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THEORY OF ELECTRON NUCLEAR DOUBLE RESONANCE IN THE PRESENCE OF AN EXTERNAL ELECTRIC FIELD

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A method of calculation is developed and general expressions are obtained for the spin-Hamiltonian constants of a paramagnetic center (PC) in the presence of an external electric field. A comparison of the theoretical and experimental results makes it possible to determine the sign and magnitude of the ion displacements near the PC—the local deformation. A method is proposed for determining the wave functions of the excited state of the PC from data on the shift of the ENDOR line under the action of an external electric field. The methods are illustrated for the example of F-centers in alkali-halide crystals. The displacements of the ions and the values of the square of the modulus of the excited-state wave function are determined at the sites where the ions are located for the first, second, and fourth coordination spheres in crystals of KCl and KBr.

INTRODUCTION

UTILIZATION of the method of electron nuclear double resonance (ENDOR) appreciably facilitates the investigation of paramagnetic centers in crystals.[1] It turned out to be possible to measure the square of the modulus of the ground-state wave function at sites where the nuclei of many coordination spheres are located and to use this data in order to investigate the structure of the energy bands.[2,3]

The nuclei of a paramagnetic center (PC) are located at sites which are devoid of a center of inversion, independently of whether the PC as a whole possesses inversion symmetry or not.[1)] Therefore one can expect shifts of the ENDOR lines which are linear in the electric field, and spin-nuclear transitions due to the effect of the electric component of the radiofrequency field.[4-7] The first electric effect in ENDOR was observed by Reichert et al.:[8,9] they observed a shift of the F-center lines in alkali-halide crystals due to the effect of a constant electric field, which is described as a change of the constant a, i.e., as the function $(\partial a/\partial E)$.

Investigation of electric effects in ENDOR opens up new possibilities for studying PC (including centers with inversion symmetry) and, in particular, their excited states.

The influence of an external electric field on the hyperfine interaction constants is considered below. A method is proposed for determining the wave function of the excited state of the PC at different lattice sites from data on the shifts of the ENDOR lines due to the effect of a constant external electric field. Specific calculations are carried out for F-centers in KCl and KBr crystals.

1. CALCULATION OF THE SPIN-HAMILTONIAN CONSTANT FOR THE INTERACTION OF A PC WITH AN EXTERNAL ELECTRIC FIELD

Since the electric effects are relatively small, it is convenient to interpret their effect as a change of the spin-Hamiltonian constant due to the influence of the external electric field. One can calculate this change if a term $-\mathbf{d}\cdot\mathbf{E}$ is added to the initial Hamiltonian, where $\mathbf{d}$ denotes the effective dipole moment of the PC.[10] In similar calculations one usually has to keep terms of higher order (than the first) in perturbation theory, thus taking excited states into account.

In connection with this, the change of the hyperfine interaction constant due to the presence of a δ-function in the initial operator is of special interest. The latter will include in the spin-Hamiltonian constant the electric effects associated with the values of the excited-state wave functions at the site where the nucleus is located.

We carry out an explicit examination for F-centers in alkali-halide crystals since for the time being the required experimental data exists only for them. A similar investigation for other PC's does not present any difficulties in principle.

In order to calculate the spin-Hamiltonian constant let us choose the initial operator in the form

$$\hat{W} = \sum_l \tau_l \delta_l \hat{\mathbf{I}}_l \hat{\mathbf{S}} - \mathbf{dE}, \tag{1}$$

$$\tau_l = \frac{16\pi}{3}\frac{\mu_l \mu}{I_l}, \quad \delta_l = \delta(|\mathbf{r} - \mathbf{R}_l|),$$

where $\mathbf{r}$, μ, $\mathbf{S}$ and $\mathbf{R}_l$, μ_l, $\mathbf{I}_l$ denote the radius vector, magnetic moment, and spin of the electron and of the l-th nucleus. The summation over l involves the nuclei of the entire crystal. Since an F-center possesses a center of inversion (the group O_h), corrections which are linear in the electric field appear in second order perturbation theory:

$$\mathscr{E}_k^{(2)} = \sum_{n\neq k} \frac{W_{kn} W_{nk}}{\mathscr{E}_k^0 - \mathscr{E}_n^0}, \tag{2}$$

[1)] The nucleus of the impurity ion (atom) constitutes an exception if it is located at a center of inversion of the crystal. By PC we understand a region of the crystal near the defect, with which the interaction of the localized electron is substantial.

where $\mathscr{E}_k^0$ denote the energies of the unperturbed states of the system. In order to carry out the calculations it is convenient to express each of the δ-functions appearing in Eq. (1) in terms of combinations of δ-functions which transform according to certain irreducible representations of the group O_h. One can find the latter by the method of actual decomposition of a reducible representation into irreducible representations,[11] although in a number of cases it is easier to determine the coefficients of the linear combinations if the generating elements of the group operate directly on combinations of δ-functions.

