

ELECTRIC EFFECTS IN PARAMAGNETIC RESONANCE

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More than ten years have passed since discovery of the electric effect in paramagnetic resonance, but the number of investigations devoted to it has been large and increasing steadily. New phenomena related to this effect have been observed, and ways of its practical utilization have been indicated. The nature of the phenomenon is now understood, and the "phenomenological" description can be regarded as developed, although the quantitative theory leaves something to be desired. The article presents a review of work on the influence of the electric field on the paramagnetic-resonance spectrum. Principal attention is paid to electric effects in electron paramagnetic resonance and in electron nuclear double resonance. Effects in nuclear magnetic resonance (including quadrupole resonance), combined resonance, and optics are discussed in less detail, but all the studies known to the author are noted. The reviewed articles are grouped by topics, without observing chronological order.

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1. GENERAL CHARACTERISTICS OF THE PHENOMENON

THE phenomena considered below were observed in 1961 in optics^[1] and in quadrupole^[2,3], nuclear magnetic^[4], and electron paramagnetic^[5] resonances. The effects consist of a linear splitting (relative to the external electric field E) of the lines in the spectrum and offered evidence of the influence of the electric field on the energy levels of the system.

Let us stop to discuss in somewhat greater detail the experiment described in^[5]. The investigations were made on silicon doped with iron-group elements. The latter are located in the interstices, so that the point symmetry of the paramagnetic centers (PC) corresponds to group T_d (isotropic g-factor). Let us consider the iron atom Fe^0 . Its effective angular momentum is $J = 1$. In the absence of an electric field, one line was observed, corresponding to the transition between two equidistant levels (Figs. 1a and 1b). Application of the field E to the sample led to a splitting of this line into two, resulting from the different shifts of the energy levels under the influence of the electric field (Figs. 1c and 1d). The distance between the components varied linearly with the field intensity E . The split components had equal intensities, which contradicts at first glance the difference in the populations of the energy levels in accordance with the Boltzmann factor. The explanation lies in the fact that there exist in the crystal two non-equivalent (interstitial) positions that differ in the inversion operation. The energy structure for the second non-equivalent position (Fig. 1e) is the inverse of that

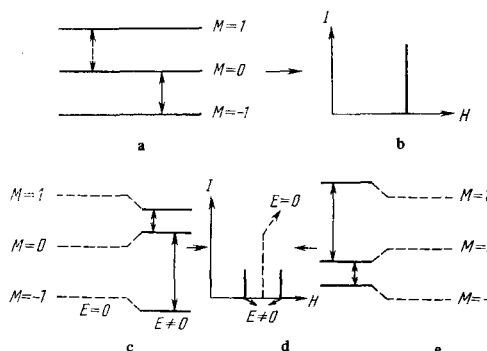


FIG. 1. Electric effect in a constant electric field. a) System of equidistant levels; b) the EPR spectrum corresponding to this system ($E = 0$); c) line splitting in the spectrum ($E \neq 0$); d, e) violation of equidistant distribution upon superposition of an external electric field (for the case of non-equivalent positions of the ions in the crystal). The arrows indicate the transitions possible under the influence of the magnetic component of a microwave. I—intensity in relative units; H—external magnetic field; M—quantum number of operator J_z .

of the first position. Therefore if there is no preferred filling of some non-equivalent position with impurity atoms, the intensities of the split components should be the same.

The new phenomenon differs from its analog and predecessor, namely the Stark effect in atoms, where, as is well known, the line splitting is quadratic in E . The difference is due to the presence of inversion symmetry in the free atoms and to the absence of such a symmetry for certain positions in the crystal. The operator of

energy of interaction of the PC with the external electric field, as will be shown below, can be represented in the form $\hat{W}_E = -\mathbf{d} \cdot \mathbf{E}$, where \mathbf{d} is the effective dipole moment of the PC.* An arbitrary matrix element of this operator is given by

$$(\hat{W}_E)_{jk} = -E \int \psi_j^* \mathbf{d} \psi_k d\tau. \quad (1.1)$$

The wave functions ψ describe the states not perturbed by the external fields. For a free atom and a PC in a crystal having an inversion center, two types of wave functions are possible, even and odd. In first-order perturbation theory the functions ψ_j and ψ_k from (1) will be of the same parity. If we perform under the integral sign a change of variables corresponding to the inversion transformation, then the product $\psi_j^* \psi_k$ does not change, and the operator \mathbf{d} reverses sign. As a result, $(\hat{W}_E)_{jk} = 0$, and there will be no effects linear in the field \mathbf{E} . Thus, effects linear in the electric field are possible for PC whose local symmetry does not contain an inversion center. This circumstance was specially pointed out by Bloembergen^[6], although analogous statements can be encountered also in earlier papers^[7,8].

The symmetry with respect to time reversal also imposes certain limitations. These concern systems with an odd number of electrons and are connected with the well known Kramers theorem (see, e.g.,^[9]). We illustrate the foregoing using as an example a system with $J = 1/2$. In the absence of external fields the corresponding term is doubly degenerate. An attempt to find the splitting of the term by an electric field leads to the secular equation

$$\begin{vmatrix} (\hat{W}_E)_{-1/2, 1/2} - \epsilon & (\hat{W}_E)_{-1/2, -1/2} \\ (\hat{W}_E)_{1/2, -1/2} & (\hat{W}_E)_{1/2, 1/2} - \epsilon \end{vmatrix} = 0. \quad (1.2)$$

The indices $\pm 1/2$ are the quantum numbers of the operator J_z , and ϵ is the energy. According to^[10], we have

$$(\hat{W}_E)_{-1/2, 1/2} = \left[\int (\hat{\Theta} \psi_{1/2})^* \hat{\Theta} \mathbf{d} \hat{\Theta}^{-1} \psi_{1/2} d\tau \right]^* E, \quad (1.3)$$

$$\hat{\Theta} \psi_{\pm 1/2} = \pm \psi_{\pm 1/2}, \quad (1.4)$$

where $\hat{\Theta}$ is the time-reversal operator.

On the basis of (1.3) and (1.4), recognizing that $\hat{\Theta} \mathbf{d} \hat{\Theta}^{-1} = -\mathbf{d}$, we obtain

$$(\hat{W}_E)_{-1/2, 1/2} = -(\hat{W}_E)_{1/2, -1/2}. \quad (1.5)$$

On the other hand, since the operator \hat{W}_E is Hermitian, we have

$$(\hat{W}_E)_{-1/2, 1/2} = (\hat{W}_E)_{1/2, -1/2}^*. \quad (1.6)$$

From a comparison of (1.5) and (1.6) we conclude that $(\hat{W}_E)_{-1/2, 1/2} = (\hat{W}_E)_{1/2, -1/2} = 0$. We can show analogously that $(\hat{W}_E)_{1/2, 1/2} = (\hat{W}_E)_{-1/2, -1/2}$, with $(\hat{W}_E)_{1/2, 1/2}$ real. As a result we obtain on the basis of (1.2)

$$\epsilon_{1,2} = (\hat{W}_E)_{1/2, 1/2}, \quad (1.7)$$

and the degeneracy remains regardless of whether the PC has an inversion center or not.* Formula (1.7) also

*For a free atom, $\mathbf{d} = e \sum_i \mathbf{r}_i$, where \mathbf{r}_i is the coordinate of the i -th electron.

†If J is a half-integer but larger than $1/2$, then the electric field can partly lift the degeneracy. There remains at least double degeneracy: the terms will be associated with functions that go over into each other, apart from the sign, under the action of the operator $\hat{\Theta}$.

Table I

Ion	Free ion*		f	Ground-term	g	$\alpha \cdot 10^7, \text{cm}^{-1}/\text{V} \cdot \text{cm}^{-1}$
	Configuration	Our classification				
Mn ²⁺	3d ⁵	⁵ D	3	1.1)	3.01	25
Cr ³⁺	3d ³	⁵ D	3	1.1)	2.97	5.4
Fe ³⁺	3d ⁵	³ F	1	1.2)	2.07	0.5
Cr ²⁺	3d ⁴	⁶ S	1	2	1.9978	0.019

f —degeneracy multiplicity of the ground term

*When ions penetrate into the crystal, the 4s-shell electrons go over to the d-shell [12, 13].

indicates that in the presence of a magnetic field the electric field can lead only to an identical shift of the levels, by virtue of which no change will take place in the paramagnetic resonance (PR) spectrum.*

To determine the magnitude of the effect, we assume that the states of the ground term are purely spin states. In this case the non-zero matrix elements of the operator \hat{W}_E , containing no spin variables, will be the diagonal matrix elements, which are equal to each other, and there will be no changes at all in the PR spectrum. To reveal the electrical effects it is necessary that the degeneracy of the principal term (in the absence of external fields) be orbital or that the states of the principal term contain an admixture of orbital states. It is convenient in this connection to distinguish between two cases:

1. The ground state of the free ion is not an S-state. Here, too, two cases are possible in turn:

1.1) Splitting of the ground-state term of the free ion by the crystal field leads to an orbitally degenerate term of the ion in the crystal.

