**Study of microwave magnetic field saturation properties of an inhomogeneous CW-EPR line in the vicinity of Rabi resonance: Possible application for *B*1 estimation**

B. Rakvin† and J. Jurec

*Ruđer Bošković Institute, Division of Physical Chemistry, Bijenička 54, Zagreb, Croatia.*

†*e-mail: rakvin@irb.hr*

**Abstract**

The spectrum of continuous wave electron paramagnetic resonance (CW-EPR) was analyzed with respect to the change in the shape of spectral lineshapes under the microwave power saturation (is intensity of MW magnetic field) when the Rabi frequency , is the electron gyromagnetic ratio) approaches to frequency of radiofrequency (RF) field . The possible effect of Rabi resonance , on spin packets system can be detected under the condition of “weak modulation near the Rabi resonance” ( where is modulation amplitude of RF field expressed in frequency units. Inhomogeneously broadened, CW-EPR, lines of the P1 (Ns0) nitrogen centers (30ppm>[Ns0] <200ppm) in HPHT diamond crystal and E’ defect in irradiated vitreous SiO2 with long spin relaxation times ( and ranged in the interval from around 2ms to 1 µs at room temperatures) were selected for saturation study. Spectra were recorded using magnetic field modulation kHz) with modulation amplitude as the first harmonic for two phase-sensitive detections, detecttion in-phase with respect to the modulation frequency and detection 90o out-of-phase with respect of the modulation frequency. The out-of-phase signal of P1 (mN=0, of nitrogen triplet) under the microwave power saturation shows two spectral components, a narrow spectral component with peak-to-peak linewidth and a broad component , respectively. These components were analyzed with regard to the change of spectral lineshape parameters (intensity amplitude, linewidth and linesplitting) in the vicinity of the Rabi resonance . For values in the close vicinity of resonance, qualitative parameters describing the narrow component show greater effective changes (collapse of linesplitting and discontinuity in linewidth) than the broad component parameters, allowing greater accuracy of the value assigned to µT) on the axis. A similar study was provided for the inhomogeneous line of the E’ center imbedded in the glassy matrix. The CW-EPR spectrum recorded at first harmonic exhibits characteristic two peaks due to nearly axial symmetric g-tensor of E’ center. The peak at described with corresponding parameters, peak amplitude and linewidth at half amplitude, was monitored as an inhomogeneous line in saturation process in the vicinity of Rabi resonance. It can be noted that peak linewidth of out-of-phase spectrum as function of clearly shows a minimum at expected position of Rabi resonance µT. The resulting changed in inhomogeneous spectral lines of P1 and E’ centers detected near Rabi resonance in the saturation process shows that both samples can be used as a standard for estimation value.

