Dynamics of the stationary triple electron-nucleus-nuclear resonance

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The mechanism and dynamics of stationary triple electron-nucleus-nuclear resonances in multilevel systems are studied. The experiment is carried out for F-centers in alkali-halide crystals. Coupling of nuclei from different coordination spheres is demonstrated. The coupling is manifest by the fact that application of a radio-frequency (RF) field of the same frequency as one of the nuclei affects the electron-nuclear double resonance (ENDOR) line intensity due to nuclei of all coordination spheres. The dependence of the change in ENDOR line intensities induced by an applied RF field on the microwave and RF wave power is investigated. The "symmetry" of effects arising on irradiation with an additional RF field at the so-called sum and difference frequencies is studied. The experiments are explained by calculations performed for a model consisting of a $S = 1/2$ electron and three nuclei $I_1 = I_2 = I_3 = 1$ with various hyperfine interaction constants. The absence of such "symmetry" of the effects in KBr crystals is ascribed to the presence of "forbidden" cross-relaxation transitions.

INTRODUCTION

The electron-nuclear double resonance method (ENDOR) is finding ever-widening applications in various physical investigations[1]. Registration of ENDOR with an additional radio-frequency (RF) field, i.e., observation of triple electron-nucleus-nuclear resonance, greatly extends the capabilities of this method, namely, it becomes possible to determine the relative values of the hyperfine interaction (HFI) constants[2], the identification of the spectra is made simpler[3,4], the intensity of the ENDOR signal is increased by one order or more for certain objects[5], and possibilities are uncovered for investigating the mechanisms whereby the ENDOR signals are produced at different nuclei surrounding a paramagnetic center and to separate the probabilities of the spin-lattice transitions (SLT) in multilevel systems[4].

An influence of the additional RF field on the nonstationary ENDOR spectra was observed in earlier experimental studies[3,5,6]. The additional RF field affects differently the spectra of the stationary and nonstationary ENDOR. The difference becomes manifest mainly in the fact that in the influence of the additional RF field, whose frequency is equal to the resonant frequency of a certain nucleus, on ENDOR from nuclei with other hyperfine constants, and also in the influence of the field on ENDOR lines pertaining to different orientations of the electron spin. The reason for these differences is that the mechanisms whereby the signals of the stationary and nonstationary ENDOR are produced are different.

A qualitative picture of the influence of the additional RF field on the ENDOR spectra is given in[2] for the extremal case of nonstationary ENDOR (all the relaxation transitions neglected). The mechanism whereby an additional RF field at the frequency of one of the ENDOR lines of a certain nucleus influences another ENDOR line of the same nucleus is explained qualitatively in[5]. A similar situation is treated more rigorously in[6]. We have shown in another paper[4], by analyzing the relaxation channels, how the additional RF field at the frequency of one nucleus influences the intensity of the ENDOR lines of another nucleus.

The present paper is devoted to the mechanism and dynamics of stationary triple electron-nucleus-nuclear resonance. We investigate F centers in alkali-halide crystals. The choice of the objects was dictated by the fact that ENDOR on these objects has been primarily investigated and is governed by the large number of nuclei with essentially different HFI constants, which permits the phenomenon to be investigated most completely. The description of the experiments (which is based on the equations for the populations of the quantum states) corresponds to the stationary case $dn_f/dt = 0$, where n_f is the instantaneous population of the f-th level. The mechanism proposed in[4] is described here quantitatively and is generalized to include the case of different ratios of the HFI constants of the nuclei whose frequencies equal the frequencies of the RF fields.

1. DERIVATION OF EXPRESSIONS FOR THE LINE INTENSITIES OF ENDOR WITH ADDITIONAL RF FIELD

Each nucleus with which the paramagnetic-center electron interacts yields, as is well known, two ENDOR lines, whose frequencies in the simplest case are equal to[1]

$$\nu_M^{(i)} = |M[a_i + b_i(3\cos^2\theta_i - 1)] - \nu_n^{(i)}| \tag{1}$$

Here M is the projection of the electron spin on the magnetic field **H**, a_i and b_i are respectively the isotropic and anisotropic constants of the HFI with the i-th nucleus, $\nu_n^{(i)}$ is its Larmor frequency, and θ_i is the angle between the direction from the paramagnetic center to the i-th nucleus and **H**. The frequencies $\nu_{-1/2}^{(i)}$ and $\nu_{1/2}^{(i)}$ are customarily called the sum and difference frequency, respectively. The induced RF transitions at the frequency $\nu_M^{(i)}$ are subject to the selection rules $\Delta M = 0$, $\Delta m_i = \pm 1$, and $\Delta m_j = 0$, where m_i is the projection of the spin of the i-th nucleus on **H**. In experiments on triple electron-nucleus-nuclear resonance, an additional unmodulated RF field at the resonant frequency of one of the nuclei is applied to the sample, in addition to the main modulated RF field that produces the ENDOR spectrum.

