was either in close association with the compensation resulting in the removal of the inversion center of the impurity site or that the impurity cation is essentially in a cubic site beyond any significant influence of the distant compensation. In view of the present investigation, some of the observations unexplainable in terms of the dissociation-association hypothesis can now be reexamined. For example, the glow curve observed[24] when Dy^{2+} ions in CaF_2 produced by γ radiation are oxidized to the trivalent state by thermal excitation is characterized by several prominent peaks. If only the nonlocal "cubic" sites are reduced, only one glow peak can be expected.[24] In view of our present discussion, the multipeaked glow curve of the $Dy^{2+} \rightarrow Dy^{3+}+e^-$ process in CaF_2 can be readily accounted for in terms of the Maxwell-Boltzmann distribution of site symmetries depicted in Sec. III.

Finally, a comment should be made on the effect of the relative sizes of the trivalent cation and the host ion which it replaces. In Table I, we detect a trend in which the tetragonal site and the trigonal site reverse in prominence as the host ion increases from Ca^{2+} to Ba^{2+}. A qualitative argument may be made on the basis of the collapse of the 8 nearest-neighbor fluoride ions about the trivalent cation as it replaces the increasingly larger divalent cation. This will have the net effect of increasing the shielding between the trivalent cation and the (1,0,0) F^- interstitial thus reducing ϵ_1. ϵ_2 on the other hand would increase as the F^- interstitial at (1,1,1) moves closer to the trivalent cation because of the inward displacement of the nearest neighbor fluoride ions, thus accounting for the observed changes in the relative abundance of the first two n.n. sites. A more quantitative approach is now being attempted through an extension of the lattice theory calculations of Franklin[25] to a calculation of ϵ_1 and ϵ_2 for the various (alkaline-earth fluoride): M^{3+} systems.

[25] A. D. Franklin, J. Phys. Chem. Solids **29**, 823 (1968).

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Effective Hamiltonian for Non-Kramers Doublets

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A method of irreducible tensor operators is described for constructing effective Hamiltonians for non-Kramers doublets. It is pointed out that this method is superior in several points to other methods. The exact effective Hamiltonians for all the non-Kramers doublets in 32 point groups are tabulated. These Hamiltonians involve the effects of magnetic and electric fields up to the second order as well as those of the hyperfine interactions. The interaction of nuclear spins with a magnetic field is taken into account to the first order. Finally, selection rules for paraelectric and paramagnetic resonances are derived by use of the effective Hamiltonians for all the non-Kramers doublets.

I. INTRODUCTION

THE doubly degenerate (not accidentally degenerate) levels of molecular systems with an even number of electrons are called non-Kramers doublets. They belong to the doubly degenerate irreducible representations of the point groups (the single groups). The purpose of the present paper is to describe a clear method of constructing an effective Hamiltonian for non-Kramers doublets and to list all the effective Hamiltonians which may be used in the analysis of electron paramagnetic resonance and optical experiments for non-Kramers doublets. In our treatment, the Jahn-Teller effect will be entirely ignored. This effect can be operative in non-Kramers doublets, but it would not be so important in the $4f$-electron systems on which experimental work has been concentrated.

So far, several studies have been done on the spin Hamiltonian for non-Kramers doublets. Bleany and Scovil[1] first introduced a spin Hamiltonian

$$\mathcal{H}=g_{\parallel}\beta H_z S_z+A_{\parallel}I_z S_z+\Delta_x S_x+\Delta_y S_y, \qquad (1)$$

* Work partly supported by the Broadcasting Science Research Laboratories of Nippon Hôsô Kyôkai.

[1] B. Bleaney and H. E. D. Scovil, Phil. Mag. **43**, 999 (1952).

with fictitious spin $S=\frac{1}{2}$ to analyze the paramagnetic resonance spectra of the lowest non-Kramers doublet of Pr^{3+} ion in a trigonal field. In this Hamiltonian, physical meanings of the last two terms $\Delta_x S_x$ and $\Delta_y S_y$ are unclear, although parameters Δ_x and Δ_y were taken to have, not unique values, but a distribution of values representing slightly different environments for different praseodymium ions. This spin Hamiltonian is different from the usual spin Hamiltonian in that the spin Hamiltonian in Eq. (1) is not invariant with respect to the time-reversal and spatial-symmetry operations which leave the real Hamiltonian invariant. These peculiar points were examined in detail by Griffith.[2]

