lower than that of the equation in question.

[3)]The derivation and analysis of the equations can be found in the work of Zakharov *et al.*[1,3]

[4)]This case corresponds to $T_{\mathbf{kk'}}=S_{\mathbf{kk'}}=\bar{S}_{\mathbf{k}}$ and it occurs, for example, in the case of a cubic antiferromagnet with the easy-plane anisotropy.

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Splitting of ENDOR lines by a strong microwave field

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The first experiments on the splitting of ENDOR lines in a solid by a strong microwave field are reported. The experiment was performed on *F* centers in KCl. The splitting was registered at ENDOR sum lines from the Cl^{35} and Cl^{37} nuclei of coordination sphere II at $T = 300$ K. The dependence of the effect on the microwave and RF field powers, on the detuning of the stationary magnetic field, and on the temperature is investigated. The maximum microwave field intensity attained in the experiment reached 0.14 Oe and corresponded to a splitting of 380 kHz. A theoretical explanation is offered for the magnitude of the splitting, for the dependence of H_1, and for intensity ratio of the split component, as well as for the independence of the splitting of the magnetic-field detuning.

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INTRODUCTION

The study of various types of double magnetic resonances in strong alternating fields that lead to coherent motion of the spins is of considerable interest, since it permits observation of qualitatively new effects that yield additional information on the investigated objects. Up to now, these resonances were investigated mainly in liquids and were used most extensively for nuclear-nuclear double resonance.[1,2] In electron-nuclear double resonance (ENDOR), the manifestation of strong alternating fields (which can be in either the microwave or the RF band) has been investigated relatively little,[2-6] and notice should be taken of the contradictory character of a number of these studies.[5,6] The phenomena connected with a strong microwave field in solutions of organic compounds were considered by Freed *et al.*[3] However, both the observed effects and the theoretical analysis for liquids, as is well known, have features that greatly encumber their interpretation; it is of therefore of interest to investigate such phenomena in solids, where the ENDOR had been most extensively used.

We have registered, for the first time ever, effects connected with the manifestation of a strong microwave field in ENDOR of solids, studied these effects, and deduced a theoretical interpretation that explains the most significant aspects of the phenomenon.

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EXPERIMENT

The measurements were performed with a superheterodyne ENDOR spectrometer for the 3-cm band ($\nu_{micro}=9280$ MHz).[7] The objects of the investigation were KCl single crystals with F centers (center concentration $\approx 5\times10^{17}$ cm^{-3}). The main parameters of the ENDOR spectrum from the ^{35}Cl of coordination sphere II (where the observed effects are most pronounced) are[8]: $a=7.08$ MHz, $b=0.51$ MHz, and $\nu_n=1.37$ MHz, where a and b are the constants of the isotropic and anisotropic hyperfine interactions, respectively, and ν_n is the nuclear Larmor frequency. For the ^{37}Cl nuclei these parameters are smaller by a factor 1.2. Details on the ENDOR spectra in this object can be found in the article by Deĭgen *et al.*[8]

The effect consists in the fact that when the microwave power is increased a splitting of the resonance lines is observed in the ENDOR spectrum. Figure 1 shows the dependence of this splitting on the microwave power for one of the summary lines of ^{35}Cl of sphere II at $T=300$ K. The maximum splitting, which is determined by the capabilities of the apparatus, is 380 kHz and corresponds to a microwave field intensity $H_1\approx0.14$ Oe in the resonator. We note that at low powers, when the splitting is small, the high-frequency component is more intense; on the other hand, their intensities become equalized when H_1 is increased. The center between the split components shifts with increasing microwave power towards higher frequencies, and its phase is the converse of that of the initial signal (i.e., an EPR-signal decrease similar to "negative" ENDOR takes place.[5,6]

The magnitude of the effect at the ^{37}Cl nuclei was somewhat larger than at the ^{35}Cl isotope. Thus, at a microwave power attenuation of 8 dB the splitting was 110 and 80 kHz for ^{37}Cl and ^{35}Cl, respectively.

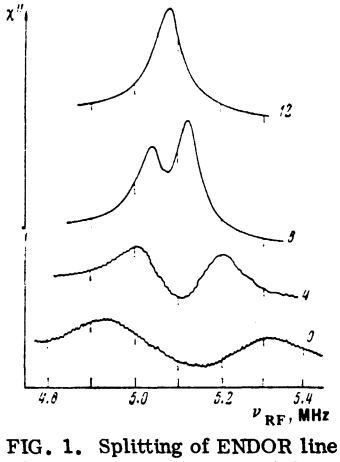

FIG. 1. Splitting of ENDOR line by microwave field ($\mathbf{H}\parallel[100]$), χ'' is the imaginary part of the magnetic susceptibility, ν_{RF} is the frequency of the applied RF signal. The numbers on the right indicate the damping of the microwave power in decibels. Zero dB corresponds to the microwave field intensity $H_1\approx0.14$ Oe in the resonator. The gain for the 12 dB line is decreased by a factor of two.

