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ANISOTROPIC EVOLUTION OF THE SPIN-TRIPLET STATES AT MAGNETIC RESONANCE CONDITIONS IN THE NON-WEAK CONSTANT FIELD: APPLICATION OF SINGLE TRANSITION OPERATORS

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Abstract

Using the known earlier formalism of the single transition operators and our original analytical technique, we have derived the equations of motion for the magnetization components, related to the separate transitions of the spin-triplet state (STS) spectrum in a single crystal. At that, we supposed that samples with STS are subjected to the action of the alternating magnetic field and of the non-weak constant field, the value of which is larger than the zero-field splitting of STS spectrum. However, only the components of the sample full magnetization, which are linearly connected with the single transition magnetization components, are the observable values. We have demonstrated that at the fulfillment of the definite condition, the free motion of the sample full magnetization after the excitation of one of the transitions is the precession at the frequency of the excited transition with an ellipse in the plane transverse to the constant field. At that, the squared absolute value of the magnetization vector contains the part, oscillating at the double frequency of the excited transition. The tensor of the dynamic susceptibility, reflecting the elliptical character of the magnetization precession at the steady state electron paramagnetic resonance (EPR), is written at the creation of the resonance conditions for each of the STS transitions. The obtained analytical angular dependence of the EPR spectrum agrees qualitatively with the corresponding experimental results.

***Keywords**: EPR, spin-triplet states, single transition operators, magnetization motion, elliptical precession.*

1 Introduction

The materials with spin-triplet states (STS) of electron spins find wide application in science and technology. The monographs [1, 2] contain the information about the compounds, in which STS are present or they can be created by means of the different methods. STS are used at the realization of the nuclear dynamic polarization [3-5], in the molecular electronics [6, 7] and in such optoelectronic devices, as light emitting diodes, transistors and solar elements [8]. STS play important role at the photosynthesis [9] and at the creation of the entangled spin states, which are of interest at the producing of the quantum processors [10,11]. EPR is one of the most important methods of the STS study during

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a few decades [12-21]; so, the investigation of the character of the sample magnetization motion under the action of the constant and the alternating magnetic fields in materials with STS has the great significance. In particular, the papers [12-18] are devoted to the EPR experiments on the STS in single crystals in the non-weak constant field (the value of this field is larger than the zero-field splitting of STS spectrum). Therefore, we would like to investigate the motion of the sample magnetization in such a case. It is of interest also to reveal the peculiarities of the free motion of the sample magnetization.

2 Materials and methods

The materials are the object of our investigation, if they are single crystals and the paramagnetic resonance in them is characterized in the zero constant field by the quadrupolar Hamiltonian

$$\mathcal{H}_Q = D\left[S_Z^2 - (1/3)S(S+1)\right] + E\left(S_X^2 - S_Y^2\right), \tag{1}$$

where S_X, S_Y, S_Z are the projections of the STS spin S=1 onto the axes **X,Y,Z** – the main axes of the quadrupolar interaction tensor; D, E are the parameters of the zero-field splitting of the spin levels (they are called also FS constants). At that, we suppose that these samples are subjected to the alternating and the non-weak constant fields[1]. Here we have in mind the STS of electron spins of any origin (STS of photoexcited mobile excitons in the pure $NaNO_2$ single crystal [12,13] and localized STS in organic molecular crystals [14-18]; of Cu^{2+} dimers [19]; of paramagnetic ions, for instance, of fulleride ions [19,20]). The main results are valid, in our opinion, also for the NMR on I=1 nuclei.

Analogously to [22], we suppose at the first stage of our consideration that the constant field $\mathbf{B}$ is parallel to one of the $\mathbf{X,Y,Z}$ axes (supposing that these axes coincide with the main axes of the g-factor of STS). At $\mathbf{B} \| \mathbf{Z}$, the Hamiltonian of the problem has the form:

$$\mathcal{H} = \mathcal{H}_0^Z + \mathcal{H}_{sh}^\alpha; \qquad \mathcal{H}_0^Z = g_Z \mu_B B S^Z + \mathcal{H}_Q \tag{2}$$

$$\mathcal{H}_Q = D_X S_X^2 + D_Y S_Y^2 + D_Z S_Z^2; \qquad \mathcal{H}_{sh}^\alpha = 2 g_\alpha \mu_B B_1 S_\alpha \cos\omega t \ . \tag{3}$$