General expressions for the ENDOR signal in multilevel systems were obtained in[7,8]. We use here the expression[7]

$$\delta_M^{(i)} = \sum_{p<k} V_{pk}\left[\frac{1+x_{pk}}{1+\alpha^{(i)}_{(pk)]M}x_{vk}} - 1\right], \quad (2)$$

where V_{pk} is the EPR signal due to the pair of states p and k; $x_{pk} = 2P_{1(pk)}W_{pk}$ is the saturation parameter, W_{pk} is the probability of the induced microwave transition, $T_{1(pk)}$ is the spin-lattice relaxation time relative to the pair of levels p and k in the absence of the main RF field, and

$$\alpha^{(i)}_{(pk)M} = T^{eff}_{1(pk)(M,i)}/T_{1(pk)} \leqslant 1, \quad (3)$$

where $T^{eff}_{1(pk)(M,i)}$ is the effective relaxation time relative to p and k when the main RF field at the frequency $\nu_M^{(i)}$ is applied to the system.

The quantities $T_{1(pk)}$ and $T^{ff}_{1(pk)(M,i)}$ are expressed in terms of the determinant of the system of equations for the populations of the quantum state and its cofactors[7]. In the presence of the additional RF field, $T_{1(pk)}$ and $T_{1(pk)(M,\,i)}$ can depend on the probabilities of the induced transitions due to this field. The extent to which $T_{1(pk)}$ is decreased by the RF field (i.e., $\alpha^{(i)}_{(pk)M}$) changes in this case, and this leads to a change in the intensity of the ENDOR signal.

To explain the laws governing the described phenomenon, let us consider a system consisting of an electron and three nuclei with spins $I_1 = I_2 = I_3 = 1$ (Fig. 1). The model is chosen from simplicity considerations, but retains at the same time the main properties of experimentally investigated systems. We assume that $a_1 > a_2$, we shall take into account[9] only the w_S transitions ($\Delta M = \pm 1$, $\Delta m_i = 0$) and the w_X transitions with reorientation of the first nucleus ($\Delta M = \pm 1$, $\Delta m_1 = 1$, $\Delta m_2 = \Delta m_3 = 0$). The role that cross relaxation plays in ENDOR dynamics has been considered in[8], where it is shown that it can be reduced to an effective enhancement of the w_S process.

Let the induced microwave transitions ($\Delta M = \pm 1$, $\Delta m_i = 0$) act in the center of the multilevel system; then the indices p and $\underline{k}$ in (2) will correspond (see Fig. 1) to the indices 5 and $\bar{5}$ (they will henceforth be omitted). The quantities $\alpha_M^{(i)}$ and $\delta_M^{(i)}$ in the absence of the additional RF fields will be designated $\alpha_M^{0(i)}$ and $\delta_M^{0(i)}$. We then have for the ratio of the intensities of the same ENDOR line in the presence and in the absence of the addition RF field

$$\frac{\delta_M^{(i)}}{\delta_M^{0\,(i)}} = \frac{1-\alpha_M^{(i)}}{1-\alpha_M^{0\,(i)}}\,\frac{1+\alpha_M^{0\,(i)}x}{1+\alpha_M^{(i)}x}. \quad (4)$$

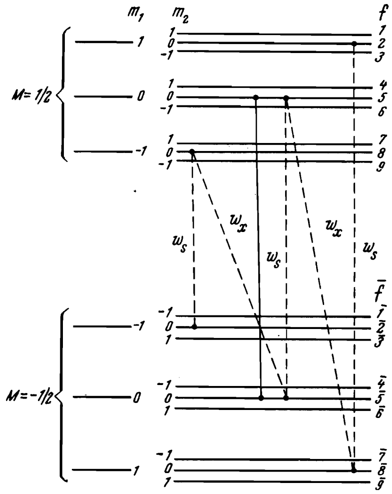

FIG. 1. Energy levels of an electron and two nuclei. The splitting of these levels due to the interaction of the electron with the third nucleus is not shown. The solid vertical line is induced microwave transition, and the dashes are some of the w_S and w_X transitions. The indices f and $\bar{f}$ that label the levels correspond to states inverted in time.