Since the experimental data are given for the first, second, and fourth coordination spheres, we carry out the appropriate calculations for these spheres. For the six nuclei of the first and fourth coordination spheres we have

$$\delta_{1,2}=\pm{}^1/_2\varphi_1+\cdots,\quad \delta_{3,4}=\pm{}^1/_2\varphi_2+\cdots,\quad \delta_{5,6}=\pm{}^1/_2\varphi_3+\cdots, \tag{3}$$

where $\varphi_1 = \delta_1 - \delta_2$, $\varphi_2 = \delta_3 - \delta_4$, and $\varphi_3 = \delta_5 - \delta_6$. Here and below we denote by dots combinations of δ-functions which are the bases of irreducible representations different from Γ_{4u} and whose explicit form is not essential in what follows. The point is that the polar vector **d** is a basis of the irreducible representation Γ_{4u}; therefore, in accordance with Eq. (2) only those combinations which transform like the vector **d** under the symmetry operations of the group will lead to nonvanishing matrix elements. Their explicit form is written down.

The directions of the coordinate axes x, y, z are chosen along the crystallographic directions [100], [010], and [001]. The following correspondence exists: $\varphi_1 \to x$, $\varphi_2 \to y$, and $\varphi_3 \to z$. Nuclei 1 and 2, 3 and 4, and 5 and 6 lie on straight lines passing through the origin of coordinates, where the first (1, 3, 5) lie on the positive directions of the axes. For the twelve nuclei of the second coordination sphere we have

$$\begin{aligned}&\delta_{1,2}=\pm{}^1/_8(\varphi_1-\varphi_2)+\cdots, &&\delta_{3,4}=\pm{}^1/_8(\varphi_1+\varphi_2)+\cdots,\\ &\delta_{5,6}=\pm{}^1/_8(\varphi_1+\varphi_3)+\cdots, &&\delta_{7,8}=\pm{}^1/_8(\varphi_2+\varphi_3)+\cdots,\\ &\delta_{9,10}=\pm(-\varphi_1+\varphi_3)+\cdots, &&\delta_{11,12}=\pm{}^1/_8(-\varphi_2+\varphi_3)+\cdots,\end{aligned} \tag{4}$$

where

$$\begin{aligned}\varphi_1&=\delta_1-\delta_2+\delta_3-\delta_4+\delta_5-\delta_6-\delta_9+\delta_{10},\\ \varphi_2&=-\delta_1+\delta_2+\delta_3-\delta_4+\delta_7-\delta_8-\delta_{11}+\delta_{12},\\ \varphi_3&=\delta_5-\delta_6+\delta_7-\delta_8+\delta_9-\delta_{10}+\delta_{11}-\delta_{12}.\end{aligned}$$

The nuclei are numbered in the following way:

$$1.2\,(R_x=\pm a,\ \ R_y=\mp a,\ R_z=0),\ \ 3.4\,(\pm a,\pm a,0),\ \ 5.6\,(\pm a,0,\pm a),$$
$$7.8\,(0,\pm a,\pm a),\ \ 9.10\,(\mp a,0,\pm a),\ \ 11.12\,(0,\mp a,\pm a),$$

where a is half the lattice constant.

Since the wave function of the ground state is a basis of the irreducible identity representation Γ_{1g}, and the vector **d** is an irreducible representation of Γ_{4u}, the summation in (2) only includes the terms Γ_{4u}. Let P_x, P_y, P_z be the wave functions of the excited state belonging to the irreducible representation Γ_{4u} so that the correspondence $P_x \to x$, $P_y \to y$, $P_z \to z$ holds. Let us represent them in the following form: $P_i = Pq_i$, where $q_i = P_i/P$ and $P = \sqrt{P_x^2 + P_y^2 + P_z^2}$ is the cubically symmetric part.

