Electron spin resonance of centers with icosahedral symmetry

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The electron spin resonance (ESR) spectrum and the spectrum of the adjoining resonances of impurity ions found in crystalline electric fields of icosahedral symmetry are predicted. The spin Hamiltonian is obtained, and its eigenvalues, the transition frequencies, and the resonant magnetic fields for an arbitrary orientation of the latter are found. The ESR spectrum is constructed and analyzed as a function of the magnitude of the total angular momentum J. A comparison with the spectra of paramagnetic centers of lower, particularly cubic, symmetry is made. The possibilities of observing the effects predicted are discussed. © *1996 American Institute of Physics.* [S1063-7761(96)01710-6]

1. INTRODUCTION

Symmetries whose elements include rotations by an angle that is a multiple of $2\pi/5=72°$ did not arouse interest for a long time, since it was assumed that the objects corresponding to them do not occur in nature on the atomic level. Such symmetries as C_5, C_{5v}, D_5, D_{5h}, Y, and Y_h, especially the last two, were not given proper attention, in contrast to, for example, the familiar 32 point groups.[1-3] However, numerous pieces of evidence have appeared in recent years, indicating that such symmetries are not only of academic interest, but also reflect real structures, which are promising for applications in some cases.[4]

For example, Morokhov *et al.*[5] discovered that small ($\leqslant 10^3$ Å) metallic particles can assume the form of a regular pentagon or have more complicated structures (icosahedral, pentagonal-pyramidal). The formation of clusters from a small number of atoms is also typical of other elements, for example, the noble gases, an icosahedral structure being possible in the case of xenon and argon. So-called quasicrystals[6,7] also have unusual symmetries: pentagonal dodecahedrons, for example, can be clearly identified in their grains. Also, the presence of small regions with atoms in an icosahedral configuration is generally characteristic of dense supercooled liquids. An icosahedral symmetry has been discovered in several molecules ($B_{12}H_{12}^{-2}$, $C_{20}H_{20}$), as well as in more complicated objects (like viruses).[8] A model of specific paramagnetic centers in the form of so-called dangling bonds in diamond-like crystals has been discussed for almost 40 years.[9] A new model based on a fivefold-coordinated silicon atom has been proposed in recent years, and the corresponding state of the unpaired electron has been termed a "floating bond."[10] A very close analog of this model is the model of another defect that appears at dislocations in silicon: a fivefold-coordinated silicon atom can be clearly identified along with a more distant sixfold-coordinated atom in the (111) plane in the region of the defect. A new class of carbon clusters (containing an icosahedron), which have rotations by 72° as symmetry elements, has recently been discovered.[11]

However, the discovery of fullerenes,[12,13] molecules of C_{60} having icosahedral symmetry, and crystals derived from them, i.e., fullerites, aroused great interest. Not only the unique structure and symmetry of these new carbon formations, but also the unusual properties of such substances are of interest. It has been shown, for example that semiconductor, metallic, and even superconducting properties can appear when atoms of other elements are implanted in them. It has been possible to implant atoms of elements belonging to different groups in the periodic table (up to the lanthanides and even uranium) directly in fullerenes.[14-16]

Thus, the existence of diverse molecular and crystalline structures with impurity atoms found in a crystalline electric field of icosahedral symmetry is possible. For this reason investigations of the energy structure, resonance properties, and other characteristics of such systems would be timely. The purpose of the present work is to predict and analyze the electron spin resonance (ESR) spectrum of such systems.

2. GROUPS OF THE ICOSAHEDRON

We distinguish between four groups of the icosahedron: the simple (Y), complete (Y_h), simple double (Y'), and complete double (Y_h') groups. Group Y consists only of rotations about the symmetry axes. There are 6 fifth-order axes with 24 rotations about these axes, 10 third-order axes with 20 rotations about them, and 15 second-order axes with 15 rotations about them. The total number of elements in the group is 60. Consideration of the inversion operation leads to the group $Y_h=Y\times C_I$ (C_I is the inversion group) containing 120 elements. The group Y' is obtained from the Y group by adding the element Q, i.e., rotation by 2π, so that $Y'=Y\times Q$. In analogy to Y_h we also have $Y_h'=Y'\times C_I$. The Y' and Y_h' groups contain 120 and 240 elements, respectively.

The characters and notation of the irreducible representations of the Y_h group are presented in Table I.[17,18] The subscripts g and u in it denote, respectively, even and odd parity of the states with respect to inversion. All the elements are numbered in the row of headings in the table, making it possible to cite rules to successively obtain all the elements of the group from a minimal number of these elements (Table II). As shown by the a geometric treatment of the icosahedron, two rotations about different fifth-order axes

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TABLE I. Characters of the irreducible representations of the Y_h group.

Irreducible representation	Class									
	$1E$	$12C_5^{1,4}$	$12C_5^{2,3}$	$20C_3^{1,2}$	$15C_2^1$	I	$12\,I\times C_5^{1,4}$	$12\,I\times C_5^{2,3}$	$20\,I\times C_3^{1,2}$	$15\,I\times C_2^1$
	1	2–13	14–25	26–45	46–60	61	62–73	74–85	86–105	106–120
A_g	1	1	1	1	1	1	1	1	1	1
A_u	1	1	1	1	1	-1	-1	-1	-1	-1
F_{1g}	3	ε_+	ε_-	0	-1	3	ε_+	ε_-	0	-1
F_{1u}	3	ε_+	ε_-	0	-1	-3	$-\varepsilon_+$	$-\varepsilon_-$	0	1
F_{2g}	3	ε_-	ε_+	0	-1	3	ε_-	ε_+	0	-1
F_{2u}	3	ε_-	ε_+	0	-1	-3	$-\varepsilon_-$	$-\varepsilon_+$	0	1
G_g	4	-1	-1	1	0	4	-1	-1	1	0
G_u	4	-1	-1	1	0	-4	1	1	-1	0
H_g	5	0	0	-1	1	5	0	0	-1	1
H_u	5	0	0	-1	1	-5	0	0	1	-1

Note. Here C_n^m is an m-fold rotation about an nth-order axis; the number in front of the notation of an element is the number of elements in the class; $\varepsilon_\pm=(1\pm\sqrt{5})/2$.

can be selected as the generating elements in the case of the Y group. To be specific, here we select elements Nos. 2 and 5, which correspond to rotations by 72° about the $b\rightarrow a$ and $d\rightarrow c$ axes, which pass through vertices of the icosahedron (Fig. 1). In the case of the Y_h group, the inversion operation $I\equiv$ No. 61 is added as a generating element, and any element after No. 61 is obtained from elements of the Y group by multiplication by I. Therefore, as a supplement to Table II we can symbolically write $60+n=I\times n$, where $n=1, 2, \ldots, 59, 60$.

The characters and notation of the irreducible representations of the Y' group are presented in Table III.[17,19] In this case elements Nos. 2 and 5 and Q can be selected as the generating elements. As in Table II, we can write a rule for successively obtaining the remaining elements of the group from them. For the sake of brevity, we shall not write out the corresponding table, noting only that the specific feature of the double group, i.e., the duality of the geometrically identical elements, must be taken into account in it. The characters of the Y_h' group are obtained from the characters of the Y' group by multiplying the latter by the characters (±1) of the C_I group, so that elements Nos. 2 and 5, Q, and I act as the generating elements here. For the sake of brevity, we shall likewise not write out the character table of the Y_h' group.

