photon part of the spectrum was found to be dominated by donor nitrogen absorption (C centers—electrically neutral single substitutional nitrogen atoms, also often called P1 centers). It is known that fast electron irradiation gives rise to vacancies in the diamond lattice, which after annealing at 800 °C become mobile and are captured by the C centers, forming NV complexes. This leads to an intense absorption by the electron-vibration system in the visible band of the absorption spectra, with a zero-phonon line (ZPL) at 637 nm (1.945 eV) due to negatively charged NV\(^-\) complexes. The concentration of NV\(^-\) centers (in cm\(^{-3}\)) was estimated from the integral absorption \(\mu_{637}\) at the 637 nm (in meV cm\(^{-1}\)) ZPL at 77 K by the expression [50] \(N_{NV^-} = 8.9 \times 10^{13}\mu_{637}\).

The concentration of C centers was determined from the absorption at 1135 cm\(^{-1}\); the concentration of A centers (a neutral nearest-neighbor pair of nitrogen atoms substituting for the carbon atoms), at 1282 cm\(^{-1}\); the concentration of C\(^+\) centers (positively charged single substitutional nitrogen atoms), at 1332 cm\(^{-1}\); and the concentration of NE1 centers (N–V–Ni–V–N systems), at 472.8 nm [51, 52]. The results of the measurements for samples SMP1–SMP4 are shown in table 1. The fifth sample was prepared from sample SMP3 by grinding it into powder with a particle size within 0.1 mm.

Figure 1(a) shows the photoluminescence of sample SMP2 excited by blue light. The image was taken using a red optical filter. The intense red luminescence is due to negatively charged NV centers.

2.2. Setup

The sample was placed in the cavity of an EPR spectrometer. The electric magnet of the spectrometer was equipped with additional coils for reverse magnetization to sweep the field through zero. The transversal component of the magnetic field did not exceed 0.1 G. In our experiments the microwave field was always equal to zero.
The samples were aligned using a manually operated goniometer. The sample was irradiated by a 400 mW laser beam at 532 nm. Laser power stability was within 1%. The direction of the light beam was perpendicular to the magnetic field vector $B_0$, as shown in figure 1(b). The laser beam was linearly polarized. We performed experiments with varied orientation of the polarization vector $E$ relative to the external magnetic field $B_0$. As demonstrated hereafter, this variation had a considerable effect on the experimental results.

The diameter of the laser beam was within 1 mm. The width of the cavity lattice slits through which the sample was irradiated was 0.5 mm.

The light from the sample passed through a quartz lightguide and an optical filter to a photomultiplier tube (PMT). The filters were selected to reduce the light intensity to a level that was acceptable for the PMT and to extract the spectral line of the negatively charged NV center. We used a set of colored and neutral glass filters that passed the light with wavelengths longer than 680 nm. The light was registered by an FEU-119 photomultiplier tube that was sensitive to the red spectral area.

The signal from the PMT was fed to the input of a lock-in amplifier. The use of the lock-in amplifier considerably improved the signal-to-noise ratio in our experiments. The modulation frequency was 12.5 kHz, and the modulation amplitude $B_M$ for all the experimental results discussed here was 0.5 G.

The phase shift $\phi$ of the modulation magnetic field relative to the reference signal from the source generator is determined by the impedance of the modulation coil and its leads, as well as by the skin effect in the cavity walls. The phase shift $\theta$ of the signal coming from the sample relative to the modulation magnetic field is determined by the temporal function of the system response to the variation in magnetic field. Varying the lock-in amplifier’s phase $\theta_{LA}$, one can determine $\theta$ and thus obtain information about the time parameters of the processes occurring in the sample. For an exponential system response, the characteristic time $\tau$ of a process is related to the phase shift $\theta$ by the expression $\tan \theta = \omega \tau$, where $\omega$ is modulation frequency.