When a "saturating" main RF field at the frequency $\nu_{1/2}^{(1)}$ or $\nu_{-1/2}^{(1)}$ is turned on, we have for $\alpha_M^{0(1)}$ the relation[7]

$$\alpha_{1/2}^{0\,(1)} = \alpha_{-1/2}^{0(1)} = \frac{(2T_1)^{-1}}{(2T^{eff}_{1\,(M,\,i)})^{-1}} = \frac{w_s}{w_s + w_x}. \quad (5)$$

Let the additional RF field act on $\nu_{1/2}^{(2)}$. Then, expanding the corresponding determinants, we obtain

$$[2T_1]^{-1} = w_s\left[1 + \frac{4zy_2 + 6z(1+z)y_2{}^2}{3+(12+8z)y_2 + 3(3+4z+z^2)y_2{}^2}\right], \quad (6)$$

Here $z = w_X/w_S$, $y_2 = W_2/w_X$, W_2 is the probability of the induced RF transition at the frequency $\nu_{1/2}^{(2)}$ of the additional RF field. If the "saturating" main RF field acts on $\nu_{1/2}^{(1)}$, then

$$[2T^{eff}_{1(1/2,1)}]^{-1} = w_s(1+z), \quad (7)$$

and if it is turned on at the frequency $\nu_{-1/2}^{(1)}$, we have accordingly

$$[2T_{1(-1/2,1)}]^{-1} = w_s\left[1 + z + \frac{4z(1+z)^2y_2 + 6z^2(2+3z+z^2)y_2{}^2}{3(1+z)^2 + z(14+20z+6z^2)y_2 + z^2(15+12z)y_2{}^2}\right] \quad (8)$$

Expressions (7) and (8) in conjunction with (6) yield $\alpha_M^{(1)}$. Substituting these $\alpha_M^{(1)}$ and $\alpha_M^{0(1)}$ from (5) in (4), we can analyze the enhancement and attenuation of the ENDOR lines by the additional RF field.

2. EXPERIMENT AND DISCUSSION OF RESULTS

The experiment was performed with a superheterodyne ENDOR spectrometer[10] operating in the 3-cm band. The investigations were performed on F centers in LiF, KBr, KCl, and NaCl crystals at room temperature. We investigated the ENDOR lines of the nuclei of the following coordination spheres: I–VIII in LiF, I, II, and IV in KBr and KCl, and I–III and V in NaCl. The additional RF field was introduced into the microwave resonator with the aid of a system of two wire loops. At the frequency of the summary ENDOR line, this field enhanced all the difference lines and attenuated all the sum lines. Application of an additional RF field at the difference line attenuated the difference lines and enhanced (with the exception of the case of KBr to be discussed below) the sum lines. The maximum amplification of the ENDOR lines was approximately 5, and the attenuation approximately 10, so that the change of the ratio of the intensities of the sum lines to the difference lines was equal to 50.

Figure 2 shows spectra illustrating the influence of the additional RF field. The upper spectrum is the usual ENDOR spectrum. The middle spectrum shows the enhancement of the sum ENDOR lines and the attenuation of the difference lines by the additional RF field. The lower spectrum pertains to the case when the frequency of the main field is equal to that of the difference ENDOR line of sphere VI, and the frequency of the additional field runs through the frequency range indicated in the figure.

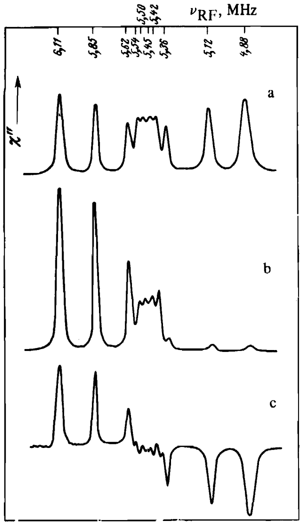

FIG. 2.

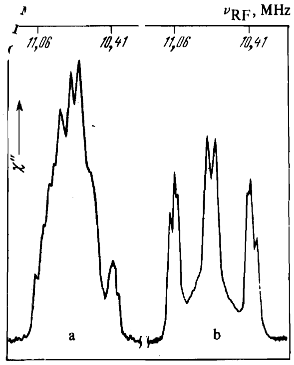

FIG. 3.