Using the matrix method of perturbations[12] one can represent the matrix elements of a product of two arbitrary polar vectors **A · B**, where **B** does not depend on the coordinates over which the integration is carried out, in the form

$$(\mathbf{AB})_{\Gamma_{1g},P_i}=\alpha B_i, \tag{5}$$

where $\alpha = (A_z)_{\Gamma_{1g},P_z}$. Substituting (1) into (2) and taking relations (3) and (5) into account, we obtain the spin-Hamiltonian for the first and fourth coordination spheres, linear in **E**:

$$\hat{\mathscr{E}}_m^{(2)}=\tau_m\mathbf{S}[E_x\mathbf{I}_{12}+E_y\mathbf{I}_{34}+E_z\mathbf{I}_{56}]\sum_n\frac{\alpha_{1n}\alpha_{2n}{}^m}{\Delta_n}, \tag{6}$$

where

$$\mathbf{I}_{ll'}=\mathbf{I}_l-\mathbf{I}_{l'},\quad \alpha_{1n}=\int\Psi_{\Gamma_{1g}}d_zP_z^{(n)}\,dV,$$

$$\alpha_{2n}{}^m=\int\Psi_{\Gamma_{1g}}(\delta_5{}^m-\delta_6{}^m)P_z^{(n)}\,dV,\ \ \Delta_n=\mathscr{E}_{\Gamma_{4u}}^{(n)}-\mathscr{E}_{\Gamma_{1g}},$$

here the index m labels the spheres (I or IV), and dV is the volume element.

Using the law governing the transformation of basis functions of the irreducible representation Γ_{4u}, we obtain

$$q_z(0,0,-a)=-q_z(0,0,a),$$
$$q_x(0,0,\pm a)=q_y(0,0,\pm a)=0,$$

so that

$$\alpha_{2n}{}^m=2\Psi_{\Gamma_{1g}}(m)P^n(m). \tag{7}$$

For the second coordination sphere we have

$$\begin{aligned}\hat{\mathscr{E}}^{(2)}={}^1/_4\tau\mathbf{S}[&E_x(\mathbf{I}_{1,2}+\mathbf{I}_{3,4}+\mathbf{I}_{5,6}-\mathbf{I}_{9,10})\\ &+E_y(-\mathbf{I}_{1,2}+\mathbf{I}_{3,4}+\mathbf{I}_{7,8}-\mathbf{I}_{11,12})+\\ &+E_z(\mathbf{I}_{5,6}+\mathbf{I}_{7,8}+\mathbf{I}_{9,10}+\mathbf{I}_{11,12})]\sum_n\frac{\alpha_{1n}\alpha_{2n}}{\Delta_n},\end{aligned} \tag{8}$$

where

$$\alpha_{2n}=\int\Psi_{\Gamma_{1g}}\varphi_3P_z^{(n)}\,dV.$$

From symmetry considerations we obtain

$$\alpha_{2n}=4\int\Psi_{\Gamma_{1g}}(\delta_7-\delta_8)P_z{}^n\,dV;$$

furthermore

$$q_z(0,-a,-a)=-q_z(0,a,a),\quad q_x(0,\pm a,\pm a)=0,$$
$$q_z(0,a,a)=q_y(0,a,a).$$

so that

$$\alpha_{2n}=\frac{8}{\sqrt{2}}\Psi_{\Gamma_{1g}}(7)P^n(7).$$

In an experiment the external electric and magnetic fields are directed along an axis passing through the vacancy and two nuclei whose ENDOR lines are observed. Assuming $E_x = E_y = 0$, $E_z = E$ for the first and fourth coordination spheres and $E_x = 0$, $E_y = E_z = E/\sqrt{2}$ for the second coordination spheres, and averaging the operators (6) and (8) over the electron spin, we obtain the following result for the spin-nuclear Hamiltonian

$$\langle\hat{\mathscr{E}}_m^{(2)}\rangle_S=\tau_mE\hat{I}_{56}^H\sum_n\frac{\alpha_{1n}\Psi_{\Gamma_{1g}}(m)\,P^n(m)}{\Delta_n}, \tag{9}$$

$$\langle\hat{\mathscr{E}}^{(2)}\rangle_S=\tau E\left[\hat{I}_{7,8}^H+\frac{1}{2}(\hat{I}_{3,4}^H-\hat{I}_{1,2}^H+I_{5,6}^H+I_{9,10}^H)\right]\sum_n\frac{\alpha_{1n}\Psi_{\Gamma_{1g}}(7)\,P^n(7)}{\Delta_n}, \tag{10}$$

where $\hat{I}^H$ denotes the projection of the vector I on the direction of quantization (the direction of the magnetic field). Formulas (9) and (10) pertain to the two types of coordination spheres under consideration.