Within the limits of the experimental accuracy (±10 kHz) the splitting was independent of the crystal orientation and of the detuning $H-H_0$ of the stationary magnetic field, where H_0 is the field corresponding to the center of the EPR line. The detuning $H-H_0$ was limited by the width of the EPR line (the ENDOR signal decreases with increasing $|H-H_0|$) and was in the range ±30 Oe. Only a slight shift of the ENDOR line frequency was observed, due to the change of the Larmor frequency H_2 (range of variation 0.1–1.0 Oe), but the effect was more pronounced at smaller H_3, since the ENDOR lines are narrower in this case.

Lowering the crystal temperature from 300 to 77 K (keeping constant other parameters such as the resonator Q, the microwave field intensity, etc.) led to a vanishing of the splitting of the ENDOR lines.

It was impossible to register reliably a splitting of the difference ENDOR lines of sphere II, which are weaker in intensity than the summary lines. All that was observed was a broadening of these lines with increasing microwave field power. No splitting of the ENDOR lines from nuclei of other coordination spheres was observed.

INTERPRETATION OF RESULTS AND DISCUSSION

A complete analysis of the electron-nuclear system following the action of strong alternating field is possible only on the basis of the equations for the density matrix. However, the use of this method entails great mathematical difficulties (especially for complicated systems such as F centers), which in many cases are of fundamental character. To describe our experiments, we present a very simple analysis that enables us to understand and explain the main results of the experiment.

We consider a system made up of electrons with spin $S=1/2$ and a nucleus with arbitrary spin I, and confine ourselves to a determination of the resonance frequencies and the ratios of the spectral-line intensities. We neglect here the relaxation processes and do not touch upon questions connected with the ENDOR mechanisms or with the line width and shape. The spin Hamiltonian of the system in question will be written in the form

$$\hat{\mathcal{H}}_0=\omega_e\hat{S}_z-\omega_n\hat{I}_z+A\hat{S}_z\hat{I}_z, \tag{1}$$

where $\omega_e=\gamma_eH_0$; $\omega_n=\gamma_nH_0$ (γ_e and γ_n are the gyromagnetic ratios of the electron and nucleus, respectively); A is a quantity that characterizes the hyperfine interaction. A weak RF field gives rise to transitions with selection rules $\Delta M=0$, $\Delta M=\pm1$, where M and m are the projections of S and I on the quantization axis. The spectrum of the nucleus with spin I will then consist of two lines (summary and difference, corresponding to $M_1=-1/2$ and $M_2=+1/2$) with frequencies

$$\omega_{1,2}=|\omega_n\pm{}^1/_2A|. \tag{2}$$

Let us see how this spectrum changes in the presence

of a strong[1)] microwave field with amplitude H_1 and frequency ω, which acts on the electron spins S. It is necessary to add to the spin Hamiltonian (1) a term corresponding to the interaction of the spins S with the strong microwave field (the interaction of this field with the nuclear spins can be neglected[1-3]):

$$\hat{\mathcal{H}}=\hat{\mathcal{H}}_0+2\gamma_e H_1 \cos\omega t\, \hat{S}_x. \tag{3}$$

To find the resonant frequencies of the system we use in this case the procedure described by Lippmaa.[2] Its gist is that the Hamiltonian (3) is written in a coordinate system that rotates with frequency ω, is then diagonalized, the resonant frequencies are obtained, and are subsequently reconverted to the laboratory frame by adding the rotation frequency of the coordinate system. Owing to the presence of the term $2\gamma_e H_1 \cos\omega t\, \hat{S}_x$ in (3), the RF field will cause, besides the transitions $\Delta M=0$, $\Delta m=\pm1$, also the transitions $\Delta M=\pm1, \Delta m=\pm1$. The frequency spectrum of the spin I will then be determined by the expression

$$\omega(M'-M'', m'-m'')=|\omega_n-M'\omega(m')+M''\omega(m'')|,$$
$$m'-m''=\pm1, \quad M'-M''=0,\pm1, \tag{4}$$
$$\omega(m)=\gamma_e H(m)=[(\omega_e-\omega+Am)^2+(\gamma_e H_1)^2]^{1/2}; \tag{5}$$

here $H(m)$ is the effective magnetic field, which is the quantization axis for the spins S in the rotating coordinate system. The direction of $H(m)$ depends on the projection m of the nuclear spin on the external magnetic field. When the nuclear spin is reoriented, the direction of the quantization axis S changes, so that transitions $m'-m''=\pm1, M'-M''=\pm1$ become possible. The probabilities of the RF transitions are then determined by the finite-rotation matrix [formula (130) of[2]] and will depend both on ω and on $\gamma_e H_1$. Obviously, in the presence of a strong microwave field the concept of sum and difference ENDOR lines becomes strictly speaking meaningless.