1.2) The ground-state term of the ion in the crystal is an orbital singlet.

2. The ground state of the free ion is an S-state.

One can expect the effect to be minimal in case 2 and maximal in case 1.1. A quantitative characteristic of the degree of admixture of orbital states may be the spectroscopic splitting factor. Table I gives the values of the g factor and of the constant α , characterizing the magnitude of the E-effect for the ions of the iron group in silicon in accordance with the data of^[5,11].

It is seen from Table I that the larger the deviation of g from the g factor of the free electron, the larger the value of α and the larger the effect.

It can be concluded that two circumstances play an important role in the formation of the electric effect: the spin-orbit interaction and the interaction of the atom with the crystal, leading to the occurrence of an admixture of orbital states and of states with different parity. A typical expression that takes into account these mechanisms and an estimate of the magnitude of the effect are given in Chap. 7.

In connection with the discovery of non-conservation of the fundamental laws in weak interactions^[14,15], attempts were made to find analogous deviations also for other types of interaction. In particular, allowance for parity nonconservation and the absence of symmetry

*See, however, the discussion given below of effects of higher-order perturbation theory (\sim EH).

with respect to time reversal for electromagnetic interactions leads to the appearance of a proper electric dipole moment (EDM) of the electron^[16]. Attempts were made to measure this quantity, but so far only its upper limits could be estimated^[17,18]. Attempts to observe the appearance of the proper EDM of the electron in PR^[16,20], in connection with a proposal made in^[21], was likewise unsuccessful. In^[20], in particular, it was shown that splitting of the PR lines in an electric field is not connected with the existence of a proper EDM of the electron d_e^p . The absence of the effect is due to the excessively small value of the latter. Thus, according to^[18], $d_e^p \leq 10^{-32}$ cgs esu. Assuming $E = 10^8$ V/cm, we obtain $d_e^p E \sim 10^{-2}$ Hz, which is 10^{10} times smaller than the splittings observed in experiment. For the same reason, in the case of nuclear resonance, the electric effects cannot be attributed to the existence of a proper EDM of the nucleus d_{nuc}^p . In fact, according to^[22,23], $d_{nuc}^p \leq 10^{-30}$ cgs esu. Assuming $E = 10^5$ V/cm, we obtain $d_{nuc}^p E < 10^{-1}$ Hz. The experimentally observed splittings are $\sim 10^4 - 10^5$ Hz.

2. ENERGY OPERATOR OF INTERACTION BETWEEN PC AND AN EXTERNAL ELECTRIC FIELD

a. Initial Operator

We denote the potential energy of the crystal with PC in an external electric field by

$$\hat{W}(r, R(E), E),$$

where r and R denote the set of electronic and nuclear coordinates, respectively. The double dependence on the field E is a reflection of the fact that, besides the direct interaction of the type $-er \cdot E$ (e is the electron charge), there is also a displacement of the nuclei into new equilibrium positions that depend on the magnitude and direction of the field E . Then the energy operator of the interaction of the system with the external electric field is given by the expression

$$\hat{W}_E = \hat{W}(r, R(E), E) - \hat{W}(r, R(0), 0), \quad (2.1)$$

and the problem consists of finding the explicit form of \hat{W}_E . It is important here to determine the new equilibrium positions $R(E)$ of the nuclei.

Since this problem cannot be solved in practice for the complicated systems considered by us, it is necessary to use approximations. Usually the electric effects are relatively small, and accordingly the displacements of the equilibrium positions of the nuclei will also be small:

$$\rho(E) = R(E) - R(0).$$

This makes possible the following:

- 1) Expand the first term of (2.1) in powers of ρ and retain a finite number of terms.
- 2) Use perturbation theory to determine the energy.
- 3) Obtain from the condition that the energy be a minimum a system of equations for the new equilibrium positions $\rho(E)$.

Considerable simplifications arise in the procedure described above^[24] if the symmetry properties of the system are used. As a result, the operator \hat{W}_E can be

represented in the form

$$\hat{W}_E = - \sum_{\alpha, k} E_k^\alpha d_k^\alpha, \quad (2.2)$$

where the summation over α and k denotes summation over the irreducible representations (IR) and within the limits of the IR, respectively. In the particular case of cubic symmetry $\hat{W}_E = -E \cdot d$. The operator d_k^α is the k -th component of the effective dipole moment of the system. It consists of two terms:

$$d_k^\alpha = d_{ke}^\alpha + d_{nuc}^\alpha, \quad (2.3)$$

where the subscripts e and nuc denote the electronic and nuclear parts, respectively*. The first term has the usual form $e \sum_i r_{ki}^\alpha$, where r_{ki}^α denotes symbolically a combination of coordinates of the i -th electron, which transforms like the k -th component of the α -th IR. The second term is a complicated function of derivatives of the potential energy with respect to the coordinates of the nuclei (ions) and their mean values^[24]. It corresponds to that term of the expansion of the potential energy in powers of $\rho(E)$ which is linear in $\rho(E) \sim E$.

Of importance in what follows is the fact that the effective dipole moment operator of the PC has the same transformation properties as the usual electron dipole moment operator. This will enable us later, without specifying its form concretely, to use only the law governing the transformation of the components under the action of operations of the group and time reversal, in analogy with the procedure used in Chap. 1.

We note once more that the field E contained in (2.1) is external with respect to the crystal. For ordinary experiments (plane-parallel plate located between electrodes connected to the current source) it does not coincide with the field E_0 measured by the instrument as the potential difference per unit length of the sample. The field E is produced by charges located on the capacitor electrodes, including the charges that compensate for the polarization of the sample. We can therefore put $E = \epsilon_0 E_0$, where ϵ_0 is the dielectric constant of the crystal.

b. Internal-field Approximation

The foregoing analysis shows that the effective dipole moment consists of two parts, electronic (d_e) and a part connected with the displacement of the nuclei (d_{nuc}). The external electric field in (2.2) is homogeneous. For numerical calculations it is necessary to know the explicit form of the operator d_{nuc} , the determination of which, as seen from the foregoing, entails rather complicated calculations.

The calculation procedure can be changed by taking the sample polarization into account in the form of a contribution made to the local electric field E_L acting on the PC. In this case the dipole-moment operator can be approximated with sufficient accuracy by the operator d_e , and the problem consists of finding E_L .

Approximately (point-like dipoles, case of cubic symmetry) one can use for the determination of E_L the Lorentz field^[25]. Since in real crystals the local field

*In a crystal model where undeformed ionic cores are considered, ions are displaced into new equilibrium positions and the second term in (2.3) characterizes the ionic part (d_{ki}^α).

can greatly differ from the field determined by the Lorentz formula^[26-28], calculation methods were developed^[29-32] for arbitrary symmetry of the crystal and for models that imitate real systems better.

It was shown in^[27] that near a defect the polarization (and with it also E_L) differs from the polarization of an ideal crystal. The local field, as follows from^[33-37], is a function of the distance, and this circumstance must be taken into account in concrete calculations, since the electron producing the PR signal can be in a sufficiently large region of the crystal adjacent to the PC (one is usually interested in the value of E_L at a lattice site).

It is seen from the foregoing that calculations of the internal electric field also entail considerable difficulties, and it is difficult to give preference beforehand to any particular approach.

c. Spin Hamiltonian

The spin Hamiltonian of PC in the presence of an external electric field can be represented in the form

$$\hat{W} = \hat{W}_0 + \hat{W}_E, \quad (2.4)$$

where \hat{W}_0 is an operator characterizing the PC in the absence of a field E (Zeeman, hyperfine, intercrystalline interaction, etc.^[38,39]), and \hat{W}_E is the operator \hat{W}_E averaged over the spatial coordinates.

Methods of obtaining the operator \hat{W}_E have by now been sufficiently well developed. The following are used: the method of equivalent operators^[40], the usual tensor formalism^[20,41,42], the perturbation-matrix method^[43-46], and the method of invariants^[47,48].

In the equivalent-operator method^[49-51] the coordinate-dependent part of the perturbation-energy operator is replaced by a combination of operators of the projections of the angular momentum J , having the same symmetry-group transformation properties. Thus, in^[40] the coordinate z , which enters in the expression for the dipole moment of the electron, is represented in the form $\{\hat{J}_x \hat{J}_y\} = \hat{J}_x \hat{J}_y + \hat{J}_y \hat{J}_x$.

In the tensor formalism, the operator \hat{W}_E is represented in the form of a linear combination of products of the operators \hat{I}_i and \hat{J}_j , and of the field components H_k and E_l , where \hat{I}_i is the spin of the nucleus. The concrete form depends on the mechanism of the interaction with the electric field. Frequently one uses, for example, the expression

$$\hat{W}_E = \sum_{ijk} R_{ijk} E_i \hat{J}_j \hat{J}_k,$$

which can be regarded as the consequence of the change (occurrence) of the intracrystalline electric field constants in the presence of the field E . The linear-combination coefficients are components of a tensor of third (fifth, seventh) rank. From the condition that the tensor be invariant on the transformations of the point symmetry of the PC one obtains^[52] the connections between the non-zero components.