As emphasized later, difficulties in constructing the spin Hamiltonian with fictitious spin $S=\frac{1}{2}$ for non-Kramers doublets lie in the fact that the basis functions of non-Kramers doublets do not have the same transformation properties as the spin functions of $S=\frac{1}{2}$ with respect to symmetry operations in space and time. It is, however, possible to find two spin functions of $S>\frac{1}{2}$ which transform in the same way as the basis functions of non-Kramers doublets.[3] Recently, Mueller[4] proposed to use the spin functions of $S=1$, in which two functions with $M_s=\pm 1$ transform as the basis functions of a non-Kramers doublet. He derived the effective-spin Hamiltonian for the C_n, D_n, and S_n symmetry groups, which involved the first- and second-order terms of magnetic and electric fields. The Hamiltonian he derived corresponding to Eq. (1) is as follows:

$$\mathcal{H}=g_{\parallel}\beta H_z S_z+D(S_z^2-1)+A_{\parallel}I_z S_z +\Delta_x(S_x^2-S_y^2)+\Delta_y(S_xS_y+S_yS_x), \quad (2)$$

in which parameter D goes to infinity after the eigenvalues of Eq. (2) are obtained. The second term in Eq. (2) is introduced to eliminate effects of the $M_s=0$ state. In this Hamiltonian, he omitted the terms $(S_xS_z+S_zS_x)$ and $(S_yS_z+S_zS_y)$ which connect the $M_s=\pm 1$ states with the $M_s=0$, even though these terms are allowed by symmetry considerations. Mueller's method excluded the aforementioned difficulties associated with the $S=\frac{1}{2}$ formalism: His effective-spin Hamiltonian is invariant with respect to the symmetry operations in space and time to which the real Hamiltonian is invariant.

The disadvantage in Mueller's method is that one must introduce extra terms, such as the second term in Eq. (2), in the Hamiltonian to eliminate unnecessary effects of the $M_s=0$ state. This disadvantage is more pronounced when one treats the effective-spin Hamiltonian for non-Kramers doublets in the cubic group. Since the basis functions of these doublets transform like two spin functions of $S=2$, one must use, instead of the $S=1$, the $S=2$ formalism to construct the effective-spin Hamiltonian.

Such a disadvantage may be removed if one uses irreducible tensor operators in place of spin operators. The use of irreducible tensor operators for constructing an effective Hamiltonian was first made by Tanabe and Kamimura,[5] and it was applied to the analysis of optical absorption lines in ruby by Sugano and Tanabe.[6] This kind of effective Hamiltonian is particularly useful for treating the states with orbital degeneracy non-Kramers doublets. In Sec. II of this paper, we shall describe the theoretical background for our method of an effective Hamiltonian and point out some merits of of this method. In Sec. III, we shall construct the effective Hamiltonians for all non-Kramers doublets by the use of irreducible tensor operators for the O_h, D_{6h}, and D_{4h} point groups. These Hamiltonians have linear and quadratic terms in the electric and magnetic fields. We shall also construct the effective Hamiltonians for the hyperfine interactions in a simple way. In Sec. IV, we shall at first give some remarks on the effective Hamiltonian derived in Sec. III. Then, the selection rules for the magnetic- and electric-dipole transitions between the split levels of non-Kramers doublets will be tabulated. Finally, the results of our method will be compared with those of others.

II. THEORETICAL BACKGROUND

We shall consider a degenerate state Γ of a system whose symmetry belongs to group G. Γ may be an irreducible representation of group G. We denote a set of wave functions of state Γ as $\varphi_1, \varphi_2, \cdots, \varphi_q$, which are the bases of irreducible representation Γ. If perturbations such as an external magnetic field, an electric field, and a distortion are applied to the system, state Γ is admixed with other states Γ' as the perturbing Hamiltonian has nonvanishing matrix elements between states Γ and Γ'. However, in principle, these matrix elements can be brought to zero by applying a unitary transformation to a set of all the wave functions of the unperturbed system. Although it is almost impossible to obtain the exact form of the unitary transformation, we assume that the matrix of the real Hamiltonian is now brought to the following form:

	ψ_1	ψ_2	$\cdots$	ψ_q		
ψ_1	×	×	$\cdots$	×		
ψ_2	×	×	$\cdots$			
$\vdots$	$\vdots$	$\vdots$		$\vdots$	0	
ψ_q	×		$\cdots$	×		
					×	×$\cdots$
			0		×	$\cdots$
					$\vdots$	

(3)

In this matrix, a subspace spanned by $\psi_1, \psi_2, \cdots, \psi_q$

[2] J. S. Griffith, Phys. Rev. **132**, 316 (1963).