3. MATRIX REPRESENTATION OF THE ELEMENTS OF THE GROUP OF AN ICOSAHEDRON

There are several ways to obtain the spin Hamiltonian describing an ESR spectrum.[20] However, they all require knowledge of the transformation properties of the basis functions of the irreducible representations or operator functions (irreducible tensor operators, equivalent operators, etc.). Stated differently, they require knowledge of the matrix representation of the group elements. A brief description of the method that we developed to obtain these matrices as applied to icosahedral symmetry is given below. The method was used in this work to find the matrices of all the elements of all the irreducible representations of each group of an icosahedron, but it can also be employed for other purposes.

TABLE II. Rule for successively obtaining all the elements of the Y group.

1	2	3	4
$14=2\times2$	$10=7\times9$	$35=2\times23$	$48=27\times35$
$20=2\times14$	$18=6\times6$	$30=2\times24$	$49=31\times35$
$8=2\times20$	$24=6\times18$	$33=2\times25$	$50=26\times29$
$17=5\times5$	$12=6\times24$	$26=36\times36$	$51=27\times29$
$23=5\times17$	$22=10\times10$	$37=27\times27$	$52=28\times30$
$11=5\times23$	$4=22\times22$	$38=28\times28$	$53=31\times32$
$3=2\times11$	$16=4\times4$	$29=39\times39$	$54=32\times33$
$7=11\times2$	$1=2\times8$	$40=30\times30$	$55=26\times28$
$15=3\times3$	$27=2\times3$	$41=31\times31$	$56=30\times35$
$21=3\times15$	$28=2\times4$	$42=32\times32$	$57=26\times31$
$9=3\times21$	$32=2\times5$	$43=33\times33$	$58=27\times32$
$19=7\times7$	$44=2\times6$	$34=44\times44$	$59=28\times33$
$25=7\times19$	$31=2\times7$	$45=35\times35$	$60=29\times34$
$13=7\times25$	$36=2\times21$	$46=27\times30$	
$6=2\times9$	$39=2\times22$	$47=26\times34$	

Note. The multiplication should be carried out from top to bottom, beginning from the first column.

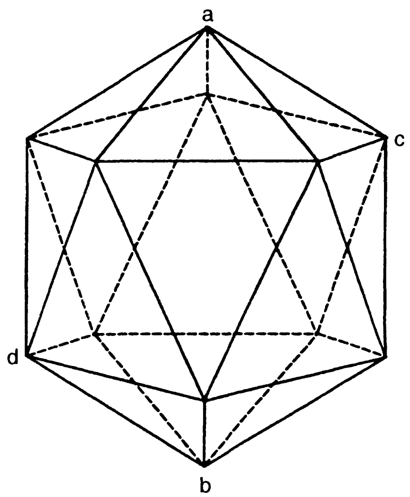

FIG. 1. Icosahedron: 20 faces, 12 vertices, and 30 edges. The letters mark the vertices through which the axes of the generating elements pass.

TABLE III. Characters of the irreducible representations of the Y' group.

	Class								
	$1E$	$1Q$	$6C_5^1$ 2–7	$6C_5^4$ 8–13	$6C_5^2$ 14–19	$6C_5^3$ 20–25	$10C_3^1$ 26–35	$10C_3^2$ 36–45	$15C_2^1$ 46–60
Irreducible representation	1	1′	$6QC_5^4$ 8′–13′	$6QC_5^1$ 2′–7′	$6QC_5^3$ 20′–25′	$6QC_5^2$ 14′–19′	$10QC_3^2$ 36′–45′	$10QC_3^1$ 26′–35′	$15QC_2^3$ 46′–60′
A	1	1	1	1	1	1	1	1	1
F_1	3	3	ε_+	ε_+	ε_-	ε_-	0	0	-1
F_2	3	3	ε_-	ε_-	ε_+	ε_+	0	0	-1
G	4	4	-1	-1	-1	-1	1	1	0
H	5	5	0	0	0	0	-1	-1	1
E_1'	2	-2	ε_+	$-\varepsilon_+$	$-\varepsilon_-$	ε_-	1	-1	0
E_2'	2	-2	ε_-	$-\varepsilon_-$	$-\varepsilon_+$	ε_+	1	-1	0
G'	4	-4	1	-1	-1	1	-1	1	0
I'	6	-6	-1	1	1	-1	0	0	0

Note. The notation is the same as in Table I. The primes on the numbers label elements obtained from the unprimed elements by multiplying the latter by Q.

Using Tables I and III, we can obtain an expansion of the irreducible representations of the rotation group D_J in the irreducible representations of the group of the icosahedron (Table IV). It is seen from Table IV, in particular, that for the angular momentum values $J=0$, 1/2, . . . ,2, 5/2 the rotation group D_J "is expanded" in only one irreducible representation of the group of an icosahedron, i.e., the representation D_J and the irreducible representation of the group of the icosahedron corresponding to it coincide. Hence it follows that the matrices of the irreducible representations of the rotation group can be chosen as the matrices of such irreducible representations. The matrix elements of the latter have the following form:[21]

$$D_J(\alpha,\beta,\gamma)_{ls}=i^{l-s}\exp[i(l\alpha+s\gamma)]\times[(J+l)!(J-l)!(J+s)!(J-s)!]^{1/2}\times\sum_k(-1)^k[k!(J-k+s)!(J-l-k)!(k-s+l)!]^{-1}\times(\cos(\beta/2))^{2J-l-2k+s}(\sin(\beta/2))^{2k-s+l}, \tag{1}$$

TABLE IV. Expansion of the D_J representation in irreducible representations of the Y and Y' groups of the icosahedron.

Integer J		Half-integer J	
J	Irreducible representation	J	Irreducible representation
0	A	1/2	E_1'
1	F_1	3/2	G'
2	H	5/2	I'
3	F_2, G	7/2	E_2', I'
4	G, H	9/2	G', I'
5	F_1, F_2, H	11/2	E_1', G', I'
6	A, F_1, G, H		

Note. The second columns show which irreducible representations are contained in the D_J representation.

where l and s take values from $-J$ to $+J$; α, β, and γ are the Euler angles, and k takes values defined by the inequalities $k\geqslant 0, k\geqslant s-l, k\leqslant J-1$, and $k\leqslant J+s$. It follows directly from a geometric analysis that for element No. 2 we have $\alpha=72°$ and $\beta=\gamma=0$ and that for element No. 5 we have $\alpha=\gamma=18°$ and $\sin\beta=2\cos\beta=2/\sqrt{5}$. These data are sufficient for constructing the matrices of the generating elements on the basis of (1) for the irreducible representations A, F_1, H, E_1', G', and I', as well as the reducible representations D_3 and $D_{7/2}$ that are used below.

To obtain the matrices of element No. 2 for the irreducible representations E_2', F_2, and G we utilized the fact that the cyclic group C_5 is a subgroup of a group of the icosahedron, and element No. 2 corresponds to an element of the C_5 group. For this purpose we preliminarily established which irreducible representations of the C_5 and C_5' groups are contained in the E_2', F_2, G, $D_3=F_2+G$, $D_{7/2}=E_2'+I'$ representations of each group of the icosahedron. The matrices of element No. 2 for the D_3 and $D_{7/2}$ representations were next obtained using Eq. (1). A comparison of the diagonal matrices thus obtained with the elements of the one-dimensional matrices of the C_5 and C_5' groups made it possible to establish which of them belong to the original irreducible representations E_2, F_2, and G. As a result, diagonal matrices of element No. 2 were obtained for the latter, and the elements of these matrices are the characters of the irreducible representations of the C_5 and C_5' groups.