We determined the value of $\phi$ from experiments with recombination fluorescence in X-irradiated nonpolar liquids because in this case the processes determining the system response to the variation in the magnetic field occur in the nanosecond time domain. Therefore, $\tau \ll 2\pi/\omega$, and the signal from the lock-in amplifier reaches its maximum when $\phi_{LA} = \phi$. As demonstrated hereafter, when measuring magnetic spectra of NV$^-$ centers one must select $\phi_{LA} = \phi + \theta_{LA}$ considerably different from $\phi$. In all the figures in this paper we show experimental results for $\theta_{LA} = 70^\circ$.

All the experiments were carried out at room temperature. An aluminum radiator was used to dissipate the heat from the sample.

### 3. Results

Figure 2 shows an experimentally registered dependence of the lock-in amplifier output signal versus the external magnetic field for sample SMP2. Further on, this dependence is referred to as the magnetic spectrum. The lock-in amplifier signal can be considered proportional to the derivative of the sample luminescence intensity with respect to the magnetic field. Figure 3 shows the integrated spectrum of sample SMP2 corresponding to the curve shown in figure 2. The integrated spectrum looks similar to previously observed [41, 42] experimental curves.

As one can see in figure 2, the spectrum consists of a wide line with a maximum (in absolute units) around 100 G and many narrow lines. The wide line describes the decay in luminescence intensity due to a decrease in the spin polarization degree of the NV$^-$ center driven by the magnetic field component perpendicular to the center’s symmetry axis. This effect is not observed in NV$^-$ centers with the symmetry axis parallel to the axis of the external magnetic field $B_0$. However, this orientation activates other polarization-reducing mechanisms, giving rise to narrow lines in the magnetic spectrum, as clearly seen in figure 2. Most of these lines have been observed before [38–42, 44]. The physical origins of these lines are different.

| Table 1. Concentrations of various defects in the studied samples (in ppm). |
|------------------|---------|--------|---------|--------|
|                  | SMP1    | SMP2   | SMP3    | SMP4   |
| [NV$^-$]         | 8.2     | 5.5    | 2.4     | 0.65   |
| [C]              | 23      | 55     | 150     | <5     |
| [C$^+$]          | 41      | <2     | 5.5     | 2.75   |
| [A]              | 30      | <5     | 125     | <5     |
| [NE1]            | 0.012   | <0.003 | <0.003  | <0.003 |
The most intense line, at \( \sim 1028 \) G, is due to a level anticrossing (LAC) of the triplet terms of the ground state of the NV\(^{-}\) center with different spin projections. The nature of the other lines has not been established with certainty. They are usually referred to as cross-relaxation lines [38]. The line in the field at \( \sim 600 \) G can be reasonably attributed to the interaction between two NV\(^{-}\) centers with different orientations [38, 44], whereas most of the lines in the region of 490–540 G are attributed to interaction of the NV\(^{-}\) centers with electrically neutral single substitutional nitrogen atoms [38, 40, 44].

Registering a magnetic spectrum with resolved narrow lines requires a very fine alignment of the crystal so that its \( \langle 111 \rangle \) axis is parallel to the external magnetic field. Any misalignment from this orientation strongly broadens the lines and reduces their magnitude. One of the indicators of the correct alignment of the crystal is the shape of the line at \( \sim 600 \) G (in our experiments the line was centered at \( \sim 590 \) G). A slight misalignment of the crystal \( \langle 111 \rangle \) axis with respect to the external magnetic field splits this line into three lines of approximately equal magnitude [44]. However, as our experiments showed, when the crystal is precisely aligned, this line may have satellites of lower magnitude (see figure 7). Another measure of crystal alignment precision is the presence of satellites at the LAC line, which disappear when the misalignment is as little as 0.2° [44].

The red circle in figure 2 marks a narrow line in the zero field never observed before. This study is focused on the properties of this line.