*Keywords:*

P1 centers in diamond

E’ centers in vitreous SiO2

EPR, ESR

Microwave field intensity B1

Electron spin relaxation

Modulation sideband

1. **Introduction**

Determination of the intensity of the microwave (MW) magnetic field ) in spectroscopic techniques such as electron paramagnetic resonance (EPR) and nuclear magnetic resonance (NMR) in combination with the method of dynamic nuclear polarization (DNP) is one of the important parameters for further application of these techniques. In a continuous wave (CW) EPR spectroscopy the intensity of traditionally can be determined by applying several methods[[1-11](#_ENREF_1)]. Recently, two methods[[9](#_ENREF_9), [10](#_ENREF_10)] have been proposed for calibration using P1 (Ns0) nitrogen centers in commercial high pressure high temperature (HPHT) diamond as a suitable calibration standard in EPR spectroscopy as well as in non-resonant structures such as DNP-enhanced NMR. For the later techniques it is important to note that one should chose as a standard the sample with long spin-spin () and spin-lattice () relaxation times as is expected for P1 (Ns0) centers even at room temperatures. These long relaxations are required to assure that the microwave power () saturation curve (signal intensity versus ) shows a maximum in the available power range. The saturation curve in CW-EPR of the commercial type-Ib diamond crystal containing (30ppm>[Ns0] <200ppm) concentration of P1 (Ns0) centers was employed to determine the maximum of saturation curve and corresponding product of P1 centers. For the central peak (=0 line, peak-to-peak linewidth ( mT) at first harmonic detection) of the P1 center the expected maximum of saturation curve was obtained at µT. In addition, these relaxation times were separately evaluated by pulse measurements at X-band MW frequency[[9](#_ENREF_9)] and the wide distribution of relaxation times was detected. Thus, the quantitative calibration of required taking into account the combination of saturation curves[[9](#_ENREF_9)]. The origin of different relaxation times was related to electron-electron spin diffusion mechanism and electron-electron dipolar coupling which contribute to the line broadening. The most recent method[[10](#_ENREF_10)] proposed HPHT type-IIa diamond crystal containing low concentration of P1 (Ns0) centers ([Ns0] <1ppm) for calibration. A low concentration of P1 centers reduces electron-electron dipolar coupling and hence contributes to narrowing of the inhomogeneous line. This significant narrowing ( µT) of the line made it possible to observe the influence of modulation sidebands (MS) on the detected spectrum when the Rabi frequency , is the electron gyromagnetic ratio) approaches to frequency of radiofrequency (RF) field . It was shown that for the first harmonic of phase-sensitive detection spectrum detected 90o out-of-phase with respect of the modulation frequency (out-of-phase spectrum) shows inversion of MS lines while passing Rabi resonance condition during the saturation process[[12](#_ENREF_12)]. The detection of this effect in the close vicinity of Rabi resonance enables the estimation of µT for applied magnetic field modulation frequency of kHz)[[10](#_ENREF_10)].

In comparing these methods, it can be seen that each of them has some advantages and disadvantages in the application itself. For example, the advantage of the first method is that it has an intense signal (HPHT diamond crystal type-Ib) and can be easily detected, while this is not the case with the second method (HPHT diamond crystal type-IIa), whose signal intensity is much weaker due to the small concentration of P1 centers. On the other hand, the second method using only one spectral component has an advantage over the first method in the precision of detection, since for the later one uses two spectral components to describe the cumulative saturation curve when determining the constant of proportionality for corresponding ,

Taking these considerations into account, it can be concluded that one can additionally improve calibration properties of HPHT diamond crystal type-Ib if a narrow spectral component could be separated from the broad inhomogeneous line by employing CW-EPR detection.

In this work, the possibility of applying CW-EPR detection of the narrow component of the inhomogeneous broadened line present in the CW-EPR spectrum of HPHT diamond crystal type-Ib will be investigated. Due to the distribution of and , it can be expected that long times within that distribution will contribute to a narrow line component incorporated within the inhomogeneous broadened line. In the saturation process, the narrow component will be used for the detection of spectral effects in the vicinity of the Rabi resonance and the evaluation of the .

The same methodology for the calibration was examined using an amorphous glassy silica sample containing E' centers that also exhibit long and at room temperature[[11](#_ENREF_11)]. A narrow inhomogeneous line component of the out-of-phase spectrum (powder spectrum due to the axial symmetry of -tensor) corresponding to was monitored in the saturation process near the Rabi resonance.

**2. Materials and methods**

The CW-EPR experiments were performed using Bruker ELEXSYS 580 spectrometer working at X-band frequency. The spectra were recorded by employing Bruker ER 4118X-MD5 microwave cavity with 200 mW source of microwave radiation. The cavity conversion constant for converting microwave power into field was obtained earlier[[10](#_ENREF_10)]. Magnetic field modulation with magnetic modulation frequency of kHz) and small modulation amplitude was applied for all monitored EPR spectra. 20mM solution of Fremy salt was used to adjusted the modulation phase, It is expected that in-phase spectrum exhibits maximum intensity in comparison to intensity of out-of-phase spectrum. The intensity of out-of-phase spectrum of this solution is low and can not be distinqush from spectral noise at room temperatures.