Two approaches were used to obtain the matrices of element No. 5. The first is based on solving the system of equations for the matrix elements. The required number of equations was found from the requirement that the matrices be unitary and by equating the sum of the diagonal elements to the values of the characters determined. This procedure was used to find the matrices of the irreducible representations E_2 and F_2. The second approach is based on a preliminary search for functions which realize the irreducible representation sought. The matrix of element No. 5 for the irreducible representation G was found by this method. Since $D_3=F_2+G$, the known matrices of the D_3 and F_2 representations were used to preliminarily find the functions $\varphi_i^{F_2}$ of the irreducible representations F_2 in the form of a linear combination of the functions $\psi_M^3(M=-3,\ldots,+3)$ of the D_3 representation by virtual expansion of the reducible representation (D_3) in the irreducible representations (F_2) (see Ref. 1):[1)]

$$\varphi_{1,3}^{F_2}=\pm\sqrt{3/5}\psi_{\pm 2}^3-\sqrt{2/5}\psi_{\pm 3}^3,\varphi_2^{F_2}=\psi_0^3. \quad (2)$$

The expression sought for the functions φ_i^G of the irreducible representation G was obtained in the following general form:

$$\varphi_i^G=\sum_{M=-3}^{3} k_{Mi}\psi_M^3. \quad (3)$$

The coefficients k_{Mi} were found from the condition that the functions (2) and (3) be orthonormalized and the condition that the functions (3) satisfy the transformation corresponding to element No. 2. As a result, we have

$$\varphi_{1,4}^G=\sqrt{3/5}\psi_{\mp 3}^3\mp\sqrt{2/5}\psi_{\mp 2}^3,\varphi_{2,3}^G=\psi_{\mp 1}^3. \quad (4)$$

The matrix sought for the irreducible representation G was obtained on the basis of (4) and the known matrix of element No. 5 of the D_3 representation. The matrices of generating elements Nos. 2 and 5 of all the irreducible representations are listed in Appendix A.[2)] Using these data and tables like Table II, we obtained (using a specially developed computer program) the matrices of all the elements for the irreducible representations of the Y, Y_h, Y', and Y_h' groups.[3)]

The matrices obtained by the methods described above are complex in the general case. However, in some cases it is convenient to use the real matrices that correspond, for example, to ordinary coordinate transformations (the irreducible representation F_1). Tensor transformation matrices, which describe a reducible representation in the general case, can be obtained inductively from the law of vector transformation. Bearing in mind the specific application in the present work, we also obtained the matrices of the irreducible representation F_1, which describe a coordinate transformation. The corresponding generating elements are presented in Appendix A (Sec. c).

To apply the methods for obtaining the spin Hamiltonian we must also know the matrices of the time-reversal operator $\hat{\theta}$ for all the irreducible representations. They can be obtained from the results presented above. In the case of the irreducible representations A, E_1', F_1, G', H, and I', which follow directly from the representations of the rotation group, the basis functions are ψ_M^J. According to Ref. 22, for these functions we have

$$\hat{\theta}\psi_M^J=(-1)^{J-M}\psi_{-M}^J. \quad (5)$$

In the case of the irreducible representations E_2', F_2, and G, we can select linear combinations of the functions ψ_M^J as the basis functions. For the irreducible representations F_2 and G they are given by Eqs. (2) and (4). For the irreducible representation E_2' virtual expansion of the reducible representation $D_{7/2}$ in the irreducible representations E_2' and I' (Ref. 1) gives

$$\varphi_{1,2}^{E_2'}=\sqrt{3/10}\psi_{\mp 7/2}^{7/2}\mp\sqrt{7/10}\psi_{\pm 3/2}^{7/2}. \quad (6)$$

The combined use of Eqs. (2), (4), (5), and (6) enables us to find the transformation law of the functions $\varphi_i^{E_2'}$, $\varphi_j^{F_2}$, and φ_k^G under the action of the operator $\hat{\theta}$.

4. MATRICES OF A PERTURBATION OPERATOR

A perturbation-matrix technique was used in this work to obtain the spin Hamiltonian. The essence of the method can be briefly described as follows.[20] Let an arbitrary matrix element of the kth component of the operator $\hat{\mathbf{V}}^\beta$ have the form

$$V_{ikj}^{\alpha\beta\gamma}=\int(\psi_i^\alpha)^*\hat{\mathbf{V}}_k^\beta\psi_j^\gamma d\tau,$$

where α, β, and γ and i, j, and k characterize the irreducible representation and the basis components within each irreducible representation, respectively, and $d\tau$ is a volume element. Performing the transformation corresponding to each element of the G group under the integral sign and summing over all the elements, we obtain

$$V_{ikj}^{\alpha\beta\gamma}=\frac{1}{N}\sum_{i'k'j'}V_{i'k'j'}^{\alpha\beta\gamma}\sum_G(G_{i'i}^\alpha)^*G_{k'k}^\gamma G_{j'j}^\beta, \quad (7)$$

where the G_{lm}^δ are the matrix elements of the operators of the group that specify the transformation properties

$$\hat{\mathbf{G}}\psi_m^\delta=\sum_l G_{lm}^\delta\psi_l^\delta, \quad \hat{\mathbf{G}}\hat{\mathbf{V}}_k^\sigma\hat{\mathbf{G}}^{-1}=\sum_{k'}G_{k'k}^\sigma V_{k'}^\sigma,$$

and N is the total number of elements in the group. Equation (7) is the starting expression, which relates the matrix elements of the perturbation operator sought to one another and specifies the matrix elements that are equal to zero. The total number of equations like (7) is equal to $S_\alpha\times S_\gamma\times S_\beta$ (where S_δ is the dimensionality of the irreducible representations δ), i.e., the total number of matrix elements. However, not all of them are independent. Some of the independent equations make it possible to express a few matrix elements in terms of others and, thus, to reduce the number of matrix elements that are subject to calculation or are used as parameters. The maximum number of independent parameters is equal to the number which indicates how many times the irreducible representation γ^* is contained in the direct product $\alpha^*\times\beta$. The results of the corresponding calculation for a group of an icosahedron are presented in Table V. The numbers in it indicate how many times the irreducible representation in the heading of the respective column is contained in the direct product of irreducible representations in the heading of the respective row. The square brackets denote symmetric products, and the curly brackets denote antisymmetric products. The table does not include trivial situations like $A\times F_1=F_1$, and the division into even and odd states has also been eliminated, since it is easily obtained from the table, if a "parity conservation law," for example, $F_{1g}\times F_{2u}=G_u+H_u$, is taken into account.

Equation (7) should be supplemented by the relation[22]

$$V_{ikj}^{\alpha\gamma\beta}=\left[\int(\hat{\theta}\psi_i^\alpha)^*\hat{\theta}\hat{\mathbf{V}}_k^\gamma\hat{\theta}^{-1}\psi_j^\beta d\tau\right]^*, \quad (8)$$

TABLE V. Expansion of direct products of irreducible representations of the Y' group.