Here the main Hamiltonian $\mathcal{H}_0^Z$ includes the following terms: $g_Z \mu_B B S^Z$ is the Zeeman interaction with the constant magnetic field; g_α are the diagonal components of the g-factor tensor; α takes the values X, Y, Z, μ_B is the Bohr magneton; $\mathcal{H}_Q$ is the alternative form of (1), at which $D_X + D_Y + D_Z = 0$. $\mathcal{H}_{sh}^\alpha$, the interaction of spins with the alternating magnetic field, directed along the α axis, is the perturbation of the main Hamiltonian. The transition to the other directions of the constant field can be realized with the help of the cyclic rearrangements of the indices in the sample parameters D_X, D_Y, D_Z and g_X, g_Y, g_Z [22].

Analogously to the paper [23], we apply to the full Hamiltonian the standard unitary transformation [24], which rotates the eigenvectors of STS by the $\Theta_Z/2$ angle. At the definite value of the Θ_Z angle this transformation diagonalizes the matrix of the main Hamiltonian $\mathcal{H}_0^Z$. The used unitary operator U has the following matrix form

[1] We would like to note that the theoretical questions related to the cases of the zero and the weak constant fields are considered in [2, pp. 181-185]; the case of the zero constant field is considered also, for instance, in [9].

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$$\mathbf{U}=\begin{pmatrix}\cos(\Theta_Z/2) & 0 & \sin(\Theta_Z/2)\\ 0 & 1 & 0\\ -\sin(\Theta_Z/2) & 0 & \cos(\Theta_Z/2)\end{pmatrix},$$

where

$$tg\Theta_Z=\left[\left(D_X-D_Y\right)/2\right]/g_Z\mu_B B. \tag{4}$$

Following [23], the transformed Hamiltonian is written in terms of the single transition operators S_α^{i-j} (or operators of the fictitious spin ½), described in [25]. Here, S_α^{i-j} is the α -component of the fictitious spin ½ related to the separate transition i-j between the STS levels i,j=1,2,3. The unitary transformed main Hamiltonian $U\mathcal{H}_0^Z U^{-1}$, which defines the STS levels, has the form:

$$U\mathcal{H}_0^Z U^{-1}=\hbar\Omega_{12}\mathbf{S}_Z^{1-2}+\hbar\Omega_{23}\mathbf{S}_Z^{2-3}, \tag{5}$$

where

$$\mathbf{S}_Z^{1-2}=-\mathbf{S}_Z^{2-1}=\frac{1}{2}\begin{pmatrix}1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 0\end{pmatrix};\quad \mathbf{S}_Z^{2-3}=-\mathbf{S}_Z^{3-2}=\frac{1}{2}\begin{pmatrix}0 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -1\end{pmatrix};$$

$$\hbar\Omega_{\substack{12\\23}}^Z=\pm D_Z+2\sqrt{\left(g_Z\mu_B B\right)^2+\left[\left(D_X-D_Y\right)/2\right]^2}\equiv 2\left(\pm D/3+\sqrt{\left(g_z\mu_B B\right)^2+E^2}\right). \tag{6}$$

The unitary transformed perturbation $U\mathcal{H}_{sh}^\alpha U^{-1}$**,** which is in the same representation, causes the transitions between the STS levels.

Further, we introduce the following notations: $M'_{X,Y,Z}=-ng_{X,Y,Z}\mu_B S_{X,Y,Z}$ are the original components of the sample full magnetization; $M_{X,Y,Z}$ are the unitary transformed components of the sample full magnetization. $M_{X,Y,Z}$ and $M'_{X,Y,Z}$ are connected by the following formulae:

$$M_X\equiv UM'_X U^{-1}=\sqrt{2}\left(C_Z M_X^{1-2}+A_Z M_X^{2-3}\right)$$

$$M_Y\equiv UM'_Y U^{-1}=\sqrt{2}\left(A_Z M_Y^{1-2}+C_Z M_Y^{2-3}\right) \tag{7}$$

$$M_Z\equiv UM'_Z U^{-1}=2\left(M_Z^{1-3}\cos\theta_Z-\left(g_Z/g_X\right)M_X^{1-3}\sin\theta_Z\right)$$

In Eqs. (7) the values

$$M_{X,Y,Z}^{i-j}=-ng_{X,Y,Z}\mu_B S_{X,Y,Z}^{i-j}, \tag{8}$$

where n is the STS concentration, are the magnetization components related to the separate STS transitions;