FIG. 2. Spectra of nuclei of coordination spheres III and V in an LiF crystal, recorded by different methods (χ'' is the imaginary part of the magnetic susceptibility. ν_{RF} is the frequency of the RF field): a—without additional RF field, b—with additional RF field at the difference line of sphere VI; c—spectrum of triple electron-nucleus-nuclear resonance with variation of the frequency of the additional RF field.

FIG. 3. a) ENDOR spectrum of sphere I in KCl crystal, constituting a mixture of the sum and difference lines. b) The same spectrum with additional RF field on the sum line of sphere II. The difference quadrupole triplet with partially resolved structure of second order is clearly distinguishable.

The signal of certain nuclei is registered in this case as the change of the intensity of the ENDOR signal of other nuclei. The intensity of the signals recorded in this manner can exceed the intensity of the signals recorded in the usual ENDOR. The spectral lines pertaining to the different electron-spin orientations are recorded in this case on opposite sides of the null line, a fact that can be used to identify the spectra and to determine the relative signs of the HFI constants. We note that the additional RF field at a frequency equal to $\nu_{\bar{n}}^{(i)}$ did not affect the intensity of the ENDOR lines in our experiments.)

Figure 3 illustrates the use of the additional RF field to separate individual components from the complex ENDOR lines due to superpositions of sum and difference lines.

We have observed experimentally a relation between nuclei of different coordination spheres in the dynamics of stationary ENDOR; this relation is manifest by the fact that the additional RF field at the frequency of a certain nucleus affects the intensities of all the ENDOR lines.

The observed relation between the nuclei and the mechanism of stationary triple electron-nucleus-nuclear resonance on different environment nuclei can be explained with the aid of the level scheme of Fig. 1 by starting from expressions (4)—(8) in the following manner. In the absence of the additional RF field, the main RF field at the frequency ν (this field acts between states 5–2 and 5–8) opens up a new channel 5–8–5 for the relaxation of the electrons from the state 5 to the state $\bar{5}$, and an analogous channel $5-\bar{8}-\bar{5}$ is opened at the frequency $\nu_{-1/2}^{(1)}$. The main field at the frequency $\nu_{1/2}$ (or $\nu_{-1/2}$) of the second or third nucleus, together with the w_s and w_x transitions, also leads to an effective coupling between states 5–2 and 5–8 (or else $\bar{5}-\bar{2}$ and $\bar{5}-\bar{8}$), by opening the previous relaxation channel $5-8-\bar{5}$ (or $5-\bar{8}-5$). Owing to the new relaxation channels we get $T_{1(M,\,i)}^{\mathrm{eff}} < T_1$, and the degree of the decrease of T_1 (i.e., $\alpha_M^{(i)}$ from (3)) determines the intensity of the ENDOR signal. It is important to note that ENDOR on nuclei with small HFI constants is due to spin-lattice transitions with reorientation of the first nucleus.

In the presence of an additional RF field at the frequency $\nu_{1/2}$ of any of the nuclei, an effective coupling is produced in similar fashion between the states 5–2 and 5–8, and this coupling opens in part the relaxation channel $5-8-\bar{5}$. Therefore the main RF field at the frequency $\nu_{1/2}$ of other nuclei produced in this case a smaller change in T_1 than in the absence of the additional RF field. The main RF field at the frequency $\nu_{-1/2}$ of each of the nuclei, to the contrary produces a larger change in T_1 (at a favorable ratio of the spin-lattice transition probabilities), since other relaxation channels are opened besides the channel $5-\bar{8}-\bar{5}$, for example the channel $5-\bar{2}-\bar{8}-\bar{5}$. Allowance for other relaxation transitions does not change the gist of the foregoing arguments.