In the perturbation-matrix method^[53-55] the spin Hamiltonian is obtained directly in matrix form. It is assumed that the problem of finding the eigenfunctions and energies in the absence of external fields has been solved. The action of external fields is regarded as a perturbation. Thus, the known quantities are the laws

governing the transformations of the initial zeroth-order approximation wave functions and of the perturbation operators, and the problem consists of determining the maximum number of linearly independent matrix elements to be calculated, using the spatial symmetry and the symmetry with respect to time reversal. For the electric fields under consideration, the perturbation operator is given by (2.2).

In the method of invariants^[56-63] the spin Hamiltonian is constructed directly for a definite type of interaction, starting from the requirement that the Hamiltonian be invariant against the operations of the considered group and time reversal. The method of invariants can be regarded as the operator analog of the perturbation-matrix method: the results of the latter are represented in operator form, in terms of the combination of the angular momentum operators.

Thus, if we specify a definite mechanism of interaction of the PC with the external electric field, knowledge of the effective angular momentum J and of the local symmetry of the PC is sufficient to obtain the spin Hamiltonian. For the most frequently encountered mechanisms we can write ($J \leq 3/2$, $I = 1/2$)

$$\hat{W}_E = \sum_{ijk} R_{ijk} E_i \hat{J}_j \hat{J}_k + \sum_{ijk} T_{ijk} E_i H_j \hat{J}_k + \sum_{ijk} V_{ijk} E_i I_j \hat{J}_k. \quad (2.5)$$

The first term describes the change produced by the field E in the intracrystalline-field constants, the second the change in the g tensor, and the third in the hyperfine interaction constants. At values $J > 3/2$ and $I > 1/2$, the right-hand side of (2.5) must be supplemented by terms containing higher power of J and I and tensors of higher rank. Thus, at $J = 5/2$ the change of the intracrystalline-field constants will be determined by the term $\sum_{ijk/m} R_{ijk/m} E_i \hat{J}_j \hat{J}_k \hat{J}_l \hat{J}_m$. Not all the mechanisms of interaction with the field E are en par for the PC under consideration. As a rule, the dominating mechanism is the change of that constant of the spin Hamiltonian \hat{W}_0 , which determines the difference between the PR spectra of the free atom (electron) and the PC in the crystal. By virtue of this, one of the terms of (2.5) suffices for the description of the electric effect*.

3. SPLITTING OF EPR LINE BY EXTERNAL ELECTRIC FIELD

a. Linear Approximation. Single Crystals.

The most typical manifestation of the electric effects is the splitting (displacement) of a line by an external static electric field. The problem of the "phenomenological" description of the spectrum consists in choosing the spin Hamiltonian and determining its constants from the experiment. The procedure presupposes a calculation of the energy levels, frequencies, resonant values of the magnetic fields, and investigations of the angular dependence of the positions of the lines in the spectrum. Usually the electric effects are sufficiently small, so that the operator \hat{W}_E can be regarded as a

*Terms with higher powers of J usually make a smaller contribution than the terms with lower powers of J . The reason is that higher powers of J correspond to higher orders of perturbation theory (an analogous situation obtains also for the constants of the spin Hamiltonian \hat{W}_0).

perturbation to the operator \hat{W}_0 from (2.4). Since \hat{W}_0 contains the Zeeman-energy operator, the zeroth-approximation levels turn out to be non-degenerate and the corrections to the energy are determined, in first-order perturbation theory, by the diagonal matrix element of the operator \hat{W}_E , calculated with the aid of the regular zeroth-approximation wave functions. If the operator \hat{W}_E depends on the field \mathbf{E} linearly, then the energy levels, transition frequencies, and resonant values of the magnetic field (H) will also be linear in \mathbf{E} . We thus have the experimentally most characteristic case of a linear dependence of the line position in the spectrum on the field \mathbf{E} .

Assume that in the absence of an electric field the connection between the klystron frequency ν and H_0 is determined by the expression

$$\nu = \nu_{pq}^0(H_0),$$

where $\nu_{pq}^0(H_0)$ is the theoretical expression for the frequency of the transition between the levels p and q , obtained by diagonalizing the operator W_0 . In the presence of a field we have

$$\nu = \nu_{pq}^0(H_0 + \Delta H) + \nu_{pq}^E(H_0 + \Delta H),$$

where ΔH is the displacement of the resonant value of the magnetic field under the influence of the electric field. For small values of ΔH ($H_0 \gg \Delta H$) we obtain

$$\Delta H = -\nu_{pq}^E(H_0) \left[\frac{\partial \nu_{pq}^0(H_0)}{\partial H_0} \right]^{-1}. \quad (3.1)$$

Usually in the investigated crystals (ruby, silicon, tungstates) there exist two non-equivalent positions (at which the paramagnetic ions are located) that differ in the inversion with respect to the location occupied by the ion. In other words, the crystalline surrounding of ion No. 1 will be exactly the same as possessed by its non-equivalent partner No. 2 if the crystal were to be inverted in a coordinate system with center at ion No. 1. By virtue of the pseudovector nature of the magnetic field, which is insensitive to the inversion operator, positions No. 1 and No. 2 in ordinary EPR (without the field \mathbf{E}) are equivalent. In the presence of an electric field, the situation changes, since the inversion operation transforms \mathbf{E} into $-\mathbf{E}$. Therefore on the basis of (3.1) and because of the linearity of $\nu_{pq}^E(H_0)$ with respect to \mathbf{E} , the increments ΔH_1 and ΔH_2 corresponding to the two non-equivalent positions will differ in sign. The latter denotes that the shift of EPR line under the influence of the field \mathbf{E} will become manifest in experiment in the form of a splitting of the line (δH). Since this splitting is not connected with the level splitting, it is sometimes called pseudo-Stark splitting. The right-hand side of (3.1) depends on the angles characterizing the directions of the vectors \mathbf{E} and \mathbf{H} relative to the crystallographic axes, so that the line splitting has an angular dependence (which has been observed in experiment) (Fig. 2, curve 2). To investigate the angular dependence and to determine the spin-Hamiltonian parameters on the basis of (3.1) it is necessary to use numerical calculations, since as a rule it is impossible to diagonalize the operator W_0 in general form for an arbitrary orientation of the magnetic field.* In the calculations of $\partial \nu_{pq} / \partial H_0$ it is

*If the energy of the intracrystalline field (\bar{W}_C) and the Zeeman energy $W_H = -\mu \cdot H$ are connected by the relation $W_C \ll W_H$ or $W_C \gg W_H$, simplifications that lead to analytic expressions for ΔH and δH are possible.

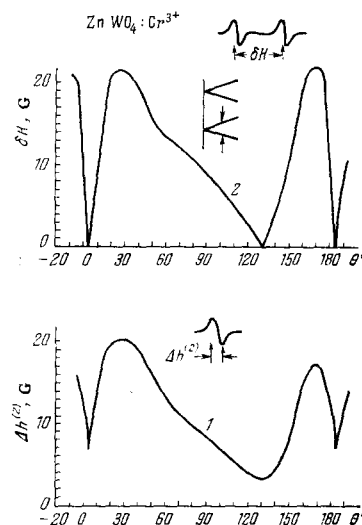


FIG. 2. Angular dependence of the half-width (1) and of the splitting (2) of the EPR line (transition $3/2 \rightarrow 1/2$) with changing field H in the x, z plane. Curves 1 ($\mathbf{E} = 0$) and 2 ($\mathbf{E} \parallel y$, $E = 220$ kV/cm) were drawn through the experimental points.

convenient to use the relation^[9]

$$\frac{\partial \nu_{pq}}{\partial H_0} = \left(\frac{\partial \hat{W}_0}{\partial H_0} \right)_{pp} - \left(\frac{\partial \hat{W}_0}{\partial H_0} \right)_{qq}.$$

Table II lists references in which splitting of PR lines under the influence of an external electric field was investigated and the spin-Hamiltonian constants were determined. For the sake of generality, references in which other procedures were used to determine the constants (e.g., spin echo) are included. They are marked by asterisks.

b. Determination of Point Symmetry of PC

The use of an electric field in PR makes it possible to obtain in principle new qualitative information concerning the nature of the PC. We have in mind the determination of the point symmetry of the PC^[108]. The use of ordinary PR for the investigation of local symmetry of PC is limited by the pseudovector nature of the magnetic field. The latter is insensitive to the space-inversion operation, and therefore in principle does not distinguish between certain point groups (e.g., isomorphic). When electric fields are used, it is possible to indicate uniquely the local symmetry of the PC. Thus, previously known data on the point group of PC were refined in^[20] and confirmed in^[41,47,91].