The diamond sample used in the present study was synthetic diamond type-Ib crystal (2.4×2.4×0.95 mm3, with polished face normal to the [100] axis) produced by Element 6. This type of crystal is transparent (light yellow) and characterized by high concentration of impurities ([Ns0] ≈90 ppm). The concertation can be obtained from mT from the plot 1/ vs [Ns0] assuming Gaussian lineshape[[13](#_ENREF_13)]. The long relaxation times for such type of crystal (type-Ib) was examined by pulsed X-band[[9](#_ENREF_9)] and W-band[[14](#_ENREF_14)] EPR spectroscopies. The [1,0,0] crystal axis is aligned along the Zeeman magnetic field with accuracy of experimental error (±1o) in the CW-EPR cavity. Thus, the expected 1:1:1 intensity of spectral lines at this orientation usually appears as triplet spectrum with non-equivalent intensities of line (with higher intensity of central line in comparison to outer lines, (=±1)) due to small misalignment of the crystal and anisotropy of 14N hyperfine splitting.

An inhomogeneous broadened spectral line of γ-irradiated SiO2 with a dose of ~5kG was used as the second model for detection of spectral effects in the vicinity of the Rabi resonance. The dominant defects that persist at room temperatures caused by such radiation is known as E’ paramagnetic centers (S=1/2)[[15](#_ENREF_15)]. This centers have been investigated in some details in crystalline quartz[[16](#_ENREF_16)]. Usually, the most common detected EPR spectra are in the polycrystalline sample showing nearly axial type anisotropy in *g*-tensor (= 2.0018, ~2.0004). Following earlier more detail investigation for the dose of ~5kG it can be expected long relaxation times ( ~ ~ 200 µs, spin concentration ~ 1.3×1016 spins/cm3)[[11](#_ENREF_11), [17](#_ENREF_17)] at ambient temperature.

**4. Detection of first harmonic out-of-phase absorption signal of P1 center in diamond**

P1, (Ns0) center is known as the most common paramagnetic impurity in natural and as-grown CVD diamonds and it was studied by various EPR methods[[18-22](#_ENREF_18)]. It exhibits S = 1/2, I = 1 (from14N nucleus) and C3v symmetry. This system can be described by four independent sites in a diamond lattice. When is aligned parallel to [100] crystallographic direction (perpendicular to the face of the type-Ib crystal), nitrogen-carbon anti-bonding orbitals (localization of unpaired electron) of all four sites make the same angle with and all four sites give identical spectrum. The in-phase spectrum is characterized with a dominant triplet line splitting due to the hyperfine interaction with the spin of the nitrogen nucleus (Fig. 1) at low MW power ( bellow saturation effects. The out-of-phase spectrum detected at the same MW power exhibits very small intensities of peaks which are comparable with the spectral noise as can be seen in Fig.1a. Figure 1b shows the both spectra recorded at an order of magnitude higher MW power. The in- phase spectrum shows almost the same intensity while the out-of-phase spectrum shows significantly larger intensity than the intensity detected at low MW power. It can be also noted that the line shape of the out-of-phase spectrum exhibits a composite character in comparison to lineshape of the in-phase-spectrum. In order to examine composite character of the spectrum the (mN=0) line of the triplet was monitored in the narrow interval of magnetic field sweep at two different MW powers (Fig.2). Two spectral components can be clearly distinguished, the narrow line component with peak-to-peak linewidth () and broad line component () as denoted in Fig.2 with one stars for the first component and with two stars for the second component, respectively. The intensity of broad component shows a faster decrease than the intensity of the narrow component in the process of further lowering of the MW power. Figure 3 shows CW-EPR out-of-phase spectra for mN=0 component as the function of microwave power in the low microwave power region (ω1<ωrf) . The amplitudes of spectra were reduced by the factor denoted on the left side of each spectrum. Note, decreasing of the central doublet splitting with increasing microvave power and disaperence of the doublet in the close vicinity of Raby resonance (ω1≈ωrf). Moreover, at the lowest MW powers, the narrow component splits into two sharp lines (Fig.3). The appearance of merging complex inhomogeneous lines in the saturation process indicates that the intensity of MW magnetic field approaches to the frequency of the magnetic field modulation (). This effect has been discussed and described in details for a type-IIa HPHT diamond crystal that contains a significantly lower concertation of P1 centers ([Ns0] <1ppm) and its CW-EPR spectrum shows only a narrow inhomogeneous line component ( [[10](#_ENREF_10)]. It can be noted that the detected closely matches the obtained in the same interval of the saturation process and indicates that the origin of the narrow spectral component is similar to the P1 spectrum of low density centers in type-IIa HPHT diamond. One can exploit this similarity to use recently developed theoretical model[[10](#_ENREF_10), [12](#_ENREF_12)] to describe the behavior of the narrow spectral component near the Rabi resonance. The dominant contribution of the first spectral component to the cumulative spectrum is expected at low MW power, while the contribution of the second spectral component can be neglected. Fig. 4 shows the out-of-phase spectrum detected at and corresponding calculated model spectrum[[10](#_ENREF_10)] using parameters (). The calculated spectrum represents a homogeneous spectrum with an effective at the expected value of and therefore the value of for monitored spectrum is defined. The largest uncertainity in evaluation of is related to the description of the inhomogeneous spectral line with the homogeneous spectral line. In order to improve this uncertainity, it is convinient to defined the qualitative parameters of these spectra (Fig. 4) as suggested earlier[[10](#_ENREF_10)]. These parameters can be monitored in the saturation process approuching the Rabi resonance condition. Each of these parameters shows a characteristic behavior at as shown in previous study[[10](#_ENREF_10)]. The qulitative parameter () describe splitting, which decreases with increasing and disappears under resonance conditions. In the same interval of , the linewidth parameter shows little changes, but in resonance condition it shows a “discontinuity“ towards larger values. Qualitative parameters corresponding to the first and second inhomogeneous spectral components in the saturation process are collected in Figure 5. The parameters of the broad component () show a continuous change throughout the