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$$\begin{aligned} A_Z &= \cos\left(\Theta_Z/2\right) - \sin\left(\Theta_Z/2\right) \\ C_Z &= \cos\left(\Theta_Z/2\right) + \sin\left(\Theta_Z/2\right) \end{aligned} . \tag{9}$$

With the help of the quantum operator equation, we have obtained the equations of motion for the operators S_α^{i-j} under the action of the full unitary transformed Hamiltonian. For this purpose, we have used the necessary commutation relations, which are brought in [25]. Then the conversion to $M_{X,Y,Z}^{i-j}$ has been done; the equations for them (see Section 3) are the initial point for the obtaining of all dynamical results; beginning from these equations, the values $M_{X,Y,Z}^{i-j}$ are considered, as classical macroscopic values. However, only the components of sample full magnetization $M_{X,Y,Z}$ are the observable ones, they are used further for the description of effects.

3 Results and discussion

The equations of motion for the 3 components of the magnetization related to the 3 transitions of the FS of EPR, following from the equations for S_α^{i-j}, have the form (as an example, below these equations are brought for the case $\mathbf{B} \parallel \mathbf{Z}$, $\mathbf{B}_1 \parallel \mathbf{X}$):

$$\begin{aligned}
\dot{M}_X^{1-2} &= -\omega_{12}^Z \left(g_X/g_Y\right) M_Y^{1-2} + \sqrt{2} A_Z \left(g_X/g_Y\right) M_Y^{1-3} \left(g_X \mu_B/\hbar\right) B_1 \cos\omega t \\
\dot{M}_Y^{1-2} &= \omega_{12}^Z \left(g_Y/g_X\right) M_X^{1-2} - \sqrt{2}\left(2C_Z\left(g_Y/g_Z\right) M_Z^{1-2} + A_Z\left(g_Y/g_X\right) M_X^{1-3}\right)\left(g_X \mu_B/\hbar\right) B_1 \cos\omega t \\
\dot{M}_Z^{1-2} &= \sqrt{2}\left(g_Z/g_Y\right)\left(2C_Z M_Y^{1-2} - A_Z M_Y^{2-3}\right)\left(g_X \mu_B/\hbar\right) B_1 \cos\omega t \\
\dot{M}_X^{1-3} &= -\omega_{13}^Z \left(g_X/g_Y\right) M_Y^{1-3} - \sqrt{2}\left(g_X/g_Y\right)\left(C_Z M_Y^{2-3} - A_Z M_Y^{1-2}\right)\left(g_X \mu_B/\hbar\right) B_1 \cos\omega t \\
\dot{M}_Y^{1-3} &= \omega_{13}^Z \left(g_Y/g_X\right) M_X^{1-3} + \sqrt{2}\left(g_Y/g_X\right)\left(C_Z M_X^{2-3} - A_Z M_X^{1-2}\right)\left(g_X \mu_B/\hbar\right) B_1 \cos\omega t \\
\dot{M}_Z^{1-3} &= \sqrt{2}\left(g_Z/g_Y\right)\left(B_Z M_Y^{1-2} + A_Z M_Y^{2-3}\right)\left(g_X \mu_B/\hbar\right) B_1 \cos\omega t
\end{aligned} \tag{10}$$

The equations for $\dot{M}_X^{2-3}, \dot{M}_Y^{2-3}$ can be obtained from the equations for $\dot{M}_X^{1-2}, \dot{M}_Y^{1-2}$ at the index $1-2 \to 2-3$ replacements and the value $A_Z \to -C_Z; C_Z \to A_Z$ replacements. The equation for $\dot{M}_Z^{2-3}$ can be obtained from the equation for $\dot{M}_Z^{1-2}$ at the index $1-2 \to 2-3$ replacements and the value $A_Z \leftrightarrow C_Z$ replacements. $\hbar\omega_{ij}^Z$ in Eqs. (10) are the notations for the quanta of the transitions between the STS levels i and j; they are equal to

$$\hbar\omega_{\substack{12\\23}}^Z = \pm\left(3/2\right) D_Z + \sqrt{\left(g_Z \mu_B B\right)^2 + \left[\left(D_X - D_Y\right)/2\right]^2} \equiv \pm D + \sqrt{\left(g_Z \mu_B B\right)^2 + E^2} \ ; \tag{11}$$

$$\hbar\omega_{13}^Z = 2\sqrt{\left(g_Z \mu_B B\right)^2 + \left[\left(D_X - D_Y\right)/2\right]^2} \equiv 2\sqrt{\left(g_Z \mu_B B\right)^2 + E^2} \ . \tag{12}$$

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The Eqs. (10) with the definitions (4,8,9,11,12) are the main result of this paper and the basis for the study of the anisotropic evolution of the sample full magnetization $\mathbf{M}$ with the components $M_{X,Y,Z}$ (see (7)) under the action of the magnetic fields[2]. At that, we suppose that the spectrum of the STS transitions is well resolved.