The possibility of distinguishing between point groups with the aid of electric fields is based on the fact that the energy operator of the interaction of the PC with the field \mathbf{E} , by virtue of the vector nature of the latter, should be different for different point groups. Therefore the problem reduces to construction of the spin-Hamiltonian \hat{W}_E . Our calculations^[45,109] of the perturbation-operator matrix $\hat{W}_H + \hat{W}_E$ for all pairs of IR of all point groups having no inversion centers have shown that the matrices of the operator \hat{W}_E are different for different isomorphic groups, whereas the matrices of the operator \hat{W}_H coincide for isomorphic groups. The difference in the energy operators gives rise to differences in the experimentally observed eigenvalues, tran-

Table II. Crystals and their impurities, investigated with the aid of electric effects

Crystal	Impurity and literature	Crystal	Impurity and literature
Si	Fe ⁰ , Fe ²⁺ 5, 11, 64 Cr ⁰ , Mn ⁺ , Cr ⁺ 11, 64 Mn ⁻ 64	CdS	Eu ²⁺ , Cd ³⁺ 64
Al ₂ O ₃	Cr ³⁺ 20, 65-67, 68 * 2Cr ³⁺ (vapor) 69, 70 Mn ²⁺ 71, 72 V ²⁺ , Mn ⁴⁺ , Ni ²⁺ , Cu ³⁺ 72 Fe ³⁺ 71-75, Ti ³⁺ 76	ZnS	Mn ²⁺ 83-96, Fe ³⁺ 97
MgO	Cr ³⁺ 20, 77 * Mn ²⁺ , Fe ³⁺ , Co ²⁺ 77 *	CdTe	Co ²⁺ 98 *
ZnWO ₄	Cr ³⁺ 47, 78, 79, Mn ²⁺ 80	Y ₃ Al ₅ O ₁₂	Fe ³⁺ 99
MgWO ₄	Cr ³⁺ 81	SrTiO ₃	Cd ³⁺ 100
CdWO ₄	Cr ³⁺ 82-84, Cu ²⁺ 85, 86 Mn ²⁺ 87, 88, Fe ³⁺ 87	NaKC ₄ H ₄ O ₆ · ·4H ₂ O	Cu ²⁺ 101
MgMoO ₄	Cr ³⁺ 89	NaKC ₄ H ₄ O ₆ · ·4H ₂ NH ₂ O	Cu ²⁺ 102
CaWO ₄	Mn ²⁺ 90, Gd ³⁺ 91 Ce ³⁺ , Nd ³⁺ , Er ³⁺ , Yb ³⁺ 92 *	KTaO ₃	Fe ³⁺ 103
SrMoO ₄	Gd ³⁺ 91	La(Zn) ₃ (NO ₃) ₉ · ·24H ₂ O	Pr ³⁺ 104 *
		Y(C ₂ H ₅ SO ₄) ₃ · ·9H ₂ O	Pr ³⁺ 105 *
		LiNbO ₃	Cr ³⁺ 106 *
		YGaG	Co ³⁺ 107 *

sition frequencies, and resonant values of the fields.

The first use of electric fields specially for the determination of an heretofore unknown point symmetry of a PC is described in^[89]. An MgMoO₄ single-crystal with Cr³⁺ impurity was investigated. The ordinary EPR spectrum of these samples was investigated earlier^[110], and the authors established the existence of five unequal PC systems, and determined also the spin-Hamiltonian constants for the two systems giving the most intense transition lines. They have also shown that the local surrounding of the Cr³⁺ ions has the symmetry of one of the point groups C₂, C_{2h}, and C_S, but were unable, as expected, to identify the group uniquely. The orders of magnitude and mutual ratios of the spin-Hamiltonian constants obtained in^[110] are approximately the same as in certain tungstates in which the effect was observed. This served as indirect indication that the effect can be observed also in MgMoO₄. The absence of the effects would be evidence of the presence of inversion in the symmetry operation of group C_{2h}.

The investigations reported in^[89] made it possible to establish that the electric field broadens the EPR lines of all five systems, thus indicating that no system of the Cr³⁺ ions has a local C_{2h} symmetry. A study of the angular dependences of the splitting was carried out by the authors for the two PC systems for which the spin-Hamiltonian constants could be determined in^[110]. It turned out that one system of lines is well described by the expressions obtained for the symmetry C₂ and the other for the symmetry C_S. The authors have therefore concluded that the first system of lines (D = 13.2 GHz) has local symmetry C₂, and the second (D = 20.82 GHz) has symmetry C_S. The results obtained in^[89] indicate great possibilities of using electric fields in a structure analysis.

c. Randomly Oriented PC

The electric effects were investigated on single crystals, where the PC have identical directions of the magnetic axes (if the existence in the crystal of several

non-equivalent positions is disregarded). At the same time, there are many substances containing PC with randomly oriented magnetic axes. These include, for example, glass-like systems, powders, solid and super-cooled solutions, and free radicals. The PC of these substances were investigated experimentally and theoretically (see, e.g.,^[110-120]). The question of the manifestation of electric effects in such substances is discussed in^[121,122]. To obtain the line shape, the resonant value of the magnetic field was determined for a PC arbitrarily oriented relative to a single coordinate system connected with the external fields **E** and **H**. The number of PC whose resonant values of the field **H** lie in the interval (H, H + ΔH) was then determined, and this yielded the intensity of the absorption line at the point H. Unlike in single crystals, the EPR line broadens under the influence of the field **E**. The line shape depends on the mutual orientation of the fields **E** and **H** and on the character of the "zero" broadening connected with the anisotropy of the g factor. Just as in the case of single crystals, the effect of resolution of isomorphous point groups takes place. The electric effects in powders were experimentally investigated in quadrupole resonance^[123], and in^[124] it was only noted that the intensity of the EPR line in quartz is altered under the influence of an external electric field.

d. Nonlinear Effects

The electric effects are investigated usually in a region where the line shift is linearly dependent on the intensity of the external electric field. The possibility of obtaining fields **E** with large intensities^[125] makes it vital to investigate the PR spectrum in the case when the operator \hat{W}_E is comparable with \hat{W}_H or \hat{W}_C . In particular, if the operator \hat{W}_E is regarded as a perturbation to a Hamiltonian of the type $\hat{W}_H + \hat{W}_C$, then it is necessary to take into account, in addition to the terms of first order of perturbation theory, also the terms of

higher order of smallness*. The terms of n -th order of perturbation theory ($n > 1$) can be estimated from the formula $h_n = h_1^n / \Delta \epsilon^{n-1}$, where $\Delta \epsilon$ is the distance between the energy levels (in the zeroth approximation) and h_1 is the correction to the energy in first order of the theory (linear in \mathbf{E}). Assuming $\Delta \epsilon = 3000$ Oe and $h_1 = 30$ Oe at $E = 100$ kV/cm, we obtain for $E = 1000$ kV/cm the values $h_2 = 30$ Oe, $h_3 = 3$ Oe, $h_4 = 0.3$ Oe, etc. Estimate shows that nonlinear effects are observable.

Deviations from linearity were observed in^[126,127]. To explain these data, we represent the frequency of the transition between two arbitrary levels, accurate to terms cubic in the electric field, in the form^[128]

$$\nu = \nu'(H) + \sum_i E_i P_i(H) + \sum_{ij} E_i E_j Q_{ij}(H) + \sum_{ijk} E_i E_j E_k L_{ijk}(H). \quad (3.2)$$

Each of the indices assumes values 1, 2, and 3, numbering the coordinate axes x , y , and z . We represent H in the form $H_0 + h$, where H_0 is the value of the field H at $E = 0$ and h is a small increment due to the field E . Expanding the right-hand side of (3.2) in powers of h and neglecting terms of higher order than h^3 , $h^2 E_i$, $h E_i E_j$, or $E_i E_j E_k$, we obtain an equation of third order in h . Solving it by successive approximations, we obtain

$$h = \sum_{i=1}^3 h_i, \quad (3.3)$$

where h_1 , h_2 , and h_3 are the terms linear, quadratic, and cubic in \mathbf{E} , respectively:

$$h_1 = \sum_i \alpha_i E_i, \quad h_2 = \sum_{i,j} E_i E_j \beta_{ij}, \quad h_3 = \sum_{i,j,k} \gamma_{ijk} E_i E_j E_k, \quad (3.4)$$

$$\alpha_i = -\frac{1}{c} P_i^0, \quad c = \left(\frac{\partial \nu'}{\partial h} \right)_0,$$

$$\beta_{ij} = -\frac{1}{c} \left[Q_{ij}^0 + \alpha_i \left(\frac{\partial P_i}{\partial h} \right)_0 + \frac{1}{2} \alpha_i \alpha_j \left(\frac{\partial^2 \nu'}{\partial h^2} \right)_0 \right].$$

The expression for γ_{ijk} is too cumbersome to be written out here. The subscript zero denotes that it is necessary to put $h = 0$ in the corresponding expressions. Formulas (3.4) illustrate the manner in which the nonlinearity arises. Thus, a quadratic dependence of h is due to three factors: the quadratic dependence of the frequency on the field \mathbf{E} , any dependence of the coefficient P on the magnetic field, and a nonlinear dependence of the frequency ν' on the field H . The relative contribution of each term to the values of β and γ changes with changing orientation of the field H in the crystal.