In ENDOR experiments there is always realized a situation wherein (accurate to the width of the spin packet) the expression $\omega_e-\omega+m_1A$ is equal to zero, where m_1 is one of the values of m. This condition is necessary, inasmuch as in ENDOR any component of the EPR line must be a resonance with the microwave field and it is precisely this component which determines the presence of the ENDOR signal.

An analysis of expressions (4) and (5) obtained for $S=1/2$ and for an arbitrary nuclear spin demonstrates the following: In the presence of a strong microwave field one can observe in the general case, eight rather than two ENDOR I lines (in the concrete situations the frequencies of certain lines coincide and their number decreases). It is important to note that in ENDOR the intensities of these eight I lines are determined not only by the values of the matrix elements of the corresponding transitions, but also significantly by the population rule. Namely, the only transitions observed in ENDOR are the transitions $m'-m''=\pm1$ defined by formula (4), for which m' or m'' is equal to m_1, i.e., they pertain to the saturated component of the EPR line $(\omega_e-\omega+m_1A)=0$. This rule is clearly illustrated in the experiments of Brik *et al.*[9]

As a result of the indicated limitations, only four ENDOR lines can have a noticeable intensity at $S=1/2$ and at arbitrary nuclear spin. Each of the lines[2)] ω_1 and ω_2 is then split into two components, whose frequencies are determined by the expressions

$$\omega_1'=|\omega_n+{}^1/_2[(A^2+(\gamma_e H_1)^2)^{1/2}+\gamma_e H_1]|, \tag{6}$$
$$\omega_1''=|\omega_n+{}^1/_2[(A^2+(\gamma_e H_1)^2)^{1/2}-\gamma_e H_1]|; \tag{7}$$
$$\omega_2'=|\omega_n-{}^1/_2[(A^2+(\gamma_e H_1)^2)^{1/2}+\gamma_e H_1]|, \tag{8}$$
$$\omega_2''=|\omega_n-{}^1/_2[(A^2+(\gamma_e H_1)^2)^{1/2}-\gamma_e H_1]|. \tag{9}$$

We note that the set of frequencies (6)–(9) will be obtained when any of the EPR line component is saturated, i.e., at any m_1. According to (6)–(9), the splitting of the ENDOR lines will be equal to $\gamma_e H_1$.

The results can be illustratively explained with the aid of the picture of the energy levels in a rotating coordinate system, for a system consisting of an electron and a nucleus with $I=1$ (see Fig. 2). Let $(\omega_e-\omega+m_1A)=0$, i.e., let the microwave field be at resonance with one of the three components of the EPR line corresponding to $m=+1$. Then the effective fields $H(m)$ will be equal to

$$H(+1)=\gamma_e H_1, \quad H(0)=(A^2+(\gamma_e H_1)^2)^{1/2}, \quad H(-1)=[(2A)^2+(\gamma_e H_1)^2]^{1/2}.$$

In the presence of a strong microwave field, the wave functions of the states $|1\rangle$, $|2\rangle$, etc. will have admixture of the wave functions of states with opposite projections of the electron spin on $H(m)$, so that eight RF transitions are possible in the system, with $\Delta m=\pm1$, $\Delta M=0$, ±1.

The frequencies of the transitions between $|3\rangle \leftrightarrow |6\rangle$, $|3\rangle \leftrightarrow |5\rangle$, $|4\rangle \leftrightarrow |6\rangle$ and $|4\rangle \leftrightarrow |5\rangle$ will be determined, as can be easily seen from the picture of the levels, by expressions (6)–(9). The intensities of the remaining four transitions shown in Fig. 2, owing to the population rule described above, will certainly be small, since