For instance, with the help of Eqs. (10) it is possible to ascertain the character of the free motion of the full magnetization $\mathbf{M}^{free}(t)$ of a sample with STS after the creation of the initial non-zero values of magnetization components $M_{X,Y}(0)$. Since at our non-zero constant field $A_Z \neq 0,\ \ C_Z \neq 0$, the solution of these equations at the excitation of the transition with the frequency ω_{12}^{Z} describes the oscillations of the transverse components $M_{X,Y}^{free}(t)$ of $\mathbf{M}^{free}(t)$ with this frequency. These oscillations obey the following equation:

$$\frac{\left[M_X^{free}(t)\right]^2}{C_Z^2 C^2 / g_Y^2} + \frac{\left[M_Y^{free}(t)\right]^2}{A_Z^2 C^2 / g_X^2} = 1, \quad \text{where} \quad C^2 \equiv \frac{\left[M_X(0)\right]^2}{C_Z^2 / g_Y^2} + \frac{\left[M_Y(0)\right]^2}{A_Z^2 / g_X^2}. \tag{13}$$

The equation (13) at $C_Z^2 / g_Y^2 \neq A_Z^2 / g_X^2$ is the canonical equation of an ellipse. This equation demonstrates that the projection of the end of the vector $\mathbf{M}^{free}(t)$ onto the *XY* plane circumscribes an ellipse in this plane. The longitudinal component of the vector $\mathbf{M}^{free}(t)$ does not change at the free motion. At that, the squared absolute value of the magnetization vector contains both the constant part and the part, oscillating at the double frequency of the excited transition:

$$\begin{aligned}\left[M^{free}(t)\right]^2 &= M_Z^2(0) + (1/2)\left(C_Z^2 / g_Y^2 + A_Z^2 / g_X^2\right)\left(\frac{M_X^2(0)}{C_Z^2 / g_Y^2} + \frac{M_Y^2(0)}{A_Z^2 / g_X^2}\right) + (1/2)\left(C_Z^2 / g_Y^2 - A_Z^2 / g_X^2\right)\times \\ &\times\left\{\left(\frac{M_X^2(0)}{C_Z^2 / g_Y^2} - \frac{M_Y^2(0)}{A_Z^2 / g_X^2}\right)\cos 2\omega_{12}^{Z} t - 2\frac{M_X(0) M_Y(0)}{(C_Z / g_Y)(A_Z / g_X)}\sin 2\omega_{12}^{Z} t\right\}\end{aligned} \tag{14}$$

In the case of the excitation of the transition with the ω_{23}^{Z} frequency, the replacements $A_Z^2 \leftrightarrow C_Z^2$ should be made in Eqs. (13). Using the definition (9), the condition $C_Z^2 / g_Y^2 \neq A_Z^2 / g_X^2$ can be written in the following form: $\sin\Theta_Z \neq \left(g_Y^2 - g_X^2\right) / \left(g_X^2 + g_Y^2\right)$, suitable for the evaluations.

At the studying of the steady state EPR, we have phenomenologically introduced the decays to the Eqs. (10). At that, we have supposed that the transverse magnetization components of an each transition decay exponentially with the rates $\left(T_2^{1-2}\right)^{-1}, \left(T_2^{2-3}\right)^{-1}, \left(T_2^{1-3}\right)^{-1}$. As is well known [26], the assumption about the exponential character of the transverse relaxation is valid, in particular, for the concentrated spin-systems with the averaging fast motion. Therefore, the results below, containing the transverse relaxation rates, are valid for the case of the fast motion in a concentrated STS system. Such situation takes place, for instance, in the pure *$NaNO_2$* single crystal [13], where the fast exciton jumps

[2] It should be noted that the equations for $M_Z^{1-2}, M_Z^{2-3}, M_Z^{1-3}$ are not independent from one another because of the existence of the following correlations for the single transition operators and the corresponding magnetization components: $S_Z^{i-k} = S_Z^{i-j} + S_Z^{j-k} \Rightarrow \dot{M}_Z^{1-3} = \dot{M}_Z^{1-2} + \dot{M}_Z^{2-3}$.