Comparing (9) and (10) with the effective Hamiltonian introduced in[9], we obtain an expression for the parameter $\partial a/\partial E$ from[9], measured experimentally:

$$\left(\frac{\partial a}{\partial E}\right)_m = 2\tau_m \Psi_{\Gamma_{1g}}(m) \sum_n \frac{\alpha_{1n} P^n(m)}{\Delta_n}. \qquad (11)$$

The index m labels the coordination spheres. To a good approximation one can write (11) in the form

$$\left(\frac{\partial a}{\partial E}\right)_m = \frac{2\tau_m \Psi_{\Gamma_{1g}}(m)}{\bar{\Delta}} \sum_{n \neq \Gamma_{1g}} \alpha_{1n} P^n(m), \qquad (12)$$

where $\bar{\Delta}$ is the average distance between the energy of the ground state and the energies of the excited states. One can show that

$$\sum_{n \neq 1} \alpha_{1n} P^n(m) = R_m \Psi_{\Gamma_{1q}}(m). \qquad (13)$$

In fact, let us consider an expansion in terms of eigenfunctions of the PC:

$$z\Psi_{\Gamma_{1g}}(r) = \sum_n c_n \Psi_n(r), \qquad (14)$$

where

$$c_n = \int \Psi_{\Gamma_{1g}}(r) z \Psi_n(r)\, dV,$$

and $c_n = 0$ if $n \neq \Gamma_{4u}$. Then

$$z\Psi_{\Gamma_{1g}}(r) = \sum_{n \neq \Gamma_{1g}} \alpha_{1n} P_z^{(n)}. \qquad (15)$$

Assuming $z_m = R_m$ for the first and fourth coordination spheres, $z_m = R_m/\sqrt{2}$ for the second sphere, and taking the symmetry of the wave functions into account, we arrive at expression (13). Substituting (13) into (12) we obtain

$$\left(\frac{\partial a}{\partial E}\right)_m = \frac{2\tau_m \Psi^2_{\Gamma_{1g}}(m)}{\bar{\Delta}} R_m. \qquad (16)$$

If it is assumed that the lattice is not deformed by either the external electric field or by the presence of a defect, formula (16) can be directly evaluated and compared with the experimental parameter $(\partial a/\partial E)_m$. The values of $\psi^2_{\Gamma_{1g}}$ are known from the ENDOR data, $\bar{\Delta}$ can be approximately replaced by the distance between the ground and the first excited levels. The results of the calculations and the corresponding experimental data[9] are presented in Table I, from which it is seen that there is good agreement between theory and experiment for the second and fourth spheres. The discrepancy (~ 30 to 40%) for the first sphere is apparently associated with a displacement of the ions due to the presence of a defect in the crystal. The magnitude and sign of this displacement can be determined. From Table I and formula (16) it is seen that the sign of the displacement of the ions of the first sphere is the same for both crystals (the ions move away from the vacancy). The magnitude of the displacement is of the order of 1 Å.

In these discussions we have not considered the effect of a displacement of the ions due to the action of the external electric field.[10] Taking this effect into account would make it possible to determine the value of the effective dipole moment d at the lattice sites. Once again it must be emphasized that the investigation carried out here may serve as a method of investigating the lattice's deformation in the region of a crystal where a PC is located.

2. DETERMINATION OF THE WAVE FUNCTION OF THE EXCITED STATE

Let us also consider PC's for which one can limit one's attention to the first term in the sum (11). A discussion of this approximation will be carried out in Section 3. In this case we obtain the following result for the wave function of the excited state at a lattice site:

$$P(m) = \frac{\Delta}{2\tau_m \Psi(m) \alpha} \left(\frac{\partial a}{\partial E}\right)_m. \qquad (17)$$

From (17) it follows that in order to determine P(m) it is necessary to know the optical absorption frequency, the ground-state wave function at the lattice site, and the matrix element for the dipole transition from the ground state to the excited state.