[3] W. Hauser, in *Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. 1, p. 297.

[4] K. A. Mueller, Phys. Rev. **171**, 350 (1968).

[5] Y. Tanabe and H. Kamimura, J. Phys. Soc. Japan **13**, 394 (1958).

[6] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

corresponds to state Γ in the unperturbed system. The matrix in this subspace will be called the Γ small matrix.

For simplicity, let us consider the case in which the perturbation is only a distortion which changes the symmetry of the unperturbed system belonging to group G into G'. Denoting symmetry operations in G' together with the operation of time reversal as T', we can show that the transformation properties of φ_i and ψ_i for operation T' are the same:

$$T'\varphi_i=\sum_{j=1}^{q}\varphi_j A_{ji}(T'),$$
$$T'\psi_i=\sum_{j=1}^{q}\psi_j A_{ji}(T'). \tag{4}$$

Then, one can show that the Γ small matrix has the following properties: (I) It is Hermitian. Therefore, it can be expressed by using q^2 real parameters. (II) Its elements are correlated by the relation

$$\begin{aligned}\mathcal{H}_{ij}&=\sum_{\sigma}\int d\tau\psi_i^*\mathcal{H}\psi_j\\&=\sum_{\sigma}\int d\tau(T'\psi_i)^*T'\mathcal{H}T'^{-1}T'\psi_j\\&=\sum_{\sigma}\int d\tau(T'\psi_i)^*\mathcal{H}T'\psi_j\\&=\sum_{\mu\nu}\mathcal{H}_{\mu\nu}A_{\mu i}^*(T')A_{\nu j}(T').\end{aligned} \tag{5}$$

In Eq. (5), $\sum_\sigma$ is the summation over the spin coordinates and $\int d\tau$ is the integration over the space coordinates of electrons. In deriving (5), we have used Eq. (4) and the relation $T'\mathcal{H}T'^{-1}=\mathcal{H}$, in which $\mathcal{H}$ is the real Hamiltonian involving the perturbation.

In the effective Hamiltonian method, one constructs an operator $\mathcal{H}_{\text{eff}}$, called the effective Hamiltonian, whose matrix with a given set of bases $\tilde{\varphi}_i(i=1, 2,\cdots, q)$ has the properties (I) and (II) of the Γ small matrix. Then, the eigenvalues of matrix of $\mathcal{H}_{\text{eff}}$ have to give, by assuming appropriate values for the parameters left undetermined, the exact splitting and shift of the energy level of the Γ state with the distortion. In this case, one should assume that the energy separations of the Γ state from other states are larger than the magnitude of the splitting and shift so that the manifold of the split components of the Γ state is well separated from those of other states Γ'.

In constructing $\mathcal{H}_{\text{eff}}$, we use irreducible tensor operators $\mathbf{X}(\Gamma_0)$ whose component $X_{\gamma_0}(\Gamma_0)$ transforms like the γ_0 base of irreducible representation Γ_0 of group G;

$$RX_{\gamma_0}(\Gamma_0)=\sum_{\gamma_0'}X_{\gamma_0'}(\Gamma_0)D_{\gamma_0'\gamma_0}^{(\Gamma_0)}(R), \tag{6}$$

where R is a symmetry operation in G and matrix $\mathbf{D}^{(\Gamma_0)}(R)$ is the matrix representation of Γ_0 for R. We choose, as a set of bases for $\mathcal{H}_{\text{eff}}$, functions $\tilde{\varphi}_i$'s which transform like wave functions φ_i's $(i=1, 2,\cdots, q)$ of state Γ for T representing R and the time-reversal operations. Then, it is evident that for T'

$$T'\tilde{\varphi}_i=\sum_{j=1}^{q}\tilde{\varphi}_j A_{ji}(T'). \tag{7}$$

Since $\tilde{\varphi}_i$'s are the bases of irreducible representation Γ, the matrix of $X_{\gamma_0}(\Gamma_0)$ with bases $\tilde{\varphi}_i$ can be calculated by the use of Clebsch-Gordan coefficients $\langle\Gamma\gamma|\Gamma'\gamma'\Gamma_0\gamma_0\rangle$. It can be shown that the matrices of $X_{\gamma_0}(\Gamma_0)$ for different $\Gamma_0\gamma_0$ are linearly independent of each other, i.e., the matrix of $X_{\gamma_0}(\Gamma_0)$ cannot be expressed by a linear combination of the matrices for other $\Gamma_0\gamma_0$.