Product	A	F_1	F_2	G	H	Product	A	F_1	F_2	G	H
$[F_1\times F_1]$	1	0	0	0	1	$[E_1'\times E_1']$	0	1	0	0	0
$\{F_1\times F_1\}$	0	1	0	0	0	$\{E_1'\times E_1'\}$	1	0	0	0	0
$F_1\times F_2$	0	0	0	1	1	$E_1'\times E_2'$	0	0	0	1	0
$F_1\times G$	0	0	1	1	1	$E_1'\times G'$	0	1	0	0	1
$F_1\times H$	0	1	1	1	1	$E_1'\times I'$	0	0	1	1	1
$[F_2\times F_2]$	1	0	0	0	1	$[E_2'\times E_2']$	0	0	1	0	0
$\{F_2\times F_2\}$	0	0	1	0	0	$\{E_2'\times E_2'\}$	1	0	0	0	0
$F_2\times G$	0	1	0	1	1	$E_2'\times G'$	0	0	1	0	1
$F_2\times H$	0	1	1	1	1	$E_2'\times I'$	0	1	0	1	1
$[G\times G]$	1	0	0	1	1	$[G'\times G']$	0	1	1	1	0
$\{G\times G\}$	0	1	1	0	0	$\{G'\times G'\}$	1	0	0	0	1
$G\times H$	0	1	1	1	2	$G'\times I'$	0	1	1	2	2
$[H\times H]$	1	0	0	1	2	$[I'\times I']$	0	2	2	1	1
$\{H\times H\}$	0	1	1	1	0	$\{I'\times I'\}$	1	0	0	1	2

which follows from the symmetry with respect to the time-reversal operator $\hat{\boldsymbol{\theta}}$. It can lead to an additional decrease in the number of parameters. Finally, when the resultant square matrix intended for determining the energy spectrum of the system is formed from individual blocks of matrix elements, the condition that it be Hermitian should be imposed.

The principal initial perturbation operator defining an ESR spectrum is the Zeeman energy operator $\hat{\mathbf{V}}_H=-\hat{\boldsymbol{\mu}}\mathbf{H}$, where $\hat{\boldsymbol{\mu}}$ and $\mathbf{H}$ are, respectively, the magnetic moment operator and the magnetic field strength. The operator $\hat{\boldsymbol{\mu}}$, which is insensitive to the inversion operation, transforms as a basis of the irreducible representation F_1. Taking this into account, we calculated the matrices $M(\alpha_1\times\alpha_2)$ of the operator $\hat{\mathbf{V}}_H$ between all the pairs of irreducible representations α_1 and α_2 that give nonzero matrix elements according to Table V on the basis of Eqs. (7) and (8) and the matrix elements G_{lm}^{δ} that we obtained (see Sec. 3). The matrices used in this work to construct the spin Hamiltonian are presented in Appendix B.

5. SPIN HAMILTONIAN

Let us take into account the character of the splitting of the atomic terms with a given J in a field of icosahedral symmetry, and let us, accordingly, construct the matrices for each J from blocks of matrices of the perturbation operator. In each of the matrices of dimensionality $2J+1$ obtained we move over to another basis representation: from symmetrized functions to functions of the angular momentum [using formulas which are the inverses of Eqs. (2), (4), and (6)]. We express the matrices obtained in terms of standard functions, i.e., the operators $\hat{\psi}_m^L$ $(m=-L,\ldots,+L)$ (Ref. 20), which are linear combinations of products of the components $\hat{\mathbf{J}}_i$ of the operator $\hat{\mathbf{J}}$ and, like spherical harmonics, comprise a basis of the irreducible representation D_L of the rotation group. The number of cofactors is indicated by the value of L. The maximum value of L for a given J equals $2J$. As a result, we obtain the following expression for the spin Hamiltonian:

$$\hat{\mathbf{W}}=\hat{\mathbf{W}}_c+\hat{\mathbf{W}}_H,\quad \hat{\mathbf{W}}_H=\hat{\mathbf{W}}_H^{(1)}+\hat{\mathbf{W}}_H^{(2)}+\hat{\mathbf{W}}_H^{(3)},\tag{9}$$

where $\hat{\mathbf{W}}_c$ and $\hat{\mathbf{W}}_H$ are, respectively, the interaction energy operators with the crystalline electric field and the external magnetic field:

$$\hat{\mathbf{W}}_c=d(\hat{\psi}_-^{6,5}-\sqrt{11/7}\hat{\psi}_0^6),\quad \hat{\mathbf{W}}_H^{(1)}=g_1(\hat{\mathbf{J}}\mathbf{H}),$$

$$\hat{\mathbf{W}}_H^{(2)}=g_2\{H_z(\hat{\psi}_0^6-\sqrt{7/6}\hat{\psi}_-^{5,5})+\sqrt{5/6}/2[H_x(\hat{\psi}_-^{5,1}+\sqrt{7/3}\hat{\psi}_+^{5,4})+iH_y(\hat{\psi}_+^{5,1}-\sqrt{7/3}\hat{\psi}_-^{5,4})]\},$$

$$\hat{\mathbf{W}}_H^{(3)}=g_3\{H_z(\hat{\psi}_0^7-2\sqrt{6/77}\hat{\psi}_-^{7,5}+\sqrt{2/7}\,[H_x(\sqrt{39/22}\hat{\psi}_+^{7,6}-\sqrt{3/44}\hat{\psi}_+^{7,4}-\hat{\psi}_-^{7,1})+iH_y(\sqrt{39/22}\hat{\psi}_-^{7,6}+\sqrt{3/44}\hat{\psi}_-^{7,4}-\hat{\psi}_+^{7,1})]\},$$

$$\psi_\pm^{L,m}=\psi_m^L\pm\psi_{-m}^L,m>0.$$

Since L is restricted by the value of J $(L\leqslant 2J)$, the number of terms appearing in (9) depends on J: for $J\leqslant 2$ only the term $\hat{\mathbf{W}}_H^{(1)}$ is nonzero; for $J\leqslant 5/2$ $\hat{\mathbf{W}}_H^{(1)}$ and $\hat{\mathbf{W}}_H^{(2)}$ are nonzero; for $J\leqslant 3$ $\hat{\mathbf{W}}_H^{(1)}$, $\hat{\mathbf{W}}_H^{(2)}$, and $\hat{\mathbf{W}}_c$ are nonzero; and for $J\geqslant 7/2$, all the terms of the spin Hamiltonian (9) are maintained.

The physical meanings of the parameters appearing in (9) are as follows: d is proportional to the energy gap between the levels ε_α in a zero magnetic field; the g_i are linear combinations of the matrix elements $(\hat{\boldsymbol{\mu}}_z)_{ij}$. Thus, we have $d=(\varepsilon_F-\varepsilon_G)/75\sqrt{3}$ and $(\varepsilon_{I'}-\varepsilon_{E_2'})/300\sqrt{3}$, respectively, for $J=3$ and 7/2; $g_1=2m_9$, m_8, $2m_6/3$, $m_4/2$, $2(m_1-10m_2/7)$, $(m_5+\sqrt{6}m_7)/7$, and $(5/6)(-m_1+11m_2/7+(2/5)\sqrt{3/7}m_3)$, respectively, for $J=1/2$, 1, 3/2, 2, 5/2, 3, and 7/2; $g_2=\sqrt{2}m_2/5\sqrt{7}$, $(\sqrt{6}m_5-m_7)/26\sqrt{21}$, and $\sqrt{7}(m_1-9m_2/7+4m_3/5\sqrt{21})/65\sqrt{2}$, respectively, for $J=5/2$, 3, and 7/2; $g_3=\sqrt{11}(m_1-5m_2+2\sqrt{3/7}m_3)/450\sqrt{39}$ for $J=7/2$. The explicit expressions presented for the parameters of the spin Hamiltonian make it possible to perform their numerical calculations in a definite approximation and a specific model of the center.