Figure

CW-EPR spectra of the HPHT diamond crystal sample with magnetic field (B0) orientation along (100) axis of the dimond lattice. Three spectral components ( mN=-1, mN=0, mN=+1) corespond to hyperfine nitrogen splitting of P1 center in the diamond. Spectra are taken with (ωrf/2π=100 kHz) modulation frequency with amplitude modulation (1µT) for two phase-sensitive detections (detecttion in-phase with respect to the modulation frequency, MP=0o red line, detection 90o out-of-phase with respect of the modulation, MP=90o blue line) at two different microwave powers a) P=0.02mW and b) P=0.32mW.

Figure

CW-ESR out-of-phase spectra obtained in the close vicinity of the central spectral component (mN=0) with the same detection parameters as described in Fig 1. Two spectra recorded at two different microwave powers exhibit two spectral components, broth component denotes with two stars (peak-to-peak amplitude, Ipp2 and peak-to-peak linewidth, Δpp2) and narrow component (Ipp1 and Δpp1) denotes with one star, respectively

Figure

CW-ESR out-of-phase spectra for mN=0 component as the function of microwave power in the low microwave power region (ω1<ωrf) . The amplitudes of spectra were reduced by the factor denoted on the left side of each spectrum. Note, decreasing of the central doublet splitting with increasing microvave power and disaperence of the doublet in the close vicinity of Raby resonance (ω1≈ωrf).

Figure

CW-ESR out-of-phase spectrum of mN=0 component of P1 center at low microwave power. Two arrows and two stars describes spectral parameters („effective splitting“ D±1 and peak-to-peak linewidth Δpp1). Dotted lines describes simulated lineshape of a homogenously broadened line detected as the first harmonic out-of-phase (calculated with parameters T1=2ms, T2=3.7µs, ω1/ωrf =0.5) by employing earliar calculation for low density P1 centres in diamond lattice. ( ref. 10 ).

monitored interval. Conversely, the parameters of the narrow components (, ) also show a continuous change in the monitored interval, but a “discontinuous” exhibit sharp increasing and approching to zerro value) behavior near the Rabi resonance at . Thus, the detected “discontuinity“ in Fig. 5 allows us to define a resonance position equal to value of =0.036mT. It can be noted that the earlier calibration of obtained by HPHT type-IIa diamond coincides with the currently detected “discontuinity“ position of the narrow inhomogeneous line component of HPHT type-Ib diamond.