Now, we construct operator $\mathcal{H}_{\text{eff}}'$ as follows:

$$\mathcal{H}_{\text{eff}}'=\sum_{\Gamma_0,\gamma_0(\Gamma\times\Gamma=\Sigma\Gamma_0)}C_{\Gamma_0\gamma_0}X_{\gamma_0}(\Gamma_0). \tag{8}$$

Since the matrix of $\mathcal{H}_{\text{eff}}'$ with bases $\tilde{\varphi}_i$ involves q^2 independent matrices, it can reproduce any Hermitian matrix of dimension q. The number of parameters q^2 may be reduced by imposing the condition that the matrix elements of $\mathcal{H}_{\text{eff}}'$ should also satisfy the relation in (5). Because of relation (7), it is evident that this condition is satisfied only if

$$T'\mathcal{H}_{\text{eff}}'T'^{-1}=\mathcal{H}_{\text{eff}}'. \tag{9}$$

Operator $\mathcal{H}_{\text{eff}}'$ satisfying (9) is the effective Hamiltonian we want to obtain.

When the perturbations involve external magnetic and electric fields $\mathbf{H}$ and $\mathbf{E}$ in addition to the distortion, one has to add to the real Hamiltonian of the distorted system the Zeeman term $\mathcal{H}_z$ and the Stark term $\mathcal{H}_s$ which are given as follows:

$$\mathcal{H}_z=\beta\mathbf{H}\cdot\sum_i(\mathbf{l}_i+2\mathbf{s}_i),$$
$$\mathcal{H}_s=e\mathbf{E}\cdot\sum_i\mathbf{r}_i, \tag{10}$$

in which $\beta=e\hbar/2mc$. Even in this case, the matrix of the real Hamiltonian can be brought to the form given in (3) and the Γ small matrix is Hermitian. Therefore, it can be reproduced by the matrix of $\mathcal{H}_{\text{eff}}'$ with bases $\tilde{\varphi}_i$. However, in this case, coefficients $C_{\Gamma_0\gamma_0}$ are given as functions of $\mathbf{H}$ and $\mathbf{E}$.

So far, symmetry operations in space and time have been considered to act on electron systems. However, we can define symmetry operations acting on both the electron system and the sources of external magnetic and electric fields. For these newly defined operations, $\mathbf{H}$ and $\mathbf{E}$ transform like $\mathbf{l}$ and $\mathbf{r}$, respectively: $\mathbf{H}$ changes its sign for time reversal as $\mathbf{l}$ does. Then, the real Hamiltonian of the distorted system involving $\mathcal{H}_z$ and $\mathcal{H}_s$ is invariant with respect to operation $\bar{T}'$, which is obtained from T' by allowing it to act on the sources of the magnetic and electric fields. Relation (5) still holds for the matrix elements of the real Hamiltonian.

Therefore, $\mathcal{H}_{\text{eff}}$ in this case is obtained by imposing the condition that $\mathcal{H}_{\text{eff}}'$ is invariant with respect to operation $\bar{T}'$. In actual problems, we expand $C_{\Gamma_0\gamma_0}$ in the power series of $\mathbf{H}$ and $\mathbf{E}$ and retain only the terms of small powers.

Our method of effective Hamiltonians has the following merits: (1) Since $\tilde{\varphi}_i$'s transform in the same way as the real wave functions ψ_i, one can discuss selection rules for the optical transitions between states Γ and $\Gamma'(\Gamma\neq\Gamma')$ by using the eigenvectors of the effective Hamiltonian. (2) The physical origin of each term in the effective Hamiltonian may be understood easily. This enables us to estimate the order of magnitudes of undetermined parameters.