An analysis of the experimental data shows that the splitting of the PR line is described sufficiently well by formula (3.3), i.e., there appear terms that are linear, quadratic, and cubic in \mathbf{E} . For a quantitative comparison, the parameters α , β , and γ were calculated for different orientations of the field H , starting from the spin Hamiltonian given in^[20]. The results of the theory are in good agreement with the experimental data^[129].

4. ELECTRIC DIPOLE TRANSITIONS AND OTHER ELECTRIC ANALOGS OF MAGNETIC PHENOMENA

a. Electric Dipole Transitions

Another manifestation of the electric effects are transitions between "magnetic" sublevels under the

*We do not assume, in general, that the operator \hat{W}_E is linear in the field E .

influence of the electric component of an electromagnetic wave. In other words, unlike the usual procedure, PR can be observed by placing the sample in a resonator at the antinode of the electric field. There is no fundamental difference between the electric effects in constant and alternating fields, since from the point of view of the theory^[43] the problem consists of having the non-zero matrix elements of the operator \hat{W}_E sufficiently large. The presence or absence of time in the perturbation operator does not play any role.

The spin Hamiltonian for the description of electric dipole transitions can be represented, in accordance with (2.4), in the form

$$\hat{W} = \hat{W}_0 + \hat{W}_E(t). \quad (4.1)$$

The first step is to determine the energy levels and the correct wave functions of the zeroth approximation (the operator \hat{W}_0). The second is the calculation of the non-diagonal matrix elements of the operator $\hat{W}_E(t)$ for the transition in question. The most interesting fact should be regarded to be the appearance of additional transitions (compared with magnetic dipole transitions) with selection rules $\Delta M = \pm 2$. Let us consider a PC with $J = 1$ and local symmetry T_d . The matrix of the perturbation operator $-\mu \cdot \mathbf{H} - \mathbf{d} \cdot \mathbf{E}$ can be represented in the form^[43]

$$M = \begin{vmatrix} -\beta H_z & \frac{1}{\sqrt{2}}(\beta T + \alpha P) & i\alpha E_z \\ \frac{1}{\sqrt{2}}(\beta T^* + \alpha P^*) & 0 & \frac{1}{\sqrt{2}}(-\beta T + \alpha P) \\ -i\alpha E_z & \frac{1}{2}(-\beta T^* + \alpha P^*) & \beta H_z \end{vmatrix}. \quad (4.2)$$

$T = H_x + iH_y$, $P = E_y + iE_x$, and β and α are the parameters of the theory (the matrix elements of the operators μ and \mathbf{d} , respectively). The coordinate axes are chosen along axes of the type (100).

Let us consider the case when the static magnetic field \mathbf{H} , which produces the system of equations, is directed along the (100) axis ($T = 0$). It follows then from (4.2) that the correct zeroth-approximation wave functions coincide with the initial zeroth-approximation functions, and the matrix (4.2) can be used directly when quantum transitions are considered. We see that an alternating electric field produces transitions with selection rules $\Delta M = \pm 1$ ($E_x(t)$) and $E_y(t)$ and $\Delta M = \pm 2$ ($E_z(t)$). For quantitative estimates of the effect one can use the spin-Hamiltonian constants obtained from experiments on the displacement of the PR line in a constant electric field. The field $\mathbf{E}(t)$ in the operator $-\mathbf{d} \cdot \mathbf{E}(t)$ is external and coincides with the electric field in the resonator. Electric dipole transitions were observed in^[11,76,98,104-107].

b. Paramagnetic-electric and Parnaelectric Resonances

Transitions under the influence of the electric and magnetic components are possible not only in a system with a constant magnetic field, but also in the case when the energy levels are produced by an external static electric field^[44]. Such an electric analog of paramagnetic resonance (paramagnetic-electric resonance) in crystals containing paramagnetic ions has not yet been observed. Interest attaches therefore to experimental and theoretical investigations of the so-called paraelec-

tric resonance^[130-138] in crystals of the NaCl type containing molecular ions (e.g., OH⁻) and having a constant electric dipole moment. An analogous effect was observed on color centers in smoky quartz^[139], and in the impurity Li ion in KCl^[140-144].

c. Passage Through Resonance by an Electric Field

The possibility of applying to the samples electric fields of high intensities has made it possible to realize a resonance of a new type^[68]. In the usual method of observing paramagnetic-resonant absorption, the passage through resonance $h\nu = f_1(H)$ is effected by an external magnetic field. Since the electric field also changes the level positions, it can be used for passage through a resonance $h\nu = f_2(H, E)$. Particular interest attaches in this variant to the case $H = 0$. Samples suitable for the realization of such an experiment are those in which the electric effect is quite strongly pronounced, for example silicon doped with iron-group elements^[44]. If the influence of the electric field is not so strongly pronounced, one can use substances that contain paramagnetic impurities, in which the splitting by the intracrystalline field is close to the frequency ν used in the experiment. A suitable medium in this respect is ruby, in which the energy gap (2D) between the Kramers doublets in zero electric fields is equal to 11.5 GHz. In addition to the very fact of registration of absorption, it turned out to be possible to determine the parameters D and R_{333} (the field E was applied along the C axis). The values of the latter, within the limits of experimental accuracy, coincided with those known in the literature^[20].

d. Magnetoelectric Effect

The existence of non-zero matrix elements of the electric dipole moment in paramagnets leads to the creation of electric polarization by a magnetic field and to magnetization by an electric field^[145]. We thus have the analog of the magnetoelectric effect predicted in^[146,147] and observed in ferromagnets^[148,149] and antiferromagnets^[150-152]. In paramagnets this effect was observed on Ni²⁺ ions in an NiSO₄ · 6H₂O crystal^[153], namely, the electromotive force produced by the electric polarization induced by an alternating magnetic field was measured.

e. Induction and Echo

In the presence of electric effects it is possible to excite precession of the EDM by external alternating electric and magnetic fields. The precession is a source of an electric field, which calculations performed in^[154] show to be measurable (effect of electric dipole induction).

The possibility was also considered^[155] of observing electric dipole echo in systems with constant electric and magnetic fields. It has been shown, in particular, that in a constant magnetic field ($J = 1$, group T_d), after application of two pulses of an alternating magnetic field (spaced by an interval τ), an echo signal is produced by the EDM at instants of time $3\tau/2$, 2τ , and 3τ . An interesting procedure for observing the electric effects in the spin-echo scheme was proposed and realized by

Mims^[156]. Just as in the usual method, two microwave pulses separated by an interval τ were applied in succession to the sample, and a spin-echo signal was observed at a time τ after the application of the second pulse. It turned out that the intensity of the signal could be varied by applying additionally to the sample an external electric field E in the time interval between the termination of the application of the second pulse and the appearance of the echo signal. In particular, the spin-echo signal disappeared completely when definite parameters (τ , E) were chosen. The vanishing of the echo signal is most characteristic in these experiments, by virtue of which it turned out to be convenient to observe the signal simultaneously for different values of τ in the form of an envelope of the echo signals. The determination of τ for the characteristic points of this curve (zeroes, maxima) has made it possible to determine the constants of the spin Hamiltonian \widehat{W}_E . This method was used to investigate^[92,156] rare-earth ions in CaWO₄.

A quantum-mechanical calculation of the resultant magnetization corresponding to Mims' experiments was carried out in^[157]. Owing to the presence of two inversion-non-equivalent positions of the ions in the crystal, a characteristic factor that depends on τ , E and the constants of the spin-Hamiltonian \widehat{W}_E appears. This factor modulates the envelope of the echo signals and determines, in particular, its zeros and maxima.

f. The Faraday, Cotton-Mouton, and Kerr Effects

A theoretical study of the microwave analogs of the Faraday and Cotton-Mouton effects^[158,162] with allowance for the electric effects was carried out in^[145]. It has been shown, in particular, that the existence of a non-zero EDM affects the magnitude and the sign of the angle of rotation of the polarization plane. A microwave analog of the Kerr effect was predicted.

g. Line Shape

Quantum kinetic equation methods^[166] were used in^[163-165] to investigate the PR line shape in the presence of external electric fields (the spin-phonon broadening mechanism). It was shown that in the presence of a perturbing static electric field the line shape has a Lorentz character, and its half-width depends linearly on the field E. A Lorentz shape occurs also in the case when the level system is produced by an external electric field or by the intracrystalline field.

5. INFLUENCE OF ELECTRIC FIELD ON THE SPECTRUM OF DOUBLE ELECTRON NUCLEAR RESONANCE (ENDOR)

a. Mechanism

If hyperfine and quadrupole interactions exist in a system, it becomes possible to act with an external electric field on the nuclear spin levels and thus influence the spectra of the nuclear-magnetic^[123] and ENDOR^[43,167] resonances. Let us consider one of the mechanisms.