For the majority of PC's the optical absorption frequency is usually known, and the ground-state wave functions are determined from ENDOR data. The situation with regard to the determination of the matrix element of the dipole transition is more complicated. For its determination one can use a comparison of the theoretical and experimental values of the integrated intensity of light absorption by the PC. In this connection, of course, it is impossible to manage without making certain approximations in the theory of optical transitions.

A. One can avoid this by considering the ratios of P(m) at different lattice sites. In this case the matrix element of the dipole transition and the absorption frequency vanish:

$$\frac{P(m)}{P(m')} = \frac{\tau_{m'} \Psi(m')}{\tau_m \Psi(m)} \left(\frac{\partial a}{\partial E}\right)_m \left(\frac{\partial a}{\partial E}\right)^{-1}_{m'}. \qquad (18)$$

Using the data taken from[13,14] for $\psi(m)$ and the parameters $\partial a/\partial E$ taken from[9], we evaluated the ratio (12) for F-centers in crystals of KCl and KBr. The obtained results are tabulated in Table II. The ratios of the ψ-functions of the ground state are also given for comparison.

B. In order to determine the absolute values of the excited-state wave function of an F-center we used the experimental data for the optical frequency $(\epsilon\Gamma_{4u} - \epsilon\Gamma_{1g})$ and the integrated intensity T_{12}/N of the light absorption calculated at a single absorbing center, which is cited in[15,16], and a very general theoretical expression for T_{12}/N derived in[17]. The parameter α was determined from a comparison of theory and experiment.

Table I. Theoretical and experimental values of $(\partial a/\partial E)_m$, $\text{Hz}/\text{V}\cdot\text{cm}^{-1}$

Crystal	Number of coordination sphere	Theory	Experiment	Crystal	Number of coordination sphere	Theory	Experiment
KCl	I	0.59	0.9+0.05	KBr	I	0.61	1.0+0.05
	II	0.28	0.25+0.03		II	2.00	2.0+0.05
	IV	0.059	0.05+0.005		IV	0.38	0.33+0.02

Table II. Ratio of the squares of the wave function at a lattice site of the first coordination sphere to the square of the wave function at sites of the second and fourth coordination spheres

Crystal	Number of coordination sphere	Ground term	Excited term	Crystal	Number of coordination sphere	Ground term	Excited term
KCl	II	6.31	9.09	KBr	II	2.50	3.37
	IV	41.0	34.8		IV	18.4	16.8

The results of a calculation of the functions P(m) are given in Table III.

We note that in[9] certain data are also given for the crystal NaCl. In contrast to the other parameters, the parameter $(\partial a/\partial E)_{\mathrm{Na}}$ was determined in the region of a quadratic dependence of the line shift on the field E. In the range of fields where the shift of the lines is smaller than or of the order of the interaction energy between nuclei, the ENDOR spectrum is complicated and a determination of the parameters presents considerable difficulties. Therefore the parameter $(\partial a/\partial E)_{\mathrm{Na}}$ was determined to an accuracy ~ 25%. Keeping this in mind and taking into account that the authors of[9] did not present values of the parameters $\partial a/\partial E$ for the crystal NaCl in the fourth coordination sphere, we did not carry out calculations for this crystal.

In conclusion we note that if in Eq. (13) we confine our attention to the first term in the sum, then for P(m) we obtain the expression

$$P(m)=R_m\Psi_{\Gamma_{1g}}(m)/\alpha, \tag{19}$$

which makes it possible to estimate the wave functions of the excited states even in those cases when no experiments exist concerning the effect of an electric field on the ENDOR spectrum.

3. DISCUSSION OF THE RESULTS

1. Let us present the arguments which indicate that the approximation made in Sec. 2 may be realized in a number of PC's. In connection with the fact that in expression (11) the matrix element of the dipole transition plays an essential role, one can surmise that the approximation we have made is valid in crystals in which the oscillator strength of the optical transitions from the ground state to the first excited state is close to unity. In particular, the F-centers in alkali-halide crystals, where according to the data the oscillator strength may be ~0.9, belong to such PC's.