III. DERIVATION OF EFFECTIVE HAMILTONIAN

As mentioned in Sec. II, the wave functions of the non-Kramers doublets transform as the basis functions of the doubly degenerate representations of the point groups (the single groups). There are 24 point groups which have the doubly degenerate representations. We list these groups in Table I. The notation used in the present paper is the same as those of Koster, Dimmock, Wheeler, and Statz.[7] In Table I, we divide these 24 groups into three series so as to fulfill the following conditions: First, the symmetry groups in each series are obtained from the highest symmetry group by the reduction of the symmetry. Second, in one series, the degeneracy of the doublets of the highest symmetry group is not removed by lowering the symmetry from the highest to the lowest. Thus, we have only three series; the cubic, the hexagonal, and the tetragonal series, the highest symmetry groups of which are O_h, D_{6h}, and D_{4h}, respectively. The advantage of dividing the symmetry groups into three is that we can use just the tensor operators of the highest symmetry group to derive all the effective Hamiltonians in each series. They are considered to be the effective Hamiltonians for the state of the highest symmetry under appropriate distortions.

In this section, the method described in Sec. II will be employed to obtain the effective Hamiltonians for all the non-Kramers doublets. As one of the examples, we first consider the system of the D_{6h} symmetry. As shown in Table I, there are four kinds of non-Kramers doublets in this system. However, as is easily seen, one can use the same effective Hamiltonian for these four states. Therefore, we confine ourselves to the Γ_5^+ doublets. Considering the relation $\Gamma_5^+\times\Gamma_5^+=\Gamma_1^+\dotplus\Gamma_2^+\dotplus\Gamma_6^+$, one obtains $\mathcal{H}_{\text{eff}}'$ as follows:

$$\mathcal{H}_{\text{eff}}'=a(\mathbf{H},\mathbf{E})V(\Gamma_1^+)+b(\mathbf{H},\mathbf{E})T(\Gamma_2^+)+c(\mathbf{H},\mathbf{E})V_x(\Gamma_6^+)+d(\mathbf{H},\mathbf{E})V_y(\Gamma_6^+), \quad (11)$$

in which $\mathbf{V}(\Gamma)$ and $\mathbf{T}(\Gamma)$ are real and purely imaginary irreducible tensor operators, respectively: In general, $\mathbf{X}(\Gamma)$ may be expressed as the sum of $\mathbf{V}(\Gamma)$ and $\mathbf{T}(\Gamma)$, and in (11) one has used the fact[5,8] that

$$\langle\Gamma\|\mathbf{T}(\Gamma_0)\|\Gamma\rangle=0 \quad \text{for} \quad \Gamma_0=\Gamma_1^+,\Gamma_6^+,$$
$$\langle\Gamma\|\mathbf{V}(\Gamma_0)\|\Gamma\rangle=0 \quad \text{for} \quad \Gamma_0=\Gamma_2^+. \quad (12)$$

The reduced matrix elements of these tensor operators with bases $\tilde{\varphi}(\Gamma_5^+,+)$ and $\tilde{\varphi}(\Gamma_5^+,-)$ may be chosen as

$$\langle\Gamma_5^+\|T(\Gamma_2^+)\|\Gamma_5^+\rangle=-\sqrt{2}i,$$
$$\langle\Gamma_5^+\|V(\Gamma_6^+)\|\Gamma_5^+\rangle=2, \quad (13)$$

so that the matrices of the tensor operators are given by

$$T(\Gamma_2^+)=\begin{array}{c}\begin{matrix}+ & -\end{matrix}\\ \begin{bmatrix}1 & 0\\ 0 & -1\end{bmatrix}\end{array}, \quad V_x(\Gamma_6^+)=\begin{array}{c}\begin{matrix}+ & -\end{matrix}\\ \begin{bmatrix}0 & -i\\ i & 0\end{bmatrix}\end{array},$$

$$V_y(\Gamma_6^+)=\begin{array}{c}\begin{matrix}+ & -\end{matrix}\\ \begin{bmatrix}0 & 1\\ 1 & 0\end{bmatrix}\end{array}. \quad (14)$$

We expand coefficients $a(\mathbf{H},\mathbf{E})$, $b(\mathbf{H},\mathbf{E})$, $c(\mathbf{H},\mathbf{E})$, and $d(\mathbf{H},\mathbf{E})$ in powers of $\mathbf{H}$ and $\mathbf{E}$, and impose the condition that $\mathcal{H}_{\text{eff}}'$ should be invariant to the symmetry operations in group D_{6h} as well as to the time-reversal operation acting on both the electron system and the sources of the fields.