Figure 4 shows magnetic spectra of sample SMP1 in low fields for various orientations of the sample and various orientations of the external magnetic field \( \mathbf{B}_0 \) with respect to the polarization vector \( \mathbf{E} \) of the excitation laser beam.
Curves (a) and (b) correspond to crystal orientation \( \mathbf{B} \parallel \langle 111 \rangle \). The crystal was aligned manually. The criterion was the presence of the narrow LAC line at \( \sim 1028 \) G with resolved satellite lines and a single narrow line at \( \sim 600 \) G (in this sample, also having satellites of a lower magnitude). This observation indicated that the alignment precision was 0.2° or better. The orientation of the other axes was not controlled. The crystal orientation in cases (a) and (b) was the same.

Curves (c) and (d) correspond to crystal orientation \( \mathbf{B} \perp \langle 111 \rangle \). This orientation was achieved in the following way: first the condition \( \mathbf{B} \parallel \langle 111 \rangle \) was ensured as previously described, and then the crystal was rotated by 90° around an axis perpendicular to \( \mathbf{B}_0 \) and oriented randomly with respect to the crystal. Therefore, crystal orientation in this case is to a large extent undetermined. For curves (c) and (d) the crystal orientation was different, as they were obtained in different experimental series.

For curves (a) and (c) the polarization vector \( \mathbf{E} \) of the laser beam is parallel to the magnetic field vector \( \mathbf{B}_0 \), whereas for curves (b) and (d) they are perpendicular to each other.

The signal magnitude for all the curves was normalized to the sample luminescence intensity in the zero field.

Curves (a) and (b) after integration with respect to the magnetic field are shown in the insert in figure 3. The lock-in measurement technique cannot determine the absolute magnitude of the effect, as it registers its first derivative. However, in additional experiments in which the luminescence intensity was measured directly, we found that the relative amplitude of the zero field line intensity was within 1% of the overall luminescence intensity.

As can be seen in figure 4, in all the cases a zero field line is observed with a magnitude varying to a small extent when the sample is rotated or the polarization of the excitation light is varied. For \( \mathbf{E} \perp \mathbf{B}_0 \) a narrow inverted line appears in the zero field. Its peak-to-peak width is about 2G.

As can be seen in figure 4, a weak inverted line in the zero field is also observed when the polarization vector of the excitation light is parallel to the field \( \mathbf{B}_0 \). This is apparently due to the fact that we can control light polarization only outside the sample. Because the light is refracted when it enters the sample, its propagation direction can change, giving rise to a nonzero perpendicular component of light polarization inside the sample. It is this component that accounts for the inverted line. As one can see in figure 5, there was no such effect in the other samples.

A peculiarity of the spectrum is the presence of a satellite line just below 20 G. The magnitude of this line is independent of the excitation light polarization. However, it disappears when the sample is rotated, as shown in figure 4(c). In figure 4(d) this line appears in a much-broadened form.

Figure 5 shows magnetic spectra of different samples for two different polarizations of the excitation light. All the spectra are normalized to the sample luminescence intensity in the zero magnetic field. In the single crystal samples SMP1–SMP4 the concentration of NV\(^-\) centers monotonically decreases. The bottom spectrum corresponds to a powdered sample prepared by grinding the single-crystal sample SMP3. For all the samples (except the powdered one) \( \mathbf{B}_0 \parallel \langle 111 \rangle \).

As can be seen in figure 5, for all the samples there is a zero field line. In samples SMP1–SMP3 the line’s amplitude is nearly the same, while in sample SMP4 (with the lowest concentration of NV\(^-\) centers) it drops

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**Figure 4.** Zero field line in sample SMP1. The \( \langle 111 \rangle \) axis is ((a) and (b)) oriented along the magnetic field \( \mathbf{B}_0 \) and ((c) and (d)) rotated by 90° relative to \( \mathbf{B}_0 \). The polarization vector of the excitation light \( \mathbf{E} \) is ((a) and (c)) parallel or ((b) and (d)) perpendicular to the magnetic field \( \mathbf{B}_0 \).
sharply and the width of the line becomes much smaller. At the same time, in all the samples an inverted narrow line appears in the zero field when the polarization vector $E$ of the excitation light changes orientation from parallel to perpendicular with respect to the external magnetic field $B_0$. When $E \parallel B_0$ the narrow inverted zero field line is absent in all the samples except SMP1. In samples SMP1–SMP3 a satellite line at 20 G is also observed; its magnitude is independent of the excitation light polarization and decays when the concentration of the NV$^-$ centers decreases.