Figure

Saturation curves for two spectral components of the mN=0 line as shown and defined in Fig.2. a) circles for peak-to-peak amplitude for narrow component (Ipp1) and triangles for broad component (Ipp2), respectively. b) triangles for peak-to-peak linewidth (Δpp2) for the broad component and diamonds for the narrow component (Δpp1), respectively. D±1 parameter values were represented by squares. The filled symbols are taken for spectral component detected at microwave power region where the effective splitting can be resolved. Continuous lines follow experimental points. The arrow denotes expected position of Rabi resonance at abscise value B1=0.0036mT (ω1 = ωrf)

**5. CW-EPR spectra of E’ center in γ-irradiated vitreous SiO2 in the vicinity of Rabi resonance**



In the above chapter the CW-EPR spectra of the paramagnetic center in crystal matrices were examined in order to reduce as much as possible the inhomogeneous broadening of the detected spectral lines. However, preparing paramagnetic centers in a polycrystalline or powder matrix is more practical and it is also a challenge to use these samples to detect Rabi resonance effects. In the present case, the E’ center in γ-irradiated vitreous SiO2 (radiation dose was chosen due to the long relaxation times ) at ambient temperatures. To record CW-EPR spectra for E’ centers, the same default spectral parameters as for P1 centers were used to facilitate the comparison of the saturation process of these centers. Figure 6 shows in-phase and out-of-phase spectra of E’ centers at low (0.002mW) and high (0.087mW) MW powers. An enhanced signal intensity for the out-of-phase spectrum can be observed at higher MW power, which is characteristic for recording the EPR spectrum of the sample with the long relaxation times under the condition of ”rapid passage”. “Rapid passage” occurs when the rate of change of the external magnetic field () or the amplitude of the magnetic field modulation is greater than the electron spin relaxation rate. This effect for E’ centers was studied earlier in the wide range of by applying a significantly (two order of magnitude) larger modulation amplitude than in the present case[[11](#_ENREF_11)]. It was shown that at high (> 0.01mT) the intensity of the out-of-phase signal has a maximum intensity and is proportional to the spin concentration[[11](#_ENREF_11)]. In order to detect possible effects near the Rabi resonance under the condition of “weak modulation near the Rabi resonance” (, the saturation process was monitored only for the interval with low values ( <0.01mT). The intensity and linewidth (*I*, , at half intensity) of the narrow peak that appeared on the of the anisotropic E’ spectrum were monitored in the saturation process (Fig.7). The intensities and linewidths of the in-phase spectrum show quite expected behavior, *I* increases maintaining the constant for increasing (<0.001mT). For further increase (>0.001mT) *I* shows the maximum and saturation effects while shows the broadening contributions. On the other hand, the out-of-phase spectra show a higher intensity than the in-phase spectra in a wide interval of (>0.002 mT) with a maximum in the vicinity of Rabi resonance. This is in consistent with the theoretical description for the condition ( where the out-of-phase spectrum shows an intensity approximately an order of magnitude higher intensity then the in-phase intensity[[12](#_ENREF_12)]. The linewidth of the out-of-phase signal decreases with increasing (0.0037) and increases for further increasing of . The obtained minimum of linewidth in the saturation process can be noted at position of where Rabi resonance is expected. The origin of this minimum can be easily explained by comparison with P1 center. It can be seen that is wider than (due to faster effective relaxation times) and thus the qualitative splitting parameter can not be resolved. In the saturation process, shows an almost constant behavior while decreases sharply and a narrowing effect is expected as cumulative effect on . At higher (>0.0037mT) the usual saturation broadening of is expected. Thus, for the same monitored interval of the narrowest inhomogeneous component shows clear “dicontinuity“ contribution, while broader component shows sharp minimun and the broader component shows only a slight broad minimum. This is in accord with earlier theoretical model where calculated qualitative parameters for faster relaxation rates show smoller effects of “discotinuity“ with a possible effet of a small shift from the resonance position[[10](#_ENREF_10)].