6. ESR SPECTRUM

We find the eigenvalues of the operator (9) in the approximation of strong magnetic fields. We select the operator $\hat{\mathbf{W}}_H^{(1)}$ as the operator of the zeroth approximation and the remaining terms as a perturbation. In first-order theory we obtain

$$E_M=g_1MH+[n_H(J,M)g_2H-\sqrt{11/7}dn_c(J,M)]\Phi(\theta,\varphi),\tag{10}$$

where

$$\Phi(\theta,\varphi)=(231x^6-315x^4+105x^2-5+42x\sin^5\theta\sin 5\varphi)/16,$$

n_H and n_c are numerical coefficients, which are equal to the diagonal matrix elements of the operators $\hat{\psi}_0^5$ and $\hat{\psi}_0^6$, respectively, i.e.,

$$n_H=\langle\hat{\psi}_0^5\rangle_{M,M}=M\{63M^4+35M^2(3-2A)+15A^2-50A+12\}/6\sqrt{14},$$

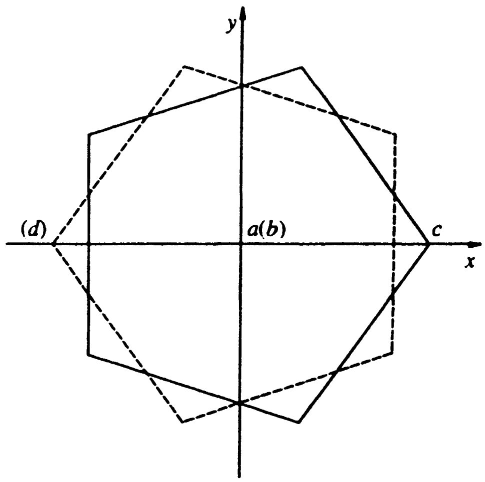

FIG. 2. Projection of an icosahedron onto the xy plane that passes through its center and is perpendicular to the z axis, which is directed toward the reader. The solid line and the letters not in brackets indicate the projection of the part of the figure located above the plane, and the dashed line and the letters in brackets indicate the projection of the part of the figure located below the plane. The $b\rightarrow a$ axis, which coincides with the z axis, is the fifth-order axis for element No. 2; the $d\rightarrow c$ axis, which passes through vertices d and c, is the fifth-order axis for element No. 5.

$$n_c=\langle\hat{\psi}_0^6\rangle_{M,M}=\sqrt{\frac{21}{11}}\{11M^6+5M^4(7-3A)+M^2(5A^2-25A+14)-5A\cdot B/21\}/4,$$

$A=J(J+1)$, $B=A^2-8A+12$, $x=\cos\theta$, θ and φ are the polar and azimuthal angles of the vector $\mathbf{H}$, and the choice of the coordinate system is shown in Fig. 2. To simplify the analysis of the spectrum, the term from $\hat{\mathbf{W}}_H^{(3)}$ containing the highest power $\hat{J}_i(L=7)$ was not included in Eq. (10); in decreasing order of magnitude, it is the next term after $\hat{W}_H^{(2)}$ which also contains the magnetic field.

On the basis of (10), for the resonant value of the magnetic field H_r of the $M\rightarrow M-1$ transition we obtain

$$H_r=H_r^{(0)}+30\Phi(\theta,\varphi)[\sqrt{3}dn_c'(J,M)-g_2H_r^{(0)}n_H'(J,M)/\sqrt{14}]/g_1, \quad (11)$$

where

$$H_r^{(0)}=h\nu/g_1,\quad n_c'(J,M)=\sqrt{11/21}[n_c(J,M)-n_c(J,M-1)]/30,$$

$$n_H'(J,M)=\sqrt{14}\,[n_H(J,M)-n_H(J,M-1)]/30.$$

The explicit expressions for n_c' and n_H' have the form

$$n_H'(J,M)=7[3M^4-6M^3+(9-2A)M^2-2M(3-A)+B/7]/12,$$

$$n_c'(J,M)=(M-1/2)[11M^4-22M^3+(49-10A)M^2+2M(5A-19)+5B/3]/20.$$

It is seen from (11) that in the absence of a perturbation ($d=g_2=0$) all the lines in the spectrum coincide and are

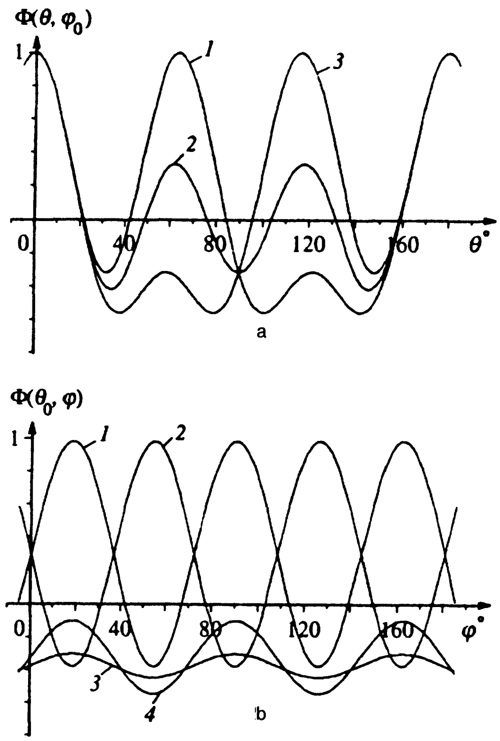

FIG. 3. Angular dependence of the ESR spectrum of paramagnetic centers of icosahedral symmetry: a — $\Phi(\theta,\varphi_0)$, $\varphi_0=18°$ (*1*), 0° (*2*), 54° (*3*); b — $\Phi(\theta_0,\varphi)$, $\theta_0=66°$ (*1*), 114° (*2*), 30° (*3*), 40° (*4*).

found at $H_r^{(0)}$ regardless of the orientation of the field $\mathbf{H}$. When $d\neq 0$ or $g_2\neq 0$ holds this line can split into $2J$ lines, each of which has an angular dependence $\Phi(\theta,\varphi)$. A characteristic feature of the latter is repetition of the spectrum every 72° as the magnetic field revolves about the z axis (at an arbitrary value of θ which does not cause the multiplier $\cos\theta\sin^5\theta$ to vanish). As the angle θ varies (at an arbitrary value of φ), the spectrum repeats every 180°. Figure 3 presents the expected angular dependence with respect to φ and θ for several fixed values of one of the angles that are characteristic of Y symmetry.

As a specific example, let us consider the most common case of impurity ions with $J=7/2$. This case corresponds, for example, to the frequently encountered paramagnetic centers based on Eu^{2+} and Gd^{3+} ions.[4)] Table VI presents the values of $n'(J,M)$ for it. The ESR spectrum calculated on the basis of (11) for $d\neq 0$ and $g_2=0$ is presented in Fig. 4a. It is seen

TABLE VI. Values of the coefficients $n'(J,M)$ for $J=7/2$ and squares of the matrix elements of the $M\rightarrow M-1$ transition.