Figure 5. Zero field line in single crystals SMP1–SMP4 and in a powdered sample prepared from SMP3. The (111) axis in all the single crystals is oriented along the magnetic field $B_0$. The polarization vector of the excitation light $E$ is (a) parallel or (b) perpendicular to the magnetic field $B_0$.

![Figure 5](image)

Figure 6 shows the dependence of the magnitude of the zero field line normalized to the sample light intensity versus the relative sample light intensity. In this experiment, the SMP1 sample was oriented in such a way that the (111) axis of the crystal was perpendicular to magnetic field $B_0$. The polarization vector of the excitation laser beam was parallel to $B_0$. The laser beam was attenuated by optical filters. A magnetic spectrum measured without attenuation filters is shown in figure 4(c).

The amplitude $S$ of the line was calculated as follows: from the zero field line spectrum a straight line was subtracted to compensate for the slope, and then the vertical peak-to-peak distance was measured. The amplitude was normalized by division by the photomultiplier tube current $I$ in the zero field, which was proportional to the sample luminescence intensity at that field. The $x$-axis shows the ratio of the current with the optical filter used, to the current with no filter $I/I_{max}$, which is proportional to the relative sample luminescence intensity in zero magnetic field.

Figure 6. The dependence of the normalized line amplitude versus relative sample luminescence intensity (closed circles). The solid line shows a parabolic approximation of the experimental data.
The scattering of the points is due to the fact that different filters not only attenuate the light but also disperse it differently. The magnitude of the zero field line depends on sample illumination, whereas the overall luminescence intensity depends on the illumination and size of the light spot that we could not control. Therefore, the measured sample light intensity is not a perfect value.

The solid line in the figure shows the best parabolic fit of the experimental data $S/I = a + b (I/I_{\text{max}}) + c (I/I_{\text{max}})^2$, where $S$ is the magnitude of the zero field line, $I$ is the PMT current at $B_0 = 0$ proportional to the sample light intensity, $a = 0.017$, $b = 0.109$, $c = -0.052$. From our experiments we can conclude that the magnitude of the zero field line has a nonlinear relationship to the intensity of the excitation light in the sample. In the low-intensity region this dependence is close to the square law.

4. Model

Our experiments revealed that the properties of the zero field line are considerably different from those of any other lines previously known for the magnetic spectrum of the NV$^-$ centers in diamond. The occurrence of this line cannot be accounted for by the processes in an isolated NV$^-$ center since it disappears quadratically with lowering of the concentration of centers. Furthermore, theoretical calculation of the magnetic spectrum of an isolated NV$^-$ center, for instance, by Rogers et al. [42], has shown no such line.

We also calculated the magnetic spectrum according to the model of geminate pairs in diamond under two-photon photoionization of the NV$^-$ center forming a neutral NV$^0$ center and a free electron similar to those discussed by Siyushev et al. [53]. If the electron is captured by a nearby positively charged nitrogen atom N$^+$ with further spin evolution in the geminate pair N$^0$–NV$^0$ followed by a spin-selective electron transfer to the NV$^0$ center, then the population of the triplet states of the thus formed NV$^-$ center with different spin projections is magnetic field dependent. Consequently, in this case the luminescence intensity will depend on the magnetic field and give a low-field line in the spectrum. This model accounts for the square-law dependence of the line’s magnitude versus excitation light intensity. However, calculations within this model fail to reproduce the properties of the line observed in the experiment. For instance, the predicted lines are inverted when crystal orientation is changed, in contrast with the experimental observation. Also, the probability of these processes is too low to give a marked line magnitude.