Figure

CW-ESR spectra for E1' center in a SiO2 sample irradiated at 5kGy. Spectra were obtained with 1µT modulation amplitude. For modulation and phase sensitive detection modulation frequency of 100kHz was employed. Spectra detected in-phase (MP=0o; red line) and out-of-phase (MP=90o; blue line) with respect to the modulation at two microwave powers a) (P=0.002mW) and b) (P=0.087mW). Spectrometer gain setting for spectra (a) was 4 times that for spectra (b).

Figure

Amplitudes (circles, in-phase open circles, out-of-phase filled circles) and linewidth at half intensity (triangles, in-phase open triangles, out-of-phase filled triangles) of the peak (denote with star in Fig. x) given as function of microwave field intensity (B1). The arrow denotes expected position of Rabi resonance at abscise value B1=0.0036mT (ω1 = ωrf).

**6. Conclusion**

The CW-EPR spectral lines of the P1 center (=0, -1, +1) in HPHT type-Ib diamond crystal contain different overlapping relaxation times. Despite the heterogeneity of the relaxation dynamics, the saturation curves of these lines show peaks at low MW power (<0.005mT) and they become suitable for use as calibration standard for DNP enhanced NMR. In order to reduce this heterogeneity and perform selectivity between different relaxation rates, the out-of-phase spectrum of this line was brought into rapid-passage condition at different MW powers. It is shown that one of the two resolved inhomogeneous lines, the narrow one ( ) exhibits detectable changes in the lineshape in the process of saturation near the Rabi resonance. The obtained lineshape effects at can be used to calibrate value. Since in this case only one narrow inhomogeneous line component is used in the determination of , and not two inhomogeneous components as in the case of the peak saturation method, higher accuracy is expected.

The ability of the E' center in the glassy SiO2 to calibrate was also investigated. Considering large relaxation times at room temperatures and the use of the low concentration of these centers, the resulting inhomogeneous line component shows a broadened linewidth than the narrow line component of the P1 center. The wider linewidth indicates a higher electron spin diffusion rate in this glassy sample than in the crystal lattice of diamond (()). Therefore, in the process of saturation, the splitting of this component into two narrower components cannot be resolved as in the case of the P1 center component at low saturation. Moreover, with further lowering in saturation, the linewidth of the E’ center shows a broadening instead of the increase of splitting that is characteristic of the P1 center. However, the obtained linewidth minimum in the saturation process (due to intrinsic coalescence of the splitting components) appears in the immediate vicinity of Rabi resonance and can be used for the calibration of .

**Acknowledgment**

This work was fully supported by the Croatian Science Foundation under the project number IP—2022-10-9292. The authors highly acknowledge the diamond samples obtained from Susumu Takahashi and Ivan Hrvoić.

**References:**

[1] E.L. Ginzton, Microwave measurements, McGraw-Hill, New York, 1957.

[2] J.H. Freed, D.S. Leniart, J.S. Hyde, Theory of Saturation and Double Resonance Effects in ESR Spectra. III. rf Coherence and Line Shapes, The Journal of Chemical Physics, 47 (1967) 2762-2773.

[3] D.P. Dalal, S.S. Eaton, G.R. Eaton, The effects of lossy solvents on quantitative EPR studies, Journal of Magnetic Resonance (1969), 44 (1981) 415-428.

[4] M.A. Hemminga, F.A.M. Leermakers, P.A. de Jager, Quantitative measurement of B1 in ESR and saturation-transfer ESR spectroscopy, Journal of Magnetic Resonance (1969), 59 (1984) 137-140.

[5] A.I. Vistnes, L.R. Dalton, Experimental methods to determine the microwave field strength in electron spin resonance, Journal of Magnetic Resonance (1969), 54 (1983) 78-88.