M	$n_c'(7/2,M)$	$n_H'(7/2,M)$	$4(J_x)^2_{M,M-1}$
7/2	3	15	7
5/2	−7	−20	12
3/2	7	1	15
1/2	0	15	16
−1/2	−7	1	15
−3/2	7	−20	12
−5/2	−3	15	7

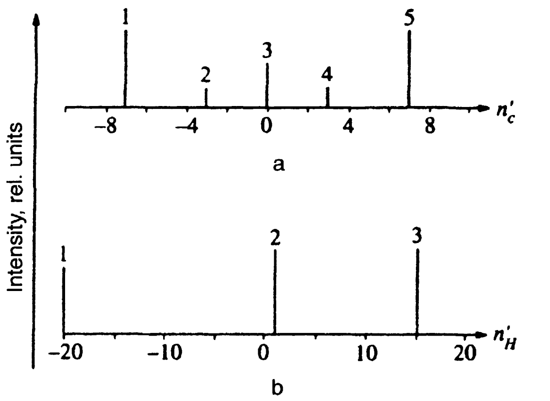

FIG. 4. ESR spectrum of a center with $J=7/2$ specified by the terms in the spin Hamiltonian with the constants d and g_1. The relative intensities were plotted with consideration of each transition (indicated below) and the square of its matrix element: a — $d \neq 0$, $g_2=0$; *1* — $5/2 \leftrightarrow 3/2$ and $-1/2 \leftrightarrow -3/2$; *2* – $-5/2 \leftrightarrow -7/2$; *3* — $1/2 \leftrightarrow -1/2$; *4* — $7/2 \leftrightarrow 5/2$; *5* — $3/2 \leftrightarrow 1/2$ and $-3/2 \leftrightarrow -5/2$; b — $d=0$, $g_2 \neq 0$; *1* — $5/2 \leftrightarrow 3/2$ and $-3/2 \leftrightarrow -5/2$; *2* — $3/2 \leftrightarrow 1/2$ and $-1/2 \leftrightarrow -3/2$; *3* — $7/2 \leftrightarrow 5/2$, $1/2 \leftrightarrow -1/2$, and $-5/2 \leftrightarrow -7/2$.

that the operator $\hat{\mathbf{W}}_c$ causes incomplete splitting of the original line ($d=0$, $g_2=0$) into five lines. When $d=0$ and $g_2 \neq 0$ hold (Fig. 4b), the lines with $H_r=H_r^{(0)}$ split into three lines. Thus, different interaction mechanisms produce different ESR spectra, making it possible to identify the different terms of the spin Hamiltonian and to determine their parameters from the spectrum.

7. DISCUSSION OF RESULTS; CONCLUSIONS

1. Let us consider the results of this paper from a somewhat different standpoint, omitting the formalism of the perturbation matrix method. The spin Hamiltonian for a definite value of J can also be obtained, if we preliminarily find $(2J+1)^2$ linearly independent operators which transform according to the irreducible representation D_L of the rotation group, the values of L being specified by the expressions

$$D_J^* \times D_J = \sum_{L=0}^{2J} D_L \text{ and } \sum_{L=0}^{2J} (2L+1) = (2J+1)^2. \quad (12)$$

Each group of operators with a given L includes $2L+1$ operators consisting of products of the L operators $\hat{\mathbf{J}}_i$. Then the virtual expansion of D_L in the irreducible representations of the point group should be performed. The sets of operators needed to derive an expression which is invariant toward all the transformations of the point group are obtained as a result.

The crystal-field operator should be invariant under any group of the icosahedron (the irreducible representation A). Its existence requires that the D_L representation contain the irreducible representation A at least once. According to Table IV, the unit representation is contained in the D_0 and D_6 representations. The former case is trivial and corresponds to the isotropic operator $\hat{\mathbf{J}}^2$, which causes identical displacement of all the levels. The latter case can arise only for $J \geqslant 3$, since, according to (12), $L_{\max}=2J$. This means that the first nonvanishing crystal-field operators are terms containing products of the operators $\hat{\mathbf{J}}_i$ in the sixth power. This result correlates with the data in Table IV, from which it also follows that the splitting of the terms in a field of icosahedral symmetry begins only from $J=3$.

Similarly, the nonzero terms of the Zeeman energy operator will contain the first and fifth powers of the operators $\hat{\mathbf{J}}_i$, since the irreducible representation F_1, according to which the operator $\hat{\mathbf{J}}$ transforms, is contained, according to Table IV, only in the D_1 and D_5 representations. The former case is possible for $J \geqslant 1/2$, and the latter case is possible for $J \geqslant 5/2$. This result correlates with the data in Table V, according to which the irreducible representation F_1 is contained once in all the direct products, except $I' \times I'$, indicating that the Zeeman energy operator is represented by only one term of the form $\hat{\mathbf{J}}\mathbf{H}$ when $J \leqslant 2$. According to Table V, when $J=5/2$, the irreducible representation F_1 is contained twice in $I' \times I'$, pointing out the presence of an additional anisotropic term $\sim H_i \hat{\mathbf{J}}_k^5$.

2. Let us compare the results obtained in this work with the known data for paramagnetic centers of other symmetries. The highest previously considered symmetry is cubic.[23] In this sense it is closer to icosahedral symmetry and is therefore of primary interest. In the case of icosahedral symmetry, the crystal-field splitting of the terms begins at higher values of J, i.e., at $J=3$ and 7/2, and if we take into account that Gd^{3+} and Eu^{2+} ions in the S state are the most common and easily observed ions, it begins in effect at $J=7/2$. This means that up to these values of J a crystal field of icosahedral symmetry does not directly manifest itself in the zero-field resonance or in the angular dependence of the ESR lines and the spectrum is isotropic. In the case of cubic symmetry the crystal-field splitting of the atomic terms begins at $J=2$ and 5/2. Thus, in the case of icosahedral symmetry the first nonvanishing crystal-field operators are terms containing $\hat{\mathbf{J}}_i$ raised to the sixth power (in the general case six cofactors of the different projections $\hat{\mathbf{J}}_k$), while in cubic symmetry these terms begin at the fourth power. In the case of icosahedral symmetry the first nonvanishing anisotropic Zeeman energy operator begins at the fifth power ($J \geqslant 5/2$), and in the case of cubic symmetry it begins at the third power ($J \geqslant 3/2$). Stated differently, probes of higher spin are needed for a direct or indirect manifestation of the crystal field in the case of icosahedral symmetry than in the case of cubic symmetry.

However, in the microscopic theory the parameters of the spin Hamiltonian associated with higher powers of the $\hat{\mathbf{J}}_i$ correspond to higher orders of perturbation theory and are, therefore, usually smaller in magnitude than the parameters associated with lower powers of the $\hat{\mathbf{J}}_i$. Thus, they are manifested less strongly in the ESR spectra. Nevertheless, these parameters have been measured fairly reliably in the case of other symmetries, such as, for example, cubic symmetry,[23] even against a background of nonzero terms with lower powers of the $\hat{\mathbf{J}}_i$ ($\sim \hat{\mathbf{J}}_i^3$ and $\hat{\mathbf{J}}_i^4$). As we have already mentioned, in the case of icosahedral symmetry, the latter terms are absent. This facilitates measurement of the parameters for the higher powers ($\sim \hat{\mathbf{J}}_i^5$ and $\hat{\mathbf{J}}_i^6$) in a pure form and is thus a favorable factor for icosahedral symmetry.

The differences in the spin Hamiltonians cause differences in the ESR spectra. For example, in contrast to the case of icosahedral symmetry, complete splitting of the lines in the spectrum appears in the case of cubic symmetry. The angular dependence of the spectral lines also has a different character. In the case of cubic symmetry it has the form

$$\Phi(\theta,\varphi)=1-5\ \sin^2\theta(\cos^2\theta+\sin^2\ \theta\ \sin^2 2\varphi/4),$$

which differs significantly from the expression following Eq. (10).