We suggest that the zero field line in the magnetic spectrum can be explained by dipole–dipole interaction between NV$^-$ centers. A similar model explaining the nature of the line at ~600 G was suggested in [44].

The ground state of the NV$^-$ center is triplet, so the center is a magnetic dipole. The magnetic dipoles of two centers interact, which can lead to transitions between the triplet sub-levels in each of the NV$^-$ centers. For this interaction to affect the luminescence quantum yield, it has to modify the overall population of both triplet states with zero projections on the symmetry axes of both centers in the interacting pair. Obviously, if the orientation of the centers is the same, the overall population will not change. However, if the orientation is different, then the dipole–dipole interaction can modify this overall population of the centers under a different degree of their polarization.

The efficiency of such a modification of the population of the terms in a pair of NV$^-$ centers substantially depends on the external magnetic field. This is due to the fact that in a zero field the transitions between the energy terms of differently oriented centers have a resonance nature, but when an external magnetic field is applied the terms in such centers shift differently and go out of resonance. This slows the mixing processes and finally stops them in higher fields. This should lead to a dip in the zero of the curve of luminescence intensity versus external magnetic field.

A different degree of polarization of differently oriented NV$^-$ centers is achieved under sample excitation by polarized light. This is due to the C$_{3v}$-symmetry of the NV$^-$ center. The transition from the ground state 3A$_2$ to an exited state 5E is forbidden when the polarization vector of the excitation light $\mathbf{E}$ is parallel to the symmetry axis. Therefore, the luminescence intensity and the degree of polarization of the center depend on the direction of vector $\mathbf{E}$ in the excitation light and grow with the transversal component of $\mathbf{E}$.

To test the outcome of this effect we performed an experiment aimed at observing the effect of variation in the excitation light polarization on the narrow lines in the magnetic spectrum of NV$^-$ centers. Figure 7 shows the magnetic spectrum of sample SMP2 for $B_0 \parallel \langle 111 \rangle$ under various polarizations of the excitation light. The figure shows a spectrum segment from 450 to 650 G. In figure 7(a) the polarization vector is perpendicular to $B_0$, whereas in figure 7(b) they are parallel. The spectra are normalized to sample luminescence intensity in the zero magnetic field. As can be seen in the figure, the spectra are almost identical and differ only in magnitudes, which are different by a factor of approximately 4. We should mention that this difference is in marked contrast with the transformation of the spectrum in low fields where the shape of the spectrum changes greatly, whereas its magnitude is altered only slightly. Since the narrow lines in the spectrum shown in figure 7 are generated only by NV$^-$ centers with symmetry axes oriented parallel to the external magnetic field, we can conclude that in our
a change in the orientation between the magnetic field and the light polarization vector should also suppress the efficiency of the excitation of the centers by a factor of 4.

The results of this experiment suggest that under polarized light excitation NV$^-$ centers oriented differently in the crystal can have considerably different ground triplet state polarizations. This means that the difference in populations of the levels for different spin projections varies considerably. Therefore, the dipole–dipole interaction between the electron spins can considerably modify the overall population of the terms with zero spin projection. Consequently, the luminescence yield in low magnetic fields changes due to the dipole–dipole interaction.

The change in sample luminescence intensity due to the dipole–dipole interaction between NV$^-$ centers is proportional to the excitation light intensity multiplied by the difference between the polarization degrees of the centers with different spatial orientation. The difference between the polarization degrees, in turn, is proportional to excitation light intensity, for moderate intensities. Therefore, the magnitude of the observed effect versus excitation light intensity should follow a square law.

As mentioned previously, the zero field line has a considerable phase shift. This phase shift cannot be accurately determined because it is slightly different for different segments of the line. As a consequence, the line cannot be nullified by adjustment of the lock-in amplifier phase $\theta_{LA}$. For sample SMP1 the phase shift is $\theta = 80 \pm 2^\circ$. One can estimate the exponential response time as $\tau = 1\tan \theta/\omega \approx 7 \times 10^{-5}\text{s}$.