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take place, and in the samples, studied in [14], where the role of the averaging fast motion is played by the isotropic exchange interaction.

Further, we have applied the Eqs. (10) in the linearized form, i.e. at $M_Z^{i-j} \approx \langle M_Z^{i-j} \rangle_{eq,neq}$, for the calculation of the dynamic susceptibility tensor (DST) at the absence of the EPR saturation. The brackets $\langle ... \rangle_{eq,neq}$ denote $Sp(...\rho_{eq,neq})$, where $\rho_{eq,neq}$ is the statistical operator describing the level population distribution at thermal equilibrium (eq) or non-equilibrium (neq) with the lattice; in the latter case – with the account for the possibility of the forced population of the STS separate levels (see below). Using the Eqs. (10) with the above-mentioned decays, we have considered the motion of sample magnetization components $M_{X,Y}^{EPR}(t)$ at the steady state EPR on the 1-2 transition. At the fulfillment of the same condition $C_Z^2 / g_Y^2 \neq A_Z^2 / g_X^2$, the projection of the end of the vector $\mathbf{M}^{EPR}(t)$ onto the *XY* plane circumscribes an ellipse in this plane:

$$\frac{\left[M_X^{EPR}(t)\right]^2}{g_X^2 C_Z^2 m^2} + \frac{\left[M_Y^{EPR}(t)\right]^2}{g_Y^2 A_Z^2 m^2} = 1 \quad , \tag{15}$$

where $m^2 \equiv \frac{1}{g_Z^2} \frac{C_Z^2 (2\gamma_X B_1)^2 \langle M_Z^{1-2} \rangle_{exc}^2}{\left[\left(\omega_{12}^Z - \omega\right)^2 + \left(T_2^{1-2}\right)^{-2}\right]}$. If the transition 2-3 is excited, then the same replacements should be made in Eq. (15), as at the magnetization free motion.

The complex DST for all transitions, which follows from the expressions for $M_{X,Y}^{EPR}(t)$, can be presented in the form of a matrix:

$$\boldsymbol{\chi}_{\alpha\beta}\begin{pmatrix}1-2\\2-3\\1-3\end{pmatrix}\Bigg|^Z = \begin{pmatrix} \chi_{XX}\begin{pmatrix}1-2\\2-3\end{pmatrix}\Bigg|^Z & i\frac{g_Y}{g_X}K_Z^{\substack{1-2\\2-3}}\chi_{XX}\begin{pmatrix}1-2\\2-3\end{pmatrix}\Bigg|^Z & 0 \\ -i\frac{g_Y}{g_X}K_Z^{\substack{1-2\\2-3}}\chi_{XX}\begin{pmatrix}1-2\\2-3\end{pmatrix}\Bigg|^Z & \left(\frac{g_Y}{g_X}K_Z^{\substack{1-2\\2-3}}\right)^2\chi_{XX}\begin{pmatrix}1-2\\2-3\end{pmatrix}\Bigg|^Z & 0 \\ 0 & 0 & \chi_{ZZ}(1-3)\Big|^Z \end{pmatrix} \tag{16}$$

Here $\boldsymbol{\chi}_{\alpha\beta}$ is the complex dynamic susceptibility, describing the response of the α-th component of the sample magnetization to the action of the alternating field along the β axis at the constant field along the *Z* axis, when the constant field value approximately corresponds to its resonance magnitude for the transition 1-2, 2-3, 1-3, respectively; $K_Z^{\substack{1-2\\2-3}} \equiv \sqrt{(1 \mp \sin\Theta_Z)/(1 \pm \sin\Theta_Z)}$. At the constant field rotation in the *ZX* plane, the dynamic susceptibilities χ_{XX} corresponding to the 1-2, 2-3 transitions are equal to (hereafter, θ and φ are the polar and the azimuthal angles of the vector $\mathbf{B}$ with respect to the $\mathbf{X,Y,Z}$ coordinate system; g-factor, for simplicity, is assumed to be isotropic):