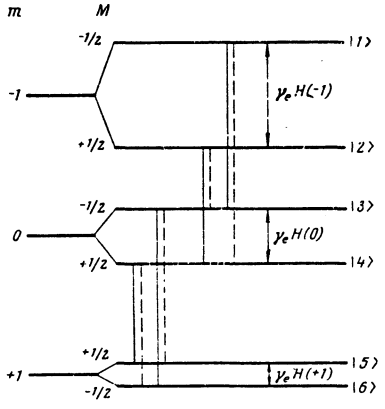

FIG. 2. Energy level scheme of the model with $S=\frac{1}{2}$ and $I=1$ in a rotating coordinate frame. The solid lines mark the transitions $\Delta m=\pm1, \Delta M=0$, the dashed ones the transitions $\Delta m=\pm1, \Delta M=\pm1$, while the lines with the arrows indicate the energy gap between the levels corresponding to different orientations of the electron spin in the effective field $H(m)$.

they take place between nuclear sublevels whose populations are not directly altered by the saturating microwave field. Thus, in place of (2) we have a spectrum whose frequencies are determined by formulas (6)–(9).

In the real system investigated by us, the F-center electron interacts with many lattice nuclei whose spins are $I=3/2$. However, we note that this interaction takes place in a rather independent fashion (the direct and indirect nuclear-nuclear interactions are small and do not appear in the experiment in our case. In the spin Hamiltonian there is no "entangling" of the terms that determine the hyperfine interaction with different nuclei, and the nuclear transitions satisfy the selection rules $\Delta m_{j\neq j'}=0$, $\Delta m_{j'}=\pm 1$, where the j number the nuclei; j' labels the nucleus at resonance with the RF fields. Therefore in the calculation of the ENDOR frequencies it suffices to consider a system consisting of an electron and one nucleus. The investigations of[8] confirm that for the system under consideration (sphere II of the F center in KCl) this is a good approximation. Since, furthermore, the obtained expressions (6)–(9) do not depend on the nuclear spins, we shall use them to describe our experiments.

The experimentally observed splitting of the ENDOR lines (see Fig. 1) is equal to $\gamma_e H_1$ and increases linearly with increasing H_1, in accord with (6)–(9). According to (6) and (7), the centered of the split components for the ENDOR "sum" line will shift towards higher frequencies with increasing H_1. This result agrees with experiment only qualitatively. In the experiment the shift is larger than according to formulas (6)–(9). Analysis of the values of the matrix elements of the corresponding RF transition by the Lippmaa formulas[2] shows that at small H_1 the ω_1' line will be more intense than ω_1''. With increasing H_1, however, the intensity of the ω_1'' line will increase and that of ω_1' will decrease.

The change in the landing point on the inhomogeneously broadening EPR line (the dependence on $H-H_0$) can be regarded as a transition from one saturable component to another. The saturable component must satisfy here the condition $(\omega-\omega_e+m_1 A)\approx 0$. The splitting of the ENDOR lines is in this case always determined by a combination of effective fields having the same magnitude, $H(m_1)=\gamma_e H_1$ and $H(m_1\pm 1)=(A^2+(\gamma_e H_1)^2)^{1/2}$. Therefore, when account is taken of the population rule, we shall always have four ENDOR lines whose frequencies are given by (6)–(9). All this causes the splitting of the ENDOR lines to be independent of $H-H_0$, as was determined in our experiments.

Thus, the foregoing analysis explains the very fact of the splitting of the ENDOR lines by a strong microwave field, as well as the magnitude of the splitting and its dependence on H_1. In addition, it becomes possible to understand qualitatively the reason for the shift of the center between the split component, the change of the ratio of their intensities with increasing H_1, and the independence of the splitting of $H-H_0$. It is impossible, however, within the framework of the analysis presented here, to explain such experimental facts as the difference between the splitting on the isotopes ^{35}Cl and ^{37}Cl, its smearing at the frequency transitions, the vanishing of the effect at $T=77$ K, and the absence of splitting on lines from nuclei of other coordination spheres; all this is apparently due to the fact that the approach employed here is not comprehensive.

The most important approximation made in the present theoretical analysis is the neglect of the relaxation processes, which are known[3] to play an important role in ENDOR. In the KCl crystal, the most important relaxation transitions are $w_s(\Delta M=\pm 1, \Delta m=0), w_x(\Delta M=\pm 1, \Delta m=\pm 1)$,[10] while the $w_n(\Delta M=0, \Delta m=\pm 1)$ transition generated by cross-relaxation[11] are also effective; the latter can be different for $M=+1/2$ and $M=-1/2$ or for nuclei from different spheres.[12] The probabilities of the w_s and w_x processes are determined respectively by the spin-orbit and hyperfine interactions, and their ratio w_s/w_x decreases with decreasing temperature.[10] This ratio will be smaller also for the isotope ^{35}Cl, since $w_x\sim a^2$.