Other symmetries lower than cubic can be examined in a similar manner, and significant differences between their ESR spectra and the spectra for icosahedral symmetry can be demonstrated. Thus, qualitatively new features not previously observed in ESR spectra appear in the case of icosahedral symmetry.

3. Although the two principal terms of the spin Hamiltonian ($\hat{\mathbf{W}}_c$ and $\hat{\mathbf{W}}_H$) that determine the ESR spectra were considered in detail in this work, the results obtained can be automatically extended to the hyperfine, quadrupole, and nuclear Zeeman interactions, since the transformation properties of the electronic ($\hat{\mathbf{J}}$) and nuclear ($\hat{\mathbf{I}}$) angular momenta, as well as of the vector $\hat{\mathbf{H}}$, are identical. This requires performing only the appropriate replacements, viz., $\hat{\mathbf{J}}\leftrightarrow\hat{\mathbf{I}}$, $\hat{\mathbf{J}}\leftrightarrow\hat{\mathbf{H}}$, and $\hat{\mathbf{I}}\leftrightarrow\hat{\mathbf{H}}$, in the corresponding expressions. For example, the hyperfine interaction operator, which is linear with respect to $\hat{\mathbf{I}}$, is obtained from $\hat{W}_H$ by the simple replacement $\mathbf{H}\rightarrow\hat{\mathbf{I}}$, and the quadrupole interaction operator for $I \geqslant 3$ is obtained from $\hat{\mathbf{W}}_c$ by replacing $\hat{\psi}^6_m\ \hat{\mathbf{J}}$ by $\hat{\mathbf{I}}$. Therefore, the results obtained in this work are transferrable to the description of both nuclear magnetic resonance spectra and nuclear quadrupole resonance spectra, if the nucleus is surrounded by a crystal field of icosahedral symmetry.

4. Although there are already a fairly large number of reports on the introduction of atoms of other elements into fullerenes, the data from radio-frequency spectroscopic experiments on such substances are still sparse.[24,25] Impurities of La and Sc in the fullerene C_{82}, which has C_2 local symmetry in each center, have been investigated for the most part. According to the authors of the papers cited, the impurity atoms have a threefold positive charge with a total electronic angular momentum $J=1/2$. A hyperfine structure of eight lines is clearly observed as a result of their interaction with ^{139}La and ^{45}Sc nuclei (the spin of each of these nuclei equals 7/2). It has been shown[26] by other methods independently of these experiments that Gd and Eu atoms exist in the fullerene C_{60} in the Gd^{3+} and Eu^{2+} states, respectively, which are distinguished by a high total angular momentum ($J=7/2$). These data point to the possibility of creating conditions for observing ESR on high-spin ions in fullerenes, particularly in C_{60}.

5. When experiments are performed, two cases should be distinguished. The first is the case of random orientation of the paramagnetic centers, in which fullerenes or other molecules containing impurity ions are in a gaseous phase, a solution, or a powder. In this case the axes of the molecules are distributed randomly in space with respect to the field **H**, and the corresponding averaging of Eq. (11) with respect to the angles θ and φ must be performed preliminarily to describe the ESR spectrum. The second case corresponds to identical orientations of all the paramagnetic centers in space. It is possible in supercooled liquids or crystals like fullerites. In this case the angular dependence of the ESR spectrum considered above is displayed directly. However, being in crystals, the impurity atoms experience not only the influence of the field of icosahedral symmetry of the nearby atoms of, for example, the fullerene, but also, possibly, the weak field of more distant atoms. The latter field can be of a lower symmetry, for example, cubic symmetry.[13] It can introduce corrections to the basic ESR spectrum defined by Eq. (11) in the form of weak splitting or displacement of the lines in the spectrum. In this case, to describe the ESR spectrum additional terms of appropriate symmetry must be introduced into the spin Hamiltonian and treated as a perturbation to the spin Hamiltonian of icosahedral symmetry.

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APPENDIX A. MATRICES OF THE GENERATING ELEMENTS OF THE GROUP OF THE ICOSAHEDRON[5)]

a) Generating element No. 2

Its nonzero elements are located on the principal diagonal. They are listed below in order from left to right (top to bottom):

the irreducible representation A: 1,

the irreducible representation F_1: $c_7^*,\ 1,\ c_7,$

the irreducible representation F_2: $-c_6,\ 1,\ -c_6^*,$

the irreducible representation G: $-c_6^*,\ c_7^*,\ c_7,\ -c_6,$

the irreducible representation H: $-c_6,\ c_7^*,\ 1,\ c_7,\ -c_6^*,$

the irreducible representation E_1': $c_6^*,\ c_6,$

the irreducible representation E_2': $-c_7^*,\ -c_7,$

the irreducible representation G': $-c_7,\ c_6^*,\ c_6,\ -c_7^*,$

the irreducible representation I': $-1,\ -c_7,\ c_6^*,\ c_6,\ -c_7^*,\ -1.$

b) Generating element No. 5

the reducible representation A: (1),

the reducible representation F_1: (complex): $\begin{pmatrix} c_{27}^* & c_{21} & -a_4^- \\ c_{21} & a_2 & -c_{21}^* \\ -a_4^- & -c_{21}^* & c_{27} \end{pmatrix}$,

the reducible representation F_2: $\begin{pmatrix} -c_{28}^* & -c_{20}^* & -a_4^+ \\ -c_{20}^* & -a_2 & c_{20} \\ -a_4^+ & c_{20} & -c_{28} \end{pmatrix}$,

the reducible representation G: $\begin{pmatrix} -c_{17} & -c_1^* & c_2^* & a_2 \\ -c_1^* & -c_{16}^* & -a_2 & c_2 \\ c_2^* & -a_2 & -c_{16} & -c_1 \\ a_2 & c_2 & -c_1 & -c_{17}^* \end{pmatrix}$,

the reducible representation H: $\begin{pmatrix} c_{10}^* & c_{24} & -c_{22}^* & -c_{25} & a_3^- \\ c_{24} & -c_{11}^* & c_{23} & -a_3^+ & c_{25}^* \\ -c_{22}^* & c_{23} & -a_1 & -c_{23}^* & -c_{22} \\ -c_{25} & -a_3^+ & -c_{23}^* & -c_{11} & -c_{24}^* \\ a_3^- & c_{25}^* & -c_{22} & -c_{24}^* & c_{10} \end{pmatrix}$,

the reducible representation E_1': $\begin{pmatrix} c_8^* & b_3^- \\ b_3^- & c_8 \end{pmatrix}$, the reducible representation E_2': $\begin{pmatrix} -c_9 & b_3^+ \\ b_3^+ & -c_9^* \end{pmatrix}$,

the reducible representation G': $\begin{pmatrix} c_{12}^* & c_4 & -c_5^* & -b_1^- \\ c_4 & c_{13}^* & b_1^+ & -c_5 \\ -c_5^* & b_1^+ & c_{13} & -c_4^* \\ -b_1^- & -c_5 & -c_4^* & c_{12} \end{pmatrix}$,

the reducible representation I': $\begin{pmatrix} -b_4^+ & c_{26} & -c_3^* & -c_{19} & c_{13}^* & b_4^- \\ c_{26} & -c_{15}^* & c_{19} & -c_{18}^* & -b_2^+ & c_{13} \\ -c_3^* & c_{19} & -c_{14}^* & b_2^- & -c_{18} & c_{19}^* \\ -c_{19} & -c_{18}^* & b_2^- & -c_{14} & -c_{19}^* & -c_3 \\ c_{13}^* & -b_2^+ & -c_{18} & -c_{19}^* & -c_{15} & -c_{26}^* \\ b_4^- & c_{13} & c_{19}^* & -c_3 & -c_{26}^* & b_4^+ \end{pmatrix}$.