Let the PC have a local symmetry T_d, a total angular momentum $J = 3/2$, and arbitrary nuclear spin I. The

spin Hamiltonian that depends on the nuclear variables can be represented in the form

$$\hat{W}_{\text{nuc}} = a(\mathbf{J}\mathbf{I}) - g_I \mu_{\text{nuc}}(\mathbf{H}\mathbf{I}). \quad (5.1)$$

The first term in (5.1) is the hyperfine-interaction operator, and the second is the operator of the nuclear Zeeman energy. We regard the operator \hat{W}_{nuc} as a perturbation to the operator of the interaction energy of the electron with the external magnetic field, which leads to a system of $(2J + 1)$ levels. It is convenient to take the second term of (5.1) into account in the first stage. It lifts the $(2I + 1)$ -fold degeneracy of each spin-electronic level. The corresponding functions are

$$\Psi_{M, m}^0 = \Psi_M^0(J_z) \chi_m^0(I_z), \quad (5.2)$$

where Ψ_m and χ_m are the electron and nuclear spin functions, and M and m are the eigenvalues of the operators \hat{J}_z and \hat{I}_z . The next step is to take into account the term $a(\mathbf{J}\mathbf{I})$. As a result we can write for the functions

$$\Psi_{\mp 3/2, m} = \Psi_{\mp 3/2, m}^0 \mp \frac{a\sqrt{3}}{2g\mu H} \sqrt{(I \pm m)(I \mp m + 1)} \Psi_{\mp 1/2, m \mp 1}^0 \quad (5.3)$$

and analogously for $\Psi_{\pm 1/2, m}$; μ is the Bohr magneton of the electron.

Let us consider the quantum transitions in the spin-nuclear system under the influence of an external alternating electric field. The perturbation operator is

$$\hat{W}_E(t) = -d\mathbf{E}(t). \quad (5.4)$$

On the basis of (5.3) and (5.4) we have for the matrix elements of the transitions

$$W_{-3/2, m+1}^{-3/2, m} = \frac{-\alpha a \sqrt{3} \sqrt{(I+m+1)(I-m)}}{2g\mu H} (E_y(t) - iE_x(t)),$$

where $i\alpha = -(\mathbf{d}_z)_{-3/2, 1/2}$. The matrix elements of the transitions $\Delta M = \pm 2$ will also differ from zero.

It can be shown analogously that the presence of hyperfine interaction leads to a nuclear-level shift that depends on the electric field. The latter leads to a shift of the ENDOR frequencies.

b. ENDOR of F-centers in Alkali-halide Crystals

One of the features of the ENDOR method^[166] is the possibility of investigating a large number of nuclei located in the PC region^[169]. Practically all the nuclei are located in places having no inversion center, regardless of whether the PC has or has not an inversion symmetry on the whole*. In this case the spin Hamiltonian describing the ENDOR spectrum contains terms that are linear in the electric field^[170-172]. They lead to a dependence of the ENDOR frequencies on the electric field, particularly to a splitting, linear in the field \mathbf{E} , of the lines belonging to two inversion-non-equivalent centers. The existence of electric effects in ENDOR greatly broadens the class of investigated PC, since the limitation connected with the inversion symmetry of the PC is lifted. For example, in the case of F centers in alkali-halide crystals, the effect exists in spite of the common symmetry O_h .

The first and so far only experiments were performed by Reichert et al.^[173-176]. They investigated F centers in NaCl, KCl, KBr, and LiF crystals. The

*An exception is the nucleus of the impurity ion if it is located at the inversion center of the PC.

effect of splitting of the ENDOR lines turned out to be connected with the change of the isotropic constant of the hyperfine interaction, $\partial a/\partial \mathbf{E}$, under the influence of the external electric field.

To explain the magnitude of the effect we present the initial perturbation operator in the form^[177,178]

$$\hat{W} = \sum_l \tau_l \delta_l \mathbf{I}_l \mathbf{S} - d\mathbf{E},$$

where $\tau_l = (16\pi/3)(\mu_l \mu / I_l)$, $\delta_l = \delta |\mathbf{r} - \mathbf{R}_l|$, \mathbf{r} , μ , \mathbf{S} and \mathbf{R}_l , μ_l , \mathbf{I}_l are the radius vector, magnetic moment, and spin of the electron, and of the l -th nucleus, respectively. Since the F center has an inversion center, the terms linear in the electric field appear in second order of perturbation theory. Fundamentally simple calculations lead to the expression

$$\left(\frac{\partial a}{\partial \mathbf{E}}\right)_i = 2\tau_l \Psi_l(l) \epsilon_0 \sum_n \frac{(dz)_{1, nz} P^n(l)}{\Delta_{n1}}, \quad (5.5)$$

where $\Psi_l(l)$ and $P^n(l)$ are the moduli of the wave functions of the ground and n -th excited states at the lattice site, Δ_{n1} is the corresponding energy difference, $(dz)_{1, nz}$ is the matrix element of the effective dipole moment of the F center, the subscripts 1 and nz correspond to the functions of the ground and n -th excited (z -component) states, and ϵ_0 is the dielectric constant of the crystal. Its appearance is connected with the fact that the experimentally measured field intensities \mathbf{E}_0 and \mathbf{E} are connected by the relation $\mathbf{E} = \epsilon_0 \mathbf{E}_0$. Taking Δ_{n1} outside the summation sign in (5.5), we obtain at a certain average value

$$\left(\frac{\partial a}{\partial \mathbf{E}}\right)_i = \frac{2\tau_l \Psi_l^2(l) \epsilon_0}{\Delta} d_i. \quad (5.6)$$

Formula (5.6) makes it possible to determine from the given $(\partial a/\partial \mathbf{E})_l$ the values of the modulus of d in the lattice site, $\Psi_l^2(l)$ are known from the ENDOR data, and Δ can be replaced approximately by the distance between the ground and first-excited terms. Neglecting the local field, the energy operator of the interaction with the electric field is written in the form

$$\hat{W}_E = -e\mathbf{r}\mathbf{E}_0. \quad (5.7)$$

\mathbf{E}_L is chosen to be here the macroscopic average field \mathbf{E}_0 . In analogy with (5.6) we have

$$\left(\frac{\partial a}{\partial \mathbf{E}}\right)_i = \frac{2\tau_l \Psi_l^2(l) eR_l}{\Delta}, \quad (5.6a)$$

where R_l is the coordinate of the l -th site.

The calculations of $(\partial a/\partial \mathbf{E})_l$ performed in this approximation^[177,178] indicate good agreement between theory and experiment for the second and fourth coordination spheres and a certain discrepancy ($\sim 30\%$) for the first sphere. The latter is connected with the deformation of the lattice near the defect (the ions are shifted away from the vacancy) and the distortion of the macroscopic field in this region. Thus, the electric effects in ENDOR make it possible to investigate local electric fields and deformations.

In the case of F centers we can confine ourselves in (5.5), with high accuracy, to a single term, namely the first excited state. We can then estimate the wave function of the excited state at the lattice site from the data on the electric effects in ENDOR^[178].

6. ELECTRIC MECHANISM OF LINE BROADENING

a. Effect of Correlation of the Width and Line Splitting

In practice crystals are not ideal. The growth and storage conditions, special working, and other factors influence the structure of the crystal and bring it closer to or farther away from ideal. In a real crystal there are always defects of various types: vacant lattice sites, impurity atoms, dislocations, mosaic structure, etc. These imperfections determine in many respects the physical properties and are being diligently studied. The defects are not distributed uniformly over the crystal, and can therefore lead to an inhomogeneous broadening of the PR lines. Such a broadening was observed and interpreted with the aid of different lattice-distortion models (see, e.g.,^[179-186]). In paraelectric resonance, line broadening is also governed by the defects^[187].

A circumstance of interest is that the aforementioned defects have an electric character. With respect to the PC, their existence leads to the appearance of a certain intracrystalline electric field determined by the relation

$$\mathbf{e} = -\text{grad}(V_p - V_{id}), \quad (6.1)$$

where V_p and V_{id} is the potential energy of the PC in a center with defects and without them, respectively. Since the radii of the PC states are usually small, one can assume the field \mathbf{E} , with high degree of accuracy, to be constant within the limits of the PC. There is thus an analogy between the external static electric field \mathbf{E} and the field produced by the defects. It is therefore of interest to investigate it in parallel and to compare the effects connected with the field \mathbf{E} (line shift, line splitting) with the line broadening, which, as expected, is due to the defect field. Such investigations were carried out^[47, 192] and led to the observation of a correlation between PR line splitting by an external electric field and the broadening of the same line. Figure 2 shows the corresponding curves, taken from^[47], for a Cr^{3+} ion in a ZnWO_4 crystal.