Let us first consider the first-order terms in external fields. Imposing the time-reversal invariance, we note that the magnetic field combines with the pure imagi-

TABLE I. Doubly degenerate representations of the point groups (the single groups).

Tetragonal series

D_{4h}	D_4	C_{4v}	D_{2d}	C_{4h}	C_4	S_4
Γ_5^+ Γ_5^-	Γ_5	Γ_5	Γ_5	$\Gamma_3^+\dotplus\Gamma_4^+$ $\Gamma_3^-\dotplus\Gamma_4^-$	$\Gamma_3\dotplus\Gamma_4$	$\Gamma_3\dotplus\Gamma_4$

Hexagonal series

D_{6h}	D_6	C_{6h}	C_{6v}	D_{3d}	D_{3h}
Γ_5^+ Γ_5^-	Γ_5	$\Gamma_5^+\dotplus\Gamma_6^+$ $\Gamma_5^-\dotplus\Gamma_6^-$	Γ_5	Γ_3^+ Γ_3^-	Γ_5
Γ_6^+ Γ_6^-	Γ_6	$\Gamma_2^+\dotplus\Gamma_3^+$ $\Gamma_2^-\dotplus\Gamma_3^-$	Γ_6	(Γ_3^+) (Γ_3^-)	Γ_6

C_6	D_3	C_{3i}	C_{3v}	C_{3h}	C_3
$\Gamma_5\dotplus\Gamma_6$	Γ_3	$\Gamma_2^+\dotplus\Gamma_3^+$ $\Gamma_2^-\dotplus\Gamma_3^-$	Γ_3	$\Gamma_5\dotplus\Gamma_6$ $\Gamma_2\dotplus\Gamma_3$	$\Gamma_2\dotplus\Gamma_3$
$\Gamma_2\dotplus\Gamma_3$		$(\Gamma_2^+\dotplus\Gamma_3^+)$ $(\Gamma_2^-\dotplus\Gamma_3^-)$		$(\Gamma_2\dotplus\Gamma_3)$ $(\Gamma_5\dotplus\Gamma_6)$	

Cubic series

O_h	O	T_d	T_h	T
Γ_3^+ Γ_3^-	Γ_3	Γ_3	$\Gamma_2^+\dotplus\Gamma_3^+$ $\Gamma_2^-\dotplus\Gamma_3^-$	$\Gamma_2\dotplus\Gamma_3$

[7] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (The MIT Press, Cambridge, Mass., 1963).

[8] S. Sugano, Y. Tanabe, and H. Kamimura, *Theory of Multiplets of Transition-Metal Ions in Crystals* (Academic Press Inc., New York, to be published).

TABLE II. The reduced matrices of the tensor operators and their matrix elements.

D_{4h} symmetry group

$$\langle\Gamma_5^{\pm}\|V(\Gamma_1^{+})\|\Gamma_5^{\pm}\rangle=\sqrt{2},\quad \langle\Gamma_5^{\pm}\|T(\Gamma_2^{+})\|\Gamma_5^{\pm}\rangle=-\sqrt{2}i,\quad \langle\Gamma_5^{\pm}\|V(\Gamma_3^{+})\|\Gamma_5^{\pm}\rangle=-\sqrt{2},\quad \langle\Gamma_5^{\pm}\|V(\Gamma_4^{+})\|\Gamma_5^{\pm}\rangle=-\sqrt{2},$$

$$V(\Gamma_1^{+})=\begin{bmatrix}\overset{+}{1} & \overset{-}{0}\\ 0 & 1\end{bmatrix},\quad T(\Gamma_2^{+})=\begin{bmatrix}\overset{+}{1} & \overset{-}{0}\\ 0 & -1\end{bmatrix},\quad V(\Gamma_3^{+})=\begin{bmatrix}\overset{+}{0} & \overset{-}{1}\\ 1 & 0\end{bmatrix},\quad V(\Gamma_4^{+})=\begin{bmatrix}\overset{+}{0} & \overset{-}{-i}\\ i & 0\end{bmatrix},$$

where $\tilde{\varphi}(\Gamma_5^{\epsilon},\pm)=\mp(i/\sqrt{2})[\tilde{\varphi}(\Gamma_5^{\epsilon},x)\pm i\tilde{\varphi}(\Gamma_5^{\epsilon},y)]$, $(\epsilon=\pm1)$.