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$$\chi_{XX}\left(B,\begin{matrix}1-2\\2-3\end{matrix}\right)\Bigg|^{ZX}=\frac{g\mu_B\mu_0}{\hbar}\left\langle M_Z^{\substack{1-2\\2-3}}(B,\theta)\right\rangle\Bigg|_{eq,neq}^{ZX}\cos\theta\times$$
$$\times\left[1\pm\sin\Theta_{ZX}(B,\theta)\right]\frac{(g\mu_B/\hbar)\left[B_{res}^{\substack{1-2\\2-3}}(B,\theta)-B\right]-i\left(T_2^{\substack{1-2\\2-3}}\right)^{-1}}{(g\mu_B/\hbar)^2\left[B-B_{res}^{\substack{1-2\\2-3}}(B,\theta)\right]^2+\left(T_2^{\substack{1-2\\2-3}}\right)^{-2}}\quad, \tag{17}$$

where

$$\sin\Theta_{ZX}(B,\theta)\approx\frac{-(D-E)+(D+3E)\cos2\theta}{\sqrt{(4g\mu_BB)^2+\left[(D-E)-(D+3E)\cos2\theta\right]^2}}\ . \tag{18}$$

At the obtaining of Eq. (17) we have assumed that at the constant field rotation the direction of the alternating field does not change and stays $2\mathbf{B}_1\cos\omega t\,\mathbf{X}$ (this fact is reflected also by the unchanged denotation χ_{XX}). The DST matrix at the constant field rotation in the other planes can be obtained from (17) with the help of the cyclic rearrangements of indices and with the replacement $\theta\to\varphi$ for the *XY* plane. It should be noted that at the constant field rotation in the *ZX* and *ZY* planes we exclude from the consideration the angles $\theta=\pi/2$ and $\theta=0$, respectively, and in the *XY* plane – the angle $\varphi=\pi/2$. $B_{res}^{\substack{1-2\\2-3}}$ are the resonance fields for the STS separate transitions (about their angular dependencies see below).

The dynamic susceptibilities corresponding to the 1-3 transition at the application of the constant field in the *ZX*, *XY*, *YZ* planes are equal to

$$\chi_{ZZ,XX,YY}(B,1-3)\Big|_{sf}^{\substack{ZX\\XY\\YZ}}=2\frac{g\mu_B\mu_0}{\hbar}\left\langle M_{\substack{Z\\X\\Y}}^{1-3}\right\rangle\Bigg|_{eq,neq}^{\substack{ZX\\XY\\YZ}}\cos(angle)\sin^2\Theta_{\substack{ZX\\XY\\YZ}}\times$$
$$\times\frac{(g\mu_B/\hbar)\left[B_{res}^{1-3}(B,\theta,\varphi,\theta)-B\right]-i\left(T_2^{1-3}\right)^{-1}}{(g\mu_B/\hbar)^2\left[B-B_{res}^{1-3}(B,\theta,\varphi,\theta)\right]^2+\left(T_2^{1-3}\right)^{-2}} \tag{19}$$

where $\sin\Theta_{ZX}(\theta)$ is defined above;

$$\sin\Theta_{XY}(\varphi)\approx-\frac{E+D\cos2\varphi}{\sqrt{(2g\mu_BB)^2+\left[E+D\cos2\varphi\right]^2}}\ ;$$

$$\sin\Theta_{ZY}(B,\theta)\approx\frac{(D+E)-(D-3E)\cos2\theta}{\sqrt{(4g\mu_BB)^2+\left[(D+E)-(D+3E)\cos2\theta\right]^2}}\ . \tag{20}$$

$\cos(angle)$ means $\cos\theta$ and $\cos(\pi/2-\theta)$ at the constant field in the planes *ZX* and *ZY*, correspondingly, and $\cos\varphi$ in the *XY* plane. It should be noted that $\chi_{ZZ,XX,YY}(B,1-3)$ at $\mathbf{B}\parallel\mathbf{Z},\mathbf{X},\mathbf{Y}$, respectively, are the EPR dynamic susceptibilities in the longitudinal geometry of an experiment, i.e. when an alternating magnetic field is parallel to a constant one.