It follows from the foregoing that the vanishing of the splitting at $T=77$ K and its smaller value for ^{35}Cl may be due to the decrease of the ratio w_s/w_x, if it is assumed that this decrease affects unfavorably the magnitude of the effect. The absence of a noticeable splitting at the difference frequencies of the coordination sphere II can be due to the influence of the effective w_n transitions, and for the signals from the nuclei of other coordination spheres it can be due also to the change in the magnitude of the w_s process.

We note in conclusion that the investigated effects are important for a correct interpretation of the ENDOR spectra, for the determination of the hyperfine interaction, and for the understanding and explanation of the dynamic regularities of ENDOR. In addition, in the presence of a rigorous theory, such experiments uncover new possibilities of obtaining detailed information on the relaxation processes of the nuclei near paramagnetic centers, which are registered only by the ENDOR method and determine, as a rule, the processes of polarization and relaxation of the bulk of the lattice nuclei.

[1)] An alternating field is regarded as strong if $\gamma_e H_1 T_2 > 1$, where T_2 is the time that characterizes the homogeneous width of the spectral lines.

[2)] The simplest model with $S=\frac{1}{2}$ and $I=\frac{1}{2}$ cannot be used to explain why the number of resonance lines is decreased to four.

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Exchange interaction between conduction electrons and localized *d*(*f*) electrons with allowance for the nonorthogonality of their wave functions

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The Hartree–Fock theory is used, subject to allowance for the nonorthogonality of the wave functions of free and bound electrons, to obtain an expression for the dependence of the energy of the exchange interaction between these electrons on the various overlap integrals and on the spin state of the interacting particles. This expression yields, in particular, a formula for the total exchange integral in the weakly nonorthogonal case when the Heisenberg spin Hamiltonian can be used. Attention is drawn to the linear nature of the dependence of this energy on the quasimomentum of the conduction electrons in magnetic semiconductors.

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The exchange interaction between the conduction electrons (holes) and localized *d* or *f* electrons governs a variety of physical properties of magnetic semiconductors.[1,2] The same interaction is responsible for a number of phenomena in magnetic metals and nonmagnetic conducting materials containing paramagnetic impurities.[3–5] The interaction is described by introducing into the Hamiltonian of the system an appropriate term which is usually expressed in the familiar Heisenberg form:

$$\mathcal{H}_{\text{Hb}}=\frac{2I}{N}\sum_{j=1}^{N}\hat{\mathbf{s}}_0\hat{\mathbf{S}}_j, \tag{1}$$

where $\hat{\mathbf{s}}_0$ and $\hat{\mathbf{S}}_j$ are the spin operators, and I is the constant of the investigated material.

It is known that this effective Hamiltonian gives rise to the same energy spectrum as a consistent microscopic description allowing for the Pauli principle and using the constant

$$I=\alpha=N\int\varphi_0^*(\mathbf{r})\varphi_j^*(\mathbf{r}')V(\mathbf{r},\mathbf{r}')\varphi_0(\mathbf{r}')\varphi_j(\mathbf{r})\,d\mathbf{r}d\mathbf{r}' \tag{2}$$

only when the wave functions of the interacting particles are orthogonal. If the nonorthogonality is weak (this may be true, for example, in the interaction between electrons localized at different atoms), Eq. (1) gives an approximately correct dependence of the energy on the spin state of the particles but in this case allowance for the nonorthogonality alters drastically the results obtained.[6,7]

It is quite clear that the assumption not only of the orthogonality of the wave functions of free and localized electrons but also of the smallness of the overlap integrals between them is not, generally, justified in describing the interaction of such electrons. The approximate orthogonality of their functions may be true only under certain specific conditions. Some of the situations under which these conditions apply to the interaction of a conduction electron with a paramagnetic impurity are discussed by Vikhnin *et al.*[5] Numerical calculations of the coefficient I, carried out using the Heisenberg Hamiltonian for rare-earth metals allowing for such a weak nonorthogonality, are reported by Watson *et al.*[7]

In some cases the nonorthogonality of the wave functions of free and bound electrons is allowed by considering virtual transitions[7,8] or introducing—in a special manner—effective potentials.[9] However, a rigorous derivation of the dependences of the relevant terms on the spin states of the interacting particles is difficult and it has not yet been carried out.

The purpose of the present paper is to use the first quantum-mechanical principles in deriving an expression for the contribution made to the energy of the system by the conduction and localized *d* or *f* electrons as a result of the exchange interaction between them, as a function of the spin state of these particles without invoking the Heisenberg Hamiltonian; moreover, attention will be drawn to the dependence of this energy contribution on the quasimomentum of the conduction elec-

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