[6] G.R. Eaton, S.S. Eaton, D.P. Barr, R.T. Weber, Quantitative EPR, Springer Vienna, 2010.

[7] M. Peric, B. Rakvin, A. Dulcic, Measurement of Microwave Field-Strength in Electron-Spin-Resonance by a Pulsed Modulation Technique, Journal of Magnetic Resonance, 65 (1985) 215-221.

[8] B. Rakvin, D. Carić, M. Kveder, Enhanced accuracy of the microwave field strength measurement in a CW-EPR by pulsed modulation technique, Journal of Magnetic Resonance, 287 (2018) 123-127.

[9] A.M. Carroll, S. Eaton, G. Eaton, K.W. Zilm, Electron spin relaxation of P1 centers in synthetic diamonds with potential as B1 standards for DNP enhanced NMR, Journal of Magnetic Resonance, 322 (2021) 106875.

[10] B. Rakvin, D. Carić, M. Kveder, CW-EPR spectra of P1 centers in HPHT diamond in the vicinity of Rabi resonance: possible standard for B1 evaluation in EPR and DNP enhanced NMR spectroscopies, Journal of Magnetic Resonance Open, 10-11 (2022) 100039.

[11] J.R. Harbridge, G.A. Rinard, R.W. Quine, S.S. Eaton, G.R. Eaton, Enhanced Signal Intensities Obtained by Out-of-Phase Rapid-Passage EPR for Samples with Long Electron Spin Relaxation Times, Journal of Magnetic Resonance, 156 (2002) 41-51.

[12] A.P. Saiko, R. Fedaruk, S.A. Markevich, Multi-photon transitions and Rabi resonance in continuous wave EPR, Journal of Magnetic Resonance, 259 (2015) 47-55.

[13] J.F. Barry, J.M. Schloss, E. Bauch, M.J. Turner, C.A. Hart, L.M. Pham, R.L. Walsworth, Sensitivity optimization for NV-diamond magnetometry, Rev Mod Phys, 92 (2020) 015004.

[14] V. Stepanov, S. Takahashi, Determination of nitrogen spin concentration in diamond using double electron-electron resonance, Physical Review B, 94 (2016) 024421.

[15] J.A. Weil, A review of electron spin spectroscopy and its application to the study of paramagnetic defects in crystalline quartz, Physics and Chemistry of Minerals, 10 (1984) 149-165.

[16] R.H. Silsbee, Electron Spin Resonance in Neutron‐Irradiated Quartz, J Appl Phys, 32 (1961) 1459-1462.

[17] B. Rakvin, D. Carić, M. Kveder, Modulation sidebands spectra within inhomogeneous CW-EPR line detected by double modulation EPR spectroscopy, Journal of Magnetic Resonance, 307 (2019) 106587.

[18] J.H.N. Loubser, J.A.v. Wyk, Electron spin resonance in the study of diamond, Reports on Progress in Physics, 41 (1978) 1201-1248.

[19] J.A.v. Wyk, E.C. Reynhardt, G.L. High, I. Kiflawi, The dependences of ESR line widths and spin - spin relaxation times of single nitrogen defects on the concentration of nitrogen defects in diamond, Journal of Physics D: Applied Physics, 30 (1997) 1790-1793.

[20] A. Cox, M.E. Newton, J.M. Baker, 13C,14N and15N ENDOR measurements on the single substitutional nitrogen centre (P1) in diamond, Journal of Physics: Condensed Matter, 6 (1994) 551-563.

[21] S. Zhang, S.C. Ke, M.E. Zvanut, H.T. Tohver, Y.K. Vohra, g tensor for substitutional nitrogen in diamond, Physical Review B, 49 (1994) 15392-15395.

[22] B. Rakvin, D. Carić, M. Kveder, Detection of narrow lines in the inhomogeneously broadened line of P1 centers in diamond by double modulation EPR spectroscopy, Appl Phys Lett, 117 (2020) 153503.