To describe the correlation effect, we note that for a group of PC having the same value of the field intensity E we can write on the basis of (3.4)^[128, 193]

$$h_i = \sum_j \alpha_j e_j. \quad (6.2)$$

Let the distribution function of the fields in the crystal be even with respect to each of the components e_i . We then have for the second moment of the curve, which characterizes the line broadening,

$$\Delta h^{(2)} = \overline{V h_i^2} = V \overline{\sum_j \alpha_j^2 e_j^2}. \quad (6.3)$$

The superior bar denotes averaging. We emphasize that in (6.3) the coefficients α_j coincide with the angular coefficients that determine the splitting of the PR line under the influence of an external static electric field. The coefficients α_j are functions of the angles characterizing the direction of the external magnetic field \mathbf{H} . At definite orientations of this field, certain α_j can vanish. Thus, for the Cr^{3+} ion in ZnWO_4 , if \mathbf{H} is perpendicular to the twofold symmetry axis (y axis) $\alpha_x = \alpha_z = 0$, we have

$$\Delta h^{(2)} = \overline{V e_y^2} \alpha_y. \quad (6.3a)$$

On the other hand, if \mathbf{E} is parallel to y we have on the basis of (3.4)

$$h_i = E_j \alpha_j. \quad (3.4a)$$

From a comparison of (6.3a) and (3.4a) it follows that the half-width and splitting have the same angular dependence, which is indeed the correlation effect in pure form (Fig. 2).

If several components of the vector \mathbf{e} are effective, it is necessary to use the general formula (6.3) to interpret the angular dependence of the line half-width. Putting in this formula $\overline{e_x^2} = \overline{e_y^2} = \overline{e_z^2} = \overline{e^2}$, i.e., assuming anisotropic distribution of the defect fields, we obtain

$$\Delta h^{(2)} = \overline{V e^2} \overline{V \sum_i \alpha_i^2}. \quad (6.3b)$$

Formula (6.3b) has made it possible to explain with high accuracy the angular dependences of the half-width of the Cr^{3+} line in ZnWO_4 for different planes in which the orientation of the field \mathbf{H} was varied.

A study of the nature of the line width with the aid of electric effects has suggested a new broadening mechanism, namely broadening due to the fields of the point defects. For the PC in ZnWO_4 ^[47] and CaWO_4 ^[192] these defects are impurity ions or vacancies that compensate for the excess charge of the paramagnetic ion. These conclusions were subsequently confirmed^[81, 84, 89, 194-196]. We note in this connection also the results of^[197, 198], where the defects that broaden the PR line were introduced artificially by replacing the second component (of a crystal of the $A_{II}B_{IV}$ type) by another ion.

If the field \mathbf{e} is sufficiently strong, so that the PC loses its individuality, a new PC is produced, and a new line appears in the PR spectrum. This is usually the case when the defect ion occupies one of the corners in the nearest coordination sphere^[199].

The correlation effect was explained^[200-202] on the basis of the spin-phonon mechanism (homogeneous broadening)*. It is shown in^[204] that the angular dependence of PR line width observed in^[47] does not occur at high temperatures, where it can be assumed that the spin-phonon mechanism predominates. The conclusion that the defect mechanism plays a dominant role in the correlation effect is confirmed in^[205].

b. Dependence of EPR Line Width on the External Electric Field

An investigation of the electric effects at large field intensities has led to observation of a dependence of the EPR line width on the field E ^[206]. The effect can be explained within the framework of the concept of existence of intracrystalline defect fields^[128]. The line broadening itself can be regarded as an effect linear in the field \mathbf{e} . If the PC is acted upon also by an external field \mathbf{E} , then bearing in mind effects that are nonlinear in the electric field (considered in Chap. 3), one should expect the appearance of effects connected with the terms of the type $e_i E_k$. This quadratic effect becomes manifest in the form of a linear dependence of the line width on the field \mathbf{E} . Nonlinear dependences of the width on the field \mathbf{E} are similarly possible*. In this case, retaining

*See also^[203] concerning the role of the spin-phonon mechanism.

†A mechanism based on the combination of deformation and an external electric field was proposed in^[207].

terms of higher order in \mathbf{E} , we can write

$$\Delta h^{(2)} = \sqrt{\sum_i \alpha_i^2 e_i^2} + \langle E \rangle + \langle E^2 \rangle + \langle E^3 \rangle + \dots; \quad (6.4)$$

$\langle E^k \rangle$ are terms containing the components of \mathbf{E} raised to the k -th power.

c. Influence of the Number of Crystal Defects on the Position of the Line in the Spectrum

In analogy with (6.3) and (6.4) we can write for the first moment

$$\Delta h^{(1)} = \sum_i \beta_{ii} \bar{e}_i^2 + 3 \sum_{i,k} \gamma_{iik} \bar{e}_i^2 E_k. \quad (6.5)$$

The first term determines the displacement of the EPR line as a function of the number of crystal defects in the absence of a field, and the second in the presence of a field \mathbf{E} . The effect connected with the first term was observed in neutron-bombarded ruby^[194]. The second term appeared in corundum^[208] containing Fe^{3+} and Mn^{2+} ions. It turns out that the splitting of the EPR line, which is linear in the field \mathbf{E} , is different for different samples that differ in the degree of perfection of the crystal lattice.

In conclusion we note that a study of the form of the absorption curve in parallel with an investigation of the line splitting in external electric fields can serve as an effective method for the investigation of crystal defects. By now, the methods of calculating the line shape and particularly its width have been sufficiently well developed. Much attention has been paid to a statistical theory^[192,198,209-212] based on knowledge of the law governing the defect distribution in the crystal*.

7. MICROSCOPIC THEORY

To calculate the spin-Hamiltonian constants characterizing the electric defects it is necessary to know the energy spectrum and the wave functions of the PC in the absence of external fields and of the initial operator of the interaction of the PC with the external electric field. If these data are available, the problem reduces to the calculation of a certain minimum number, determined by the symmetry properties, of the matrix elements^[43,44].

The difficulties in the determination of the energy spectrum and wave functions lie principally in the fact that the problem is of the many-body type, namely, the PC is a complicated formation consisting of a large number of nuclei and electrons of the crystal in the region of the defect. For the sake of simplicity, the analysis is confined to a small number of coordination spheres, but even in this quasimolecular case the problem is far from easy. The problems that arise here are analogous to those in the theory of molecules, which according to^[214] are still far from completely solved. The most promising is the method of molecular orbitals. The specific nature of the difficulties arising here and the level of the attained results is sufficiently well illustrated by a series of papers devoted to the calculation of complexes of the crystal KNiF_3 ^[215-217]. When the atoms of the entire crystal are taken into account, a more complicated problem of "deep levels" arises and,

*A review dealing with the calculation of the shape of an inhomogeneously broadened PR line is contained in^[213].

as seen from^[218-220], has not yet been solved.

The difficulty in the choice of the operator \hat{W}_E lies in the existence of the so-called "ionic" interaction mechanism. As seen from Chap. 2, to obtain the corresponding part of the energy operator it is necessary to know the positions of the ions in the presence of an external electric field, which in turn presupposes knowledge of the potential energy of the interaction of the atoms in a non-ideal crystal.

The electric effect is a sufficiently "fine" effect ($\sim 10^6 - 10^7$ Hz in EPR and $\sim 10^4$ Hz in ENDOR), and is most sensitive to the structure of the PC and the accuracy of the calculation. It is therefore logical to hope for success in a quantitative calculation of this effect if the wave functions and the energy structure of the PC explain sufficiently well the "coarser" effects such as the splitting by an intracrystalline field $10D_Q$, the spin-Hamiltonian constants D , \mathcal{E} , etc. It can be noted in this connection that a large amount of calculation is necessary to obtain sufficiently good agreement with experiment for the parameter $10D_Q$ ($\sim 10^{13}$ Hz)^[217].

The calculations of the electric effects were based on the theory of the crystal field^[72,90,105,221-232]. The main purpose of these calculations was to obtain general expressions and numerical values for the tensor components characterizing the electric effect. Owing to the approximate character of the model and the complexity of the calculations, the matter usually reduces to an estimate of the effect, to obtaining certain relations between the parameters determining the different mechanisms, and to the use of experimental data for the calculation of the "intermediate" parameters (e.g., the odd components of the intracrystalline electric field).

To illustrate the calculation method, to explain the role of different mechanisms, and to establish the connection with the already known results of the calculation of the spin-Hamiltonian constants^[38] it is convenient to start from the theory of the crystal field. We represent the energy operator of the PC in the form

$$\hat{W} = \hat{W}_0 + \hat{W}_c^e + \hat{W}_c^o + \hat{W}_{SO} + \hat{W}_H + \hat{W}_E. \quad (7.1)$$

The first term is the energy of the free atom, and the second and third constitute the energy of its interaction with the crystal. Bearing in mind that the absence of an inversion center is important for the electric effects, we have separated the even (e) and odd (o) components of the crystal field. The remaining terms are respectively the spin-orbit and Zeeman interactions and the interaction with the external electric field. We confine ourselves to the case of the iron-group elements. As the zeroth approximation we can choose the first three terms in (7.1) and regard the remainder as a perturbation. Let the main term of the initial zeroth-approximation operator ($\hat{W}_0 + \hat{W}_c^e + \hat{W}_c^o$) be an orbital singlet. Without violating the general scheme of perturbation theory, we turn on temporarily the operator W_E in the zeroth-approximation Hamiltonian. The perturbation operator, which depends on the electron spins, will be ($\hat{W}_{SO} + \hat{W}_H$), and the calculation of the spin-Hamiltonian constants does not differ in principle in any way from the published one^[38]. In particular, the components of the crystal-field tensor D are given by the expression

$$D_{ij} = \lambda^2 \sum_{n \neq 0} \frac{\langle L_i \rangle_{0n} \langle L_j \rangle_{n0}}{\Delta_{n0}}, \quad (7.2)$$

where $\Delta_{n_0} = \epsilon_n - \epsilon_0$, L_i is the i -th component of the angular-momentum operator, the subscript 0 denotes the states (Ψ_0) of the main term, and n denote the states of the excited term (Ψ_n). Owing to the absence of an inversion center, the functions Ψ_0 and Ψ_n have no definite parity, a fact that can be represented in the form

$$\Psi_q = \Psi_q^0 + \sum_{q' \neq q} \frac{(W^0)_{q'q}}{\Delta_{qq'}} \Psi_q^0. \quad (7.3)$$