In the effective mass approximation one can derive certain quantitative criteria whose fulfilment ensures the validity of the approximation which was made. Let us write the wave functions of the ground state and of the first excited state in the form

$$\Psi_{\Gamma_{1g}}=N_0u_0(\mathbf{r})\frac{\gamma^{3/2}}{\sqrt{\pi}}e^{-\gamma r} \tag{20}$$

$$\Psi_{\Gamma_{4u}}=N_0u_0(\mathbf{r})\frac{\beta^{5/2}}{\sqrt{\pi}}ze^{-\beta r},$$

where $u_0(\mathbf{r})$ denotes the Bloch function at the bottom of the conduction band; the factors associated with $u_0(\mathbf{r})$ are the "smoothed" wave functions of the F-center; N_0 is a constant normalization factor. Then

Table III. Values of the wave functions at lattice sites (Å^{-3})

Crystal	Number of coordination sphere	Ground term	Excited term	Crystal	Number of coordination sphere	Ground term	Excited term
KCl	I	0.67	2.3	KBr	I	0.59	1.95
	II	0.106	0.25		II	0.236	0.58
	IV	0.016	0.066		IV	0.032	0.116

Eq. (19) can be rewritten in the form

$$e^{(\beta-\gamma)R_m}=32\varkappa^5/(1+\varkappa)^5, \tag{21}$$

where $\kappa=\beta/\gamma$. Equation (21) is exactly satisfied for $\kappa=1$. If one of the theorems about sums is used, which for the wave functions (20) is written in the form

$$\sum_n \alpha_{1n}^2=1/\gamma^2,$$

then in order to confine our attention to the first term in this sum it is necessary to satisfy the equation $2^{10}\kappa^5/(1+\kappa)^{10}=1$, which also holds for $\kappa=1$. From here it follows that the approximation we made in Sec. 2 may be valid provided γ and β do not differ very strongly from each other.

The values obtained by us for the ψ-functions of the ground and excited states are given in Table III. Using these values we estimated the parameters γ and β (from the ratios of the ψ-functions at sites of the same kind), and it was found that the difference does not exceed 10%. Then from Eq. (21) it follows that our approximation is valid for $R_m \lesssim 10$ Å.

2. In Table II the inequality

$$\Psi_{\mathrm{I}}^2/\Psi_{\mathrm{II}}^2<P_{\mathrm{I}}^2/P_{\mathrm{II}}^2, \tag{22}$$

attracts our attention since, at first glance, it contradicts the idea that the excited-state wave function should be attenuated more slowly than the ground-state wave function. At the same time inequality (13) indicates that the wave function P, having cubic symmetry, can be "stretched" along an axis of the type [100] more strongly than the ψ-function of the ground state.

The concept of damping can give the inequality

$$\Psi_{\mathrm{I}}^2/\Psi_{\mathrm{IV}}^2>P_{\mathrm{I}}^2/P_{\mathrm{IV}}^2, \tag{23}$$

because the nuclei of the first and fourth coordination spheres are located on a single axis. The fact that inequality (14) is not strong may indicate that the maximum of the ψ-cloud is located near the vacancy so that the ratio $\psi_{\mathrm{I}}/\psi_{\mathrm{IV}}$ corresponds to a region of a smoother decrease of the ψ-function. This property is confirmed by the data in Table III, according to which $P_m^2>\psi_m^2$.

Thus, one can make two basic conclusions:

a) There is a strong localization of the ψ-cloud near the vacancy, where its maximum is located at a distance which is smaller than half the lattice constant.

b) The P-cloud is deformed more strongly than the ψ-cloud.

3. The values of the wave functions of the excited state obtained in this work may serve as additional reference points for the construction of a microscopic theory of PC, and also for an investigation of the structure of the conduction band by the method proposed in[3].

4. If in addition to an isotropic constant there are

other spin-Hamiltonian constants influencing appreciably the electric effects (the case of distant spheres, other PC's), one can extract the parameter $\partial a/\partial E$ by using the dependence of the splitting of the ENDOR lines under the action of the field E on the orientation of the external magnetic field with respect to the crystallographic axes.

Let us illustrate what has been said for the example of the anisotropic constant b in the coordination sphere with six nuclei distributed along an axis of the type [100]. The constant b appears in the expression for the ENDOR frequency together with the angular factor $(3\cos^2\theta - 1)$, where θ is the angle between the direction of the magnetic field and the direction [100].

Choosing θ such that $3\cos^2\theta = 1$, one can eliminate the constant b and together with it the parameter $\partial b/\partial E$.

In conclusion we note that together with an investigation of the effect of an external electric field on the ENDOR spectrum, the effect of the pressure[18] has also been studied experimentally. A theoretical calculation of this effect, analogous to the calculation carried out in the present article, would be of interest. The results of the calculation and of the experiments might serve as an additional method for investigation of the excited states.

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25