Suppose the response time $\tau$ is determined by the energy of the dipole–dipole interaction between two NV$^-$ centers, which can be crudely estimated by a dimension factor $V = (g\mu_B)^2/(hr^3)$, where $g$ is free electron g-value, $\mu_B$ is Bohr’s magneton, $h$ is Planck’s constant, and $r$ is separation between the centers. Assuming $V = 1/\tau$ we get $r \approx 15\text{nm}$, which is of the same order of magnitude as the average separation between the centers in the sample.

On the other hand, $\tau$ is of the same order of magnitude as the typical phase spin relaxation times in such samples [54]. Therefore, it cannot be ruled out that it is phase relaxation time that determines the phase shift.

To check our assumption we performed experiments using an incoherent non-polarized light source to excite the sample. As a source of this kind we used a 10 W green LED. The LED light was focused on the sample by a lens. The sample luminescence intensity was comparable to that observed under laser irradiation with the attenuation filters installed when we detected the zero field line. In this experiment we successfully observed both the broad line with a maximum at 100 G and narrow lines in the magnetic spectrum above 400 G. There was no zero field line at all. This experiment supports our hypothesis, although it cannot be taken as its final proof.

We performed numerical calculations of magnetic spectra for pairs of NV$^-$ centers. Our calculations for a very simplified model of light-induced transitions but with rigorous accounting for dipole–dipole interaction between two NV$^-$ centers (see appendix) showed an appearance of the zero field line in the magnetic spectrum.
and correct transformation of the spectrum with the change of excitation light polarization vector (Figure 8).

They are similar to our experimental data (see the insert in Figure 3).

We have not found a straightforward explanation for the appearance of the satellite lines at approximately 20 G. The nature of the satellite lines might be similar to that of the satellites of the line at \( \sim 600 \) G. The splitting values and amplitude ratios relative to the main line are very close in both cases. Moreover, it is possible that the two drastic decreases in the relaxation time at \( B_0 = 0 \) and \( \sim 600 \) G versus the magnetic field dependence \([38]\) can both be explained in terms of dipole–dipole interaction between two NV\(^-\) centers. Earlier the line at 600 G was explained by the effect of cross-relaxation due to the dipole–dipole interaction of NV\(^-\) centers with different orientations \([38]\). This 600 G line is observed only when \( B_0 \parallel \langle 111 \rangle \), i.e., only for certain orientations of the crystal. In this case energy splitting between the \( T_0 \) and \( T_{+}^\pm \) levels of the symmetry axis of the NV\(^-\) centers along \( \langle 111 \rangle \) coincides with the splitting in NV\(^-\) centers directed in another way. In our model we actually use the same cross-relaxation mechanism due to dipole–dipole interaction. In contrast with the line at 600 G the zero field line appears in experiment as well as in modeling for any orientation of the crystal relative to the magnetic field. This is because the splitting between the \( T_0 \) and \( T_{+}^\pm \) levels in the zero magnetic field does not depend on NV\(^-\) center orientation, and therefore all NV\(^-\) centers are in resonance.

5. Conclusion

The low-field feature in the magnetic spectrum of diamonds containing NV\(^-\) centers has been discovered. This feature, referred to as the zero field line, has the following properties:

1. The amplitude of the line weakly depends on sample orientation.
2. The shape of the line strongly depends on excitation light polarization. If the polarization is perpendicular to the external magnetic field, an inverted line in the zero field appears.
3. When the concentration of the NV\(^-\) centers in the sample decreases sharply, the magnitude of the line drops. At the same time, the width of the line decreases.
4. At higher concentrations of NV\(^-\) centers, an additional line appears at about 20 G in the spectrum. This line is observed only for \( B_0 \parallel \langle 111 \rangle \). Its magnitude is independent of excitation light polarization.
5. The amplitude of the zero field line reaches its maximum at a large (about 80°) phase shift \( \theta_{LA} \) of the lock-in amplifier, suggesting that the processes accounting for the rise of this line are quite slow (microsecond time domain).
6. The line is also observed in a powdered sample, where its magnitude is comparable to that of the line in the single crystal.