Recognizing that the enhanced ENDOR lines pertain to opposite orientations of the electron spin, we have established that the signs of the HFI constants of the nuclei of the investigated spheres are equal. We note that, contrary to the prediction of Baker and Blake[6], the stationary component of the ENDOR signal with an additional field contains information on the relative signs of the HFI constants. The magnitudes of the described effects are determined by the probability ratios of the different spin-lattice transitions. At some ratios of these probabilities, the additional RF field can decrease the intensity of the ENDOR lines pertaining to both orientations of the electron spin. (For example, accordding to formulas (5)—(8) and (4) with $z > 1$, the additional RF field at the frequency $\nu_{1/2}^{(2)}$ will attenuate both $\delta_{1/2}^{(1)}$ and $\delta_{-1/2}^{(1)}$. This situation can be easily understood by using the reasoning presented above, namely, the decrease of T_1 by the additional field is such that $\alpha_{-1/2}^{0(1)} < \alpha_{-1/2}^{(1)}$.) Even in this case, however, it is possible to determine the relative signs of the HFI constants, since $\delta_{-M}^{(i)}/\delta_{-M}^{0(i)}$ is larger than $\delta_M^{(i)}/\delta_M^{0(i)}$ if an additional RF field is applied at the frequency $\nu_M^{(j)}$ of a certain nucleus, regardless of the probability ratio of the spin-lattice transitions.

The enhancement and attenuation of the ENDOR line by the additional RF field depend little on the microwave power. When the microwave power changes by 25 dB, the effects change within 30%. If the HFI constants of the nuclei at resonance with the RF fields are larger than the width of the spin packet (the theoretical analysis pertains to this case), then the enhancement and attenuation increase monotonically with increasing microwave power, in agreement with formula (4). The intensity of the main RF field likewise exerted only an insignificant influence on the magnitude of the effects.

The most interesting is the dependence of the effects on the intensity of the additional RF field. With increasing intensity, the effects increase monotonically, reaching a certain limiting value. Figure 4 shows the characteristic dependence of the magnitude of the effects on the intensity of the additional RF field. The theoretical plots were constructed for the first nucleus in accordance with

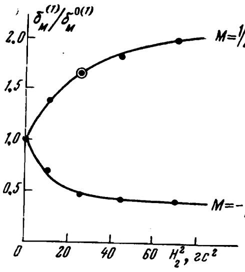

FIG. 4. Plot of the enhancement and attenuation of ENDOR lines of sphere I in KCl crystal against the intensity of the additional RF field at the sum line of sphere II. Solid lines–Theory, points–experiment, ⊙–point at which the theoretical and experimental values are assumed equal. The abscissas represent the square of the intensity of the additional RF field.

formula (4) at x = 1, when the additional RF field corresponded to the frequency $\nu_{-1/2}^{(2)}$. The value of the parameter z necessary to reconcile the theory with experiment turned out to be 0.3.

We have investigated the "symmetry" of the effect following application of an additional RF field at the sum and difference frequencies of the same nuclei. In our model, if the additional RF field is turned on at the frequency $\nu_{-1/2}^{(2)}$, then expressions (6)—(8) retain their form, but in formulas (7) and (8) it is necessary to make the substitution $1/2 \leftrightarrow -1/2$. Thus, the enhancement of $\delta_{-1/2}^{(1)}$ and the attenuation of $\delta_{1/2}^{(1)}$ by the additional RF field at the frequency $\nu_{1/2}^{(2)}$ will be equal to the enhancement of $\delta_{1/2}^{(1)}$ and attenuation of $\delta_{-1/2}^{(1)}$ by the additional RF field at the frequency $\nu_{-1/2}^{(2)}$ (when the probabilities of the RF frequencies at these frequencies are equal). It can be shown in general form that the indicated "symmetry" of the effect should take place if the probabilities of the spin-lattice transitions acting in the system (including the effective spin-lattice transitions) satisfy the condition

$$w_{fi} = w_{\bar{f}\bar{i}}, \tag{9}$$

where f and $\bar{f}$ denote states that are inverted in time.

This "symmetry" was observed for the LiF crystal, within the limits of experimental accuracy. In the case of the KBr crystal, however, the additional RF field at the sum frequencies produced stronger effects than at the difference frequencies. More over, at certain orientations of the crystal relative to the magnetic field, the additional RF field at the difference frequency of the nuclei of sphere I produced not an enhancement but an attenuation of the ENDOR line of the same nuclei at the sum frequency.

As shown in[11], in the KBr crystal, owing to the deflection of the quantization axis of the nuclei of coordination sphere IV from the direction of the external magnetic field, "forbidden" cross relaxation transitions play an important role. According to[11], they give rise to effective spin-lattice transitions that do not satisfy the condition (9). The inclusion of these effective SLT (the magnitude of which depends on the orientation of the crystal) in the picture of the relaxation transitions explains the indicated anomalies for the KBr crystal.

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