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We would like to discuss now the application of our DST for the interpretation of the experimental angular dependence of EPR signal intensity from [13]. There, the EPR signal emerged from the excitonic STS in the molecular single crystal of the pure $NaNO_2$, and the applied constant field was sufficiently larger than the FS constants. It should be noted here that the level 2 of the metastable triplet state of $NaNO_2$ was optically excessively populated during the experiments of [12, 13] at the constant field rotation from the **X** axis to the **Y** axis. We have calculated the average values of the longitudinal components of the fictitious spins, proportional to the population differences of the corresponding STS transitions, under such conditions. It can also be seen that in [13] the EPR spectra are the field derivatives of the absorption signals on the 1-2, 2-3 transitions, describing the response of the *Y*-th component of the sample magnetization to the action of the alternating field along the **Y** axis at the constant field in the *XY* plane. We have calculated numerically these signals with the help of the FS constants, experimentally obtained in [13]. At that, we have used for the angular dependencies of the resonance fields $B_{res}^{2-3\,1-2}(B,\theta)$, entering the Eq. (17), the well known results, obtained in the first order of the perturbation theory for the case when the anisotropy terms are a perturbation to the Zeeman term (see, for instance, [27]). In addition, we have supposed that the forced population of the STS level 2 is 5 times more effective than the "depopulation" of an each level owing to the other causes. Then we were able to plot the angular dependence of these signals, which qualitatively agrees with Fig. 2 from из [13]:

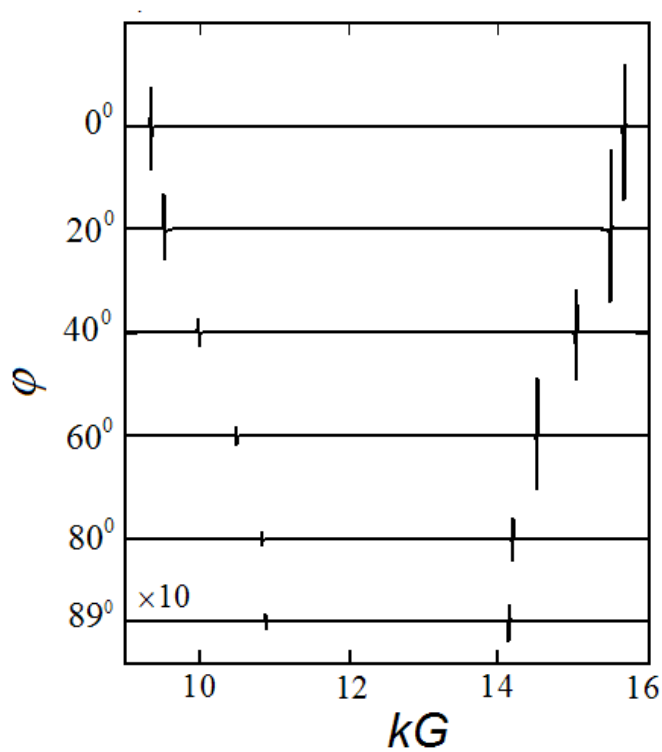

Fig. 1 The EPR spectra plotted according to Eqs. (17), (18) of this paper with the necessary cyclic rearrangements of the indices for the triplet excitons in the pure $NaNO_2$ single crystal at 1.3 K under conditions of the optic excitation described in [12]. The spectra are calculated numerically with the help of the FS constants, experimentally obtained in [13]. The constant field rotates in the *XY* plane; at $\varphi = 0$ it is parallel to the **X** axis. For the lowest plot, the intensity is increased 10 times. Note the opposite character of the low-field (emissive) and high-field (absorptive) lines

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The qualitative agreement of the shape and the intensity ratios of the separate lines of the EPR spectra (Fig. 1 from this paper) with the experimental shape and ratios of the Fig. 2 from [13] shows that our analytical investigation is carried out correctly.

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4 Conclusions

Summarizing, the following results are obtained in this paper:

The method is suggested of the obtaining of the equations of motion for the magnetization components of the separate STS transitions of a single crystal under the action of the alternating and non-weak constant magnetic fields without accounting for the decay. It is demonstrated how these equations can be used for the revealing of the character of the full magnetization motion of a sample with STS at the excitation of the separate transitions of the FS. The dynamic susceptibility tensor is calculated at the absence of the EPR saturation. The results of this calculation describe qualitatively the experimental angular dependence of the EPR spectra from the triplet excitons in the pure $NaNO_2$ single crystal observed in [13] in the sufficiently strong constant field.

It is possible that the results obtained here will be useful for the interpretation of the corresponding experiments on nuclear spins I=1, having quadrupolar moment and being under conditions of the non-zero electric field gradient.

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