Figure 8. The theoretically calculated magnetic spectrum (see appendix for details). \( D_{\perp, \parallel} = 26 \) MHz, \( \theta_{B0} = \phi_{B0} = 0, k_a = k_b = 1, \delta = 0.5 \) in both cases. (a) \( w_{1a} = w_{2a} = w_{1b} = 2 \) MHz, \( w_{2b} = 21 \) MHz; (b) \( w_{1a} = w_{1b} = 2 \) MHz, \( w_{2a} = 21 \) MHz. This set of parameters simulates \( E \parallel B_0 \) for (a) and \( E \perp B_0 \) for (b).
(7) The magnitude of the line strongly depends on excitation light intensity. In addition, for low intensities this dependence is close to a square law.

We suggest that this line appears due to the magnetic dipole–dipole interaction between NV centers oriented differently in the crystal, which modifies the polarization degree of the ground triplet state.

NV centers in diamond can act as a physical realization of qubits. A particularly promising case is a regular arrangement of the centers in the crystal, which gives rise to the appearance of the entangled states of the qubit network. The detection of the state of the system is carried out by means of optical methods. Therefore, an important phenomenon to study is the influence of the dipole–dipole interaction of NV centers on their luminescence and dependence of the luminescence on the external magnetic field. Also, this is topical for nanoscale magnetometry using NV centers.

In addition, the dependence of the magnetic spectrum of interacting NV centers on the polarization of the exciting light gives the possibility of optical control of the pair of qubits.

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## Appendix

We present the following model of two interacting NV centers. First we restricted ourselves by considering only the lowest triplets of each NV center. Polarization of NV centers due to optical pumping in our model is provided by different values of transition probabilities from the T0 state to the T+,T− states and back from the T+,T− states to the T0 state. We denote these probabilities as w1 (transition T0 → T+,T−) and w2 (transition T+,T− → T0) for the first (A) NV center and w1b and w2b for the second (B) NV center. The probabilities w1a and w2a are not equal to each other, which provides polarization of the A center. The same takes place for the B center. In addition, these probabilities for the two centers are different from each other, which provides different spin polarization of centers A and B with different orientation of two NV centers in the crystal. Centers with identical orientation have the same polarization and do not contribute to the low-field feature. These probabilities (w1a, w2a, w1b, and w2b) define the matrix W of transition probabilities in the collective-states basis of the two NV centers.

The spin Hamiltonian $\hat{H}$ of the system is as follows:

$$\hat{H} = \hat{H}_{0a} + \hat{H}_{0b} + \hat{H}_{d-d}, \quad (A.1)$$

where $\hat{H}_{0a}$ is:

$$\hat{H}_{0a} = D_1 \hat{S}_a^2 + B_0 S_a. \quad (A.2)$$

Here the first term is the Hamiltonian of the zero field splitting, whereas the second term describes the Zeeman interaction with the external magnetic field $B_0$. Parameter $D$ was taken equal to $D = 2870$ MHz. In (A.2) $\hat{S}_a$ is the operator of the z projection of the NV center spin ($S = 1$), and the z-axis is the direction of the symmetry axis of NV center A. The Hamiltonian $\hat{H}_{0b}$ for the second center is constructed in the same way.

For the sake of simplicity we define the collective-spin-states basis of two NV centers, with quantization of each spin along its own symmetry axis. Thus, the form of the zero-splitting Hamiltonian in (A.2) is identical. Let us define the right Cartesian coordinate system where the z-axis is directed along the A center symmetry axis and the x-axis lies in the plane that is formed by the symmetry axes of the A and B centers. The angle between the A and B symmetry axes was taken equal to $\theta = \arccos(1/3) \approx 70.5^\circ$. The direction of the magnetic field in the coordinate system is defined by angles $\theta_a$, $\phi_b$. Since we consider the second center B in its own quantization axis, the direction of $B_0$ is different and is recalculated taking into account the mutual arrangement of the quantization axes of the centers.