c) Generating element of the irreducible representation F_1 (real):

No. 2 $\begin{pmatrix} a_8 & -a_6 & 0 \\ a_6 & a_8 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, No. 5 $\begin{pmatrix} a_9 & -a_7 & a_4^- \\ a_7 & a_8 & -a_5 \\ a_4^- & a_5 & a_2 \end{pmatrix}$,

where

$$
\begin{array}{lll}
a_1=1/5, & a_6=R^+/2q, & b_1^{\pm}=iN^{\pm}/5,\\
a_2=1/p, & a_7=R^+/2qp, & b_2^{\pm}=iR^{\pm}/5q,\\
a_3^{\pm}=(3\pm p)/10, & a_8=(p-1)/4, & b_3^{\pm}=iR^{\pm}/pq,\\
a_4^{\pm}=(p\pm 1)/2p, & a_9=(3p+1)/4p, & b_4^{\pm}=iU^{\pm}/5pq,\\
a_5=R^+/qp, & &
\end{array}
$$

$$
\begin{array}{ll}
c_{1,2}=a_2/2+iN^{\pm}/2p, & c_{16,17}=a_4^{\pm}/2+b_3^{\mp}/2,\\
c_3=1/qp+iN^+/5q, & c_{18,19}=a_4^{\pm}/q+qb_2^{\mp}/2,\\
c_{4,5}=t/2p+itN^{\pm}/10, & c_{20,21}=a_4^{\pm}/q+qb_3^{\mp}/2,\\
c_{6,7}=(p\pm 1)/4+iR^{\mp}/2q, & c_{22,23}=t(p\pm t)/10q+itR^{\mp}/10,\\
c_{8,9}=(p\pm 1)/4+iR^{\mp}/2pq, & c_{24,25}=a_3^{\pm}+b_2^{\pm},\\
c_{10,11}=(p\pm 1)/20+iU^{\pm}/10q, & c_{26}=(3+p)/4p+b_2^{+}/2,\\
c_{12,13}=a_4^{\pm}/2+pb_4^{\pm}/2, & c_{27,28}=(3\pm p)/4p+b_3^{\mp}/2,\\
c_{14,15}=a_4^{\pm}/2+b_2^{\mp}/2, &
\end{array}
$$

$$
i=\sqrt{-1},\quad p=\sqrt{5},\quad t=\sqrt{3},\quad q=\sqrt{2},\quad R^{\pm}=\sqrt{5\pm p},
$$
$$
N^{\pm}=\sqrt{5\pm 2p},\quad U^{\pm}=\sqrt{25\pm 11p},
$$

and * denotes complex conjugation.

APPENDIX: B. MATRIXES OF THE PERTURBATION OPERATOR $\hat{V}_H$

$$
M(I'\times I')=\begin{pmatrix}
D_1H_z & D_3T^* & 0 & 0 & -D_6T & m_2H_z\\
D_3T & D_2H_z & D_4T^* & 0 & 0 & D_6T\\
0 & D_4T & -m_1H_z & D_5T^* & 0 & 0\\
0 & 0 & D_5T & m_1H_z & -D_4T^* & 0\\
-D_6T^* & 0 & 0 & D_4T & -D_2H_z & D_3T^*\\
m_2H_z & D_6T^* & 0 & 0 & D_3T & -D_1H_z
\end{pmatrix},
$$

$$
M(E_2'\times I')=m_3\begin{pmatrix}
3T^*/2p & 0 & 0 & T/q & -H_z & -T^*/2p\\
-T/2p & H_z & T^*/q & 0 & 0 & -3T/2p
\end{pmatrix},
$$

$$
M(H\times H)=m_4\begin{pmatrix}
-H_z & T^*/2 & 0 & 0 & 0\\
T/2 & -H_z/2 & tqT^*/4 & 0 & 0\\
0 & tqT/4 & 0 & tqT^*/4 & 0\\
0 & 0 & tqT/4 & H_z/2 & T^*/2\\
0 & 0 & 0 & T/2 & H_z
\end{pmatrix},
$$

$$
M(G\times G)=m_5\begin{pmatrix}
-H_z & 0 & -T & 0\\
0 & -H_z & 0 & T\\
-T^* & 0 & H_z & 0\\
0 & T^* & 0 & H_z
\end{pmatrix},
$$

$$
M(G'\times G')=m_6\begin{pmatrix}
-H_z & T^*/t & 0 & 0\\
T/t & -H_z/3 & 2T^*/3 & 0\\
0 & 2T/3 & H_z/3 & T^*/t\\
0 & 0 & T/t & H_z
\end{pmatrix},
$$

$$M(F_2\times G)=m_7\begin{pmatrix} T/2 & T^*/2 & 0 & -H_z \\ 0 & T/q & T^*/q & 0 \\ H_z & 0 & -T/2 & -T^*/2 \end{pmatrix},$$

$$M(F_1\times F_1)=m_8\begin{pmatrix} -H_z & T^*/q & 0 \\ T/q & 0 & T^*/q \\ 0 & T/q & H_z \end{pmatrix},$$

$$M(E_1'\times E_1')=m_9\begin{pmatrix} -H_z & T^* \\ T & H_z \end{pmatrix},$$

where

$$D_1=-5m_1+7m_2,\quad D_2=-3m_1+5m_2,$$

$$D_3=p\langle m_1-3m_2/2),$$

$$D_4=q(2m_1-5m_2/2),\quad D_5=3m_1-5m_2,$$

$$T=H_z+iH_y,\quad m_1=-(\hat{\mu}_z)_{44},\quad m_2=-(\hat{\mu}_z)_{16},$$

$$m_3=-(\hat{\mu}_z)_{22},\quad m_4=-(\hat{\mu}_z)_{55},$$

$$m_5=-(\hat{\mu}_z)_{44},\quad m_6=-(\hat{\mu}_z)_{44},\quad m_7=-(\hat{\mu}_z)_{31},$$

$$m_8=-(\hat{\mu}_z)_{33},\quad m_9=-(\hat{\mu}_z)_{22},$$

$$(\hat{\mu}_z)_{ik}=\int \psi_i^*\hat{\mu}_z\psi_k d\tau,$$

and ψ_l is the lth basis function of the respective irreducible representation. The common factor m_i before the entire matrix means that all of its matrix elements must be multiplied by m_i.

[1)]Here and in the following the first (second) subscript corresponds to the upper (lower) sign.

[2)]The matrices of the elements I and Q for all the irreducible representations differ from the matrix of the unit element only with respect to the common sign.

[3)]These results are fairly lengthy, therefore, we shall not present them in this paper.

[4)]The treatment also applies qualitatively to such frequently encountered ions with $J=5/2$ as Mn^{2+} and Fe^{3+}, since it is sufficient to set $d=0$ for them in (11).

[5)]The following notation is introduced for convenience: a denotes only real matrix elements, b denotes only imaginary elements, and c denotes complex matrix element.

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