Ψ_q^0 is the wave function corresponding to the operator $\hat{W}_0 + \hat{W}_C^e$; $\hat{W}_C^0 + \hat{W}_E$. Analogously

$$\epsilon_q = \epsilon_q^0 + \sum_{q' \neq q} \frac{(\hat{W}^0)_{qq'} (W^0)_{q'q}}{\Delta_{qq'}}. \quad (7.4)$$

Substituting (7.3) and (7.4) in (7.2) we obtain the increment to D_{ij} :

$$\Delta D_{ij} = \lambda^2 \left[\sum_{npq} \frac{(L_i)_{0n} (W^0)_{nq} (L_j)_{qp} (W^0)_{p0}}{\Delta_{n0}^0 \Delta_{nq}^0 \Delta_{qp}^0} + \dots \right]. \quad (7.5)$$

Equation (7.5) contains explicitly a typical term containing the lowest power of $(W^0)_{q'q''}$. It is seen from (7.5) that the correction ΔD_{ij} is determined by the fourth order of perturbation theory, if we choose $W_0 + W_C^e$ as the zeroth-approximation operator and regard the remaining terms of (7.1) as the perturbation. Separating explicitly the part linear in E , we represent (7.15) in the form

$$\Delta D_{ij} = \sum_s E_s R_{sij},$$

where

$$R_{sij} = \lambda^2 \sum_{npq} \frac{(L_i)_{0n} (L_j)_{qp}}{\Delta_{n0}^0 \Delta_{nq}^0 \Delta_{qp}^0} \left[(W_C^0)_{nq} (d_s)_{p0} + (d_s)_{nq} (W_C^0)_{p0} \right].$$

To estimate the magnitude of the effect we put $\lambda = 10^2 \text{ cm}^{-1}$, $(W_C^0)_{nq} = (W_C^0)_{p0} = 10^4 \text{ cm}^{-1}$, $(L_i)_{0n} = (L_j)_{qp} = 1$, $(d_s)_{p0} = (d_s)_{nq} = 10^{-17} \text{ cgs esu}$, $\Delta_{n0}^0 = 10^4 \text{ cm}^{-1}$, $\Delta_{nq}^0 = \Delta_{qp}^0 = 10^5 \text{ cm}^{-1}$, and $E = 10^5 \text{ V/cm}$. As a result we obtain $\Delta D_{ij} = 1 \text{ G}$; the experimentally observed splitting is of the order of several Gauss*.

For simplicity we have disregarded the contribution from the spin-spin interaction. But since λ^2/Δ_{n0} is proportional to the spin-spin interaction constant, it can be assumed that the contribution of the latter is significant^[234]. It is known that the spin-orbit interaction in a free atom differs from the one in a crystal. In principle it can vary also under the influence of an external electric field. This electric-effect mechanism was considered in^[235]. It turned out to be smaller by several orders of magnitude than the mechanism determined by formula (7.5).

In the molecular-orbital method, the scheme of the calculation remains essentially the same. One can start from a formula of the type (7.2), in which the functions Ψ_0 and Ψ_n are molecular orbitals "polarized" by the external electric field. In^[20] the "electronic" and "ionic" mechanisms were considered separately. In the former case the crystal lattice was assumed to be undeformed. In the latter, the displacements of the ions under the influence of the field E were estimated and the

calculations were performed for the new equilibrium positions with "unpolarized" orbitals. The wave functions were taken from^[236].

In conclusion we note that by virtue of the complexity of the allowance for the ionic mechanism, there exist so far no consistent quantities of calculations of the ion displacements, and consequently of the correction connected with the ionic mechanism. The estimates are usually based on the assumption that the Lorentz formula holds for the effective field in the region where the ions are located. The dependence of the polarization on the external electric field is determined in this case by the macroscopic relation $P = (\epsilon_0 - 1)E/4\pi$. The peculiarities of the local center and particularly the possible dependence of ϵ on r are neglected in these calculations. Recognizing that the electric effect is sensitive to the mutual placement of the ions (especially when covalence is taken into account^[20]), it is advisable to estimate the sensitivity of the tensor components to small changes of the calculated displacements of the ions from the equilibrium positions.

8. RELATED RESONANCES

a. Combined Resonance

In 1960, É. I. Rashba indicated the possibility of realizing electric dipole transitions between spin sublevels of the Landau levels^[237]. This effect, which he called combined resonance (CR), was observed also experimentally. Just as in the phenomena considered above, an important role is played here by the spin-orbit interaction. The work on CR is reviewed in^[238]. Among the papers not included in that review, we mention^[239-246], where references to other work can also be found.

b. Optics

An attempt to observe the electric effect in optics was undertaken already in^[7]. Its authors did not observe the effect and concluded that the local centers investigated by them had inversion centers. The effects first appeared in ruby^[1]. Further investigations^[247-250] confirmed the conclusions of^[1] that the line-splitting effect is connected, just as in EPR, with the existence of two non-equivalent positions of the Cr^{3+} ions in the corundum lattice. Experimental and theoretical investigations of the pair of Cr^{3+} ions in corundum were reported in^[251-253]. The effect on impurity atoms with unfilled f -shells was investigated in^[254-256], and complex color centers of γ -irradiated alkali-halide crystals were investigated in^[257, 258].

Just as in EPR, the mechanism of the effect is connected with the shifting of the energy levels between which the transition takes place by the external electric field. Since these levels have an "orbital" character (unlike in EPR), the effect is due to second-order of perturbation theory (see (7.4)) and is proportional to the matrix elements of the operators \hat{W}_E and \hat{W}_C^0 . The macroscopic theory is based on the crystal-field approximation^[224-226, 228, 248, 249]. Just as in EPR, a "phenomenological" approach based on the perturbation-matrix method is possible. Such an analysis was carried out in^[256].

*Expression (7.5) includes terms that contain two energy differences ($\sim 10^4 \text{ cm}^{-1}$), corresponding to levels having the same parity. This increases ΔD_{ij} by one order of magnitude.

c. Nuclear Magnetic and Quadrupole Resonances

The effect in nuclear quadrupole resonance was first observed in^[2,3], although attempts to observe it were undertaken also earlier^[259,260]. A change was observed in the quadrupole-interaction constants of the halogen nuclei in NaBrO₃, KClO₃, and NaClO₃ crystals. The study of these components was continued in^[261,262]. Corundum^[263,264], gallium arsenide^[265-267], and other more complicated compounds^[268-272] were also investigated. Just as in EPR, electric dipole transitions with selection rules $\Delta M = \pm 2$ were observed^[262,263,265,266].

From the point of view of the phenomenological description, NMR is analogous to EPR (the nuclear Zeeman energy corresponds to the electron Zeeman energy, and the energy of the quadrupole interaction corresponds to the energy of interaction with the intracrystalline field). In the experiments they measured the tensor components characterizing the change (occurrence) of the quadrupole-interaction constant^[273], although in^[8,274] it is indicated that a linear-in-E shift of the nuclear screening factor is possible if the nucleus is not in an inversion center.

The quantitative theory^[3,267,275-278] * starts from two possible mechanisms, the polarization of the electron shells and the change of the mutual positions of the nuclei. The first is taken into account by calculating the correction that must be made to the wave function because of the perturbation operator \hat{W}_E , and by subsequently averaging the energy operator of the quadrupole interaction \hat{W}_Q ^[279] on the perturbed functions (the approach is equivalent to taking into account mixed terms of the type $\langle \hat{W}_Q \rangle < \langle \hat{W}_E \rangle$ in the energy in second order of perturbation theory). The effect of the ion displacement (ρ) on the equilibrium position is proportional to ρ/a^4 , where a is the equilibrium internuclear distance (from the considered nucleus). The value of ρ was estimated by starting from the macroscopic polarization of the sample.

d. Nuclear Magnetic Resonance and Hyperfine Structure

The dependence of the position of the lines in the NMR spectrum of F¹⁹ in MnF₂ crystals on the external electric field was investigated in^[4,280]. The effect linear in the field E is connected with the change of the hyperfine-interaction constants^[281].

In conclusion, mention should be made of^[282], where the possibilities afforded by electric effects in the determination of the effective field acting on the electron is discussed.

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*An effect quadratic in E is considered in^[277].

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