Dipole–dipole interaction is defined as

$$\hat{H}_{d-d} = D_{d-d} \left( 3 \left( \hat{S}_a \mathbf{n} \right) \left( \hat{S}_b \mathbf{n} \right) - \hat{S}_a \hat{S}_b \right). \quad (A.3)$$

Here $D_{d-d}$ is the parameter characterizing the dipole–dipole interaction, which is defined by the distance between the centers. Vector $\mathbf{n}$ is a unity vector that connects these two NV centers; its direction is defined by angles $\theta$ and $\phi$ in the coordinate system previously described. Operator $\hat{S}_a$ is the spin operator of the first NV center.
center, whereas \( \hat{S}_{ib} \) is the spin operator of the second center rotated by angle \( \theta_0 = \arccos(1/3) \):
\[
\hat{S}_{ab} = \cos \theta_0 \hat{S}_{ab} + \sin \theta_0 \hat{S}_{bh},
\]
\[
\hat{S}_{bh} = \hat{S}_{bh},
\]
\[
\hat{S}_{ab} = -\sin \theta_0 \hat{S}_{ab} + \cos \theta_0 \hat{S}_{ab}.
\]
This is the case because we are considering the spin operators of the centers as operators in their own spin-states basis, with quantization along their own symmetry axis.

The equation for the collective density matrix \( \rho \) of the two centers is as follows:
\[
\frac{d\rho}{dt} = \hat{L}\rho + \hat{W}\rho, \tag{A.7}
\]
where \( \hat{W} \) is the matrix of transitions induced by light; its elements are defined through probabilities \( w_{1ab}, w_{2ab} \). Liouvillian \( \hat{L} \) describes the evolution of the density matrix \( \rho \) as a vector in the Liouville space due to the Hamiltonian \( \hat{H} \).

To obtain the stationary density matrix (at \( t \to \infty \)) we solve a slightly different equation:
\[
\frac{d\rho(t)}{dt} = \left( \hat{L} + \hat{W} \right) \rho(t) - s\rho(t). \tag{A.8}
\]
This is actually the calculation of the Laplace transform \( \rho(s) \) of the density matrix \( \rho(t) \):
\[
\rho(s) = \int_0^\infty \rho(t) e^{-st} dt. \tag{A.9}
\]
Taking the small parameter \( s \) we can calculate stationary density matrix:
\[
\rho(t \to \infty) = \lim_{s \to 0} (s\rho(s)). \tag{A.10}
\]
Thus the starting density matrix is not crucial, i.e., \( \rho(t = 0) \); it can be taken, for instance, as the unity matrix, which means that at instant \( t = 0 \) all collective spin states are equally populated.

The spectrum is calculated as follows:
\[
I\left[B_0\right] = k_b \left[n_{0a} + \delta \cdot \left(n_{a+} + n_{-a}\right)\right] + k_b \left[n_{0b} + \delta \cdot \left(n_{ab} + n_{-ab}\right)\right]. \tag{A.11}
\]
where \( n \) is the population of the corresponding level of spin A and spin B; for instance, \( n_{0a} \) is population of the \( T_0 \) level of spin A. We consider that the intensity of luminescence is proportional to the sum of the populations of the \( T_0 \) levels, as well as the fraction \( \delta \) of the sum of the populations of the \( T_+ \) and \( T_- \) levels. Coefficients \( k_a \) and \( k_b \) are necessary for taking into account different orientations of NV- centers relative to the polarization vector \( \mathbf{E} \) of the excitation light. The fraction \( \delta \) reflects the fact that the quantum yield of luminescence from the excitation of the \( T_+ \) and \( T_- \) levels is smaller than that from the \( T_0 \) levels.

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