D_{6h} symmetry group[a]

$$\langle\Gamma_5^{\pm}\|V(\Gamma_1^{+})\|\Gamma_5^{\pm}\rangle=\sqrt{2},\quad \langle\Gamma_5^{\pm}\|T(\Gamma_2^{+})\|\Gamma_5^{\pm}\rangle=-\sqrt{2}i,\quad \langle\Gamma_5^{\pm}\|V(\Gamma_6^{+})\|\Gamma_5^{\pm}\rangle=2,$$

$$V(\Gamma_1^{+})=\begin{bmatrix}\overset{+}{1} & \overset{-}{0}\\ 0 & 1\end{bmatrix},\quad T(\Gamma_2^{+})=\begin{bmatrix}\overset{+}{1} & \overset{-}{0}\\ 0 & -1\end{bmatrix},\quad V_x(\Gamma_6^{+})=\begin{bmatrix}\overset{+}{0} & \overset{-}{-i}\\ i & 0\end{bmatrix},\quad V_y(\Gamma_6^{+})=\begin{bmatrix}\overset{+}{0} & \overset{-}{1}\\ 1 & 0\end{bmatrix}.$$

O_h symmetry group

$$\langle\Gamma_3^{\pm}\|V(\Gamma_1^{+})\|\Gamma_3^{\pm}\rangle=\sqrt{2},\quad \langle\Gamma_3^{\pm}\|T(\Gamma_2^{+})\|\Gamma_3^{\pm}\rangle=-\sqrt{2}i,\quad \langle\Gamma_3^{\pm}\|V(\Gamma_3^{+})\|\Gamma_3^{\pm}\rangle=2,$$

$$V(\Gamma_1^{+})=\begin{bmatrix}\overset{+}{1} & \overset{-}{0}\\ 0 & 1\end{bmatrix},\quad T(\Gamma_2^{+})=\begin{bmatrix}\overset{+}{1} & \overset{-}{0}\\ 0 & -1\end{bmatrix},\quad V_1(\Gamma_3^{+})=\begin{bmatrix}\overset{+}{0} & \overset{-}{1}\\ 1 & 0\end{bmatrix},\quad V_2(\Gamma_3^{+})=\begin{bmatrix}\overset{+}{0} & \overset{-}{i}\\ -i & 0\end{bmatrix},$$

where $\tilde{\varphi}(\Gamma_3^{\epsilon},\pm)=\mp(i/\sqrt{2})[\tilde{\varphi}(\Gamma_3^{\epsilon},1)\pm i\tilde{\varphi}(\Gamma_3^{\epsilon},2)]$, $(\epsilon=\pm1)$

$\tilde{\varphi}(\Gamma_3^{+},1)\propto 3z^2-r^2$, $\tilde{\varphi}(\Gamma_3^{+},2)\propto\sqrt{3}(x^2-y^2)$, $\tilde{\varphi}(\Gamma_3^{-},1)\propto\sqrt{3}xyz(x^2-y^2)$, $\tilde{\varphi}(\Gamma_3^{-},2)\propto -xyz(3z^2-r^2)$.

[a] The tensor operators and their matrices for the $\Gamma_6^{\pm}$ doublets are the same as those for the $\Gamma_5^{\pm}$.

nary operator $T(\Gamma_2^{+})$. Further imposing the D_{6h}-symmetry invariance, we have the term $T(\Gamma_2^{+})H_z$, since H_z transforms as Γ_2^{+}. On the other hand, the electric field is invariant to the time reversal, so that it combines with the real tensor operators $V(\Gamma_1)$, $V_x(\Gamma_6^{+})$, and $V_y(\Gamma_6^{+})$. However, the first-order terms of the electric field are not invariant with respect to the symmetry operations of the D_{6h} group. Next, let us consider the second-order terms of the external field. It is not difficult to see that there are six invariants given as follows:

$$\sum_{mm',\gamma\gamma'} H_mH_{m'}V_{\gamma}(\Gamma_6^{+})\langle\Gamma_5m\Gamma_5m'\,|\,\Gamma_6\gamma'\rangle\langle\Gamma_6\gamma'\Gamma_6\gamma\,|\,\Gamma_1e_1\rangle$$
$$=(1/\sqrt{2})\{H_+^2V_+(\Gamma_6^{+})+H_-^2V_-(\Gamma_6^{+})\}$$
$$=\tfrac{1}{2}\{(H_x^2-H_y^2)V_y(\Gamma_6^{+})+2H_xH_yV_x(\Gamma_6^{+})\},\quad (15)$$

$$H_z^2V(\Gamma_1^{+})\langle\Gamma_2e_2\Gamma_2e_2\,|\,\Gamma_1e_1\rangle=H_z^2V(\Gamma_1^{+}),\quad (16)$$

$$\sum_{mm'} H_mH_{m'}V(\Gamma_1^{+})\langle\Gamma_5m\Gamma_5m'\,|\,\Gamma_1e_1\rangle$$
$$=\sqrt{2}H_+H_-V(\Gamma_1^{+})$$
$$=-(1/\sqrt{2})(H_x^2+H_y^2)V(\Gamma_1^{+}),\quad (17)$$

and the terms replaced (H_x,H_y) by (E_x,E_y) in the above expressions, where

$$V_{\pm}(\Gamma_6^{+})=\mp(i/\sqrt{2})[V_x(\Gamma_6^{+})\pm iV_y(\Gamma_6^{+})]$$

and $H_{\pm}=\mp(1/\sqrt{2})(H_x\pm iH_y)$.

To illustrate the method of deriving the effective Hamiltonians for other symmetry groups in the hexagonal series, we consider the case of the D_{3h} symmetry group as an example. From the compatibility relations between the D_{6h} and the D_{3h} symmetry group, the irreducible representations of Γ_1^{+} and Γ_4^{-} of the D_{6h} group are reduced to Γ_1 of the D_{3h} group. Therefore, in addition to the seven invariants of the D_{6h} group obtained above, there should be terms of the Γ_4^{-} symmetry of D_{6h} which are invariants in the D_{3h} group. The Γ_4^{-} term is linear in the electric field and given by

$$\sum_{m\gamma} E_mV_{\gamma}(\Gamma_6^{+})\langle\Gamma_5m\Gamma_6\gamma\,|\,\Gamma_4e_4\rangle$$
$$=(i/\sqrt{2})[E_-V_+(\Gamma_6^{+})-E_+V_-(\Gamma_6^{+})]$$
$$=-(1/\sqrt{2})[E_xV_y(\Gamma_6^{+})-E_yV_x(\Gamma_6^{+})],\quad (18)$$

where $E_{\pm}=\mp(i/\sqrt{2})(E_x\pm iE_y)$. Thus, the effective Hamiltonian for the non-Kramers doublet of the D_{3h} point group is given by

$$\begin{aligned}\mathcal{H}_{\text{eff}}=&\,g_{\parallel}\beta H_zT(\Gamma_2^{+})+R[E_xV_y(\Gamma_6^{+})-E_yV_x(\Gamma_6^{+})]\\&+G_1[(H_x^2-H_y^2)V_y(\Gamma_6^{+})+2H_xH_yV_x(\Gamma_6^{+})]\\&+\bar{G}_1[(E_x^2-E_y^2)V_y(\Gamma_6^{+})+2E_xE_yV_x(\Gamma_6^{+})]\\&+M_1H_z^2V(\Gamma_1^{+})+M_2(H_x^2+H_y^2)V(\Gamma_1^{+})\\&+\bar{M}_1E_z^2V(\Gamma_1^{+})+\bar{M}_2(E_x^2+E_y^2)V(\Gamma_1^{+}),\end{aligned}\quad (19)$$

where $g_{\parallel}\beta$, R, G_1, $\bar{G}_1$, M_1, M_2, $\bar{M}_1$, and $\bar{M}_2$ are real numbers. The last four terms in Eq. (19) only give the shifts of the energy levels. These terms are necessary for studying optical spectra of paramagnetic ions in crystals.

In this way, we can derive the effective Hamiltonians for all the symmetry groups in the hexagonal series. For the cubic and tetragonal series, we use the tensor operators whose necessary matrices are given in Table II. In order to obtain the matrices of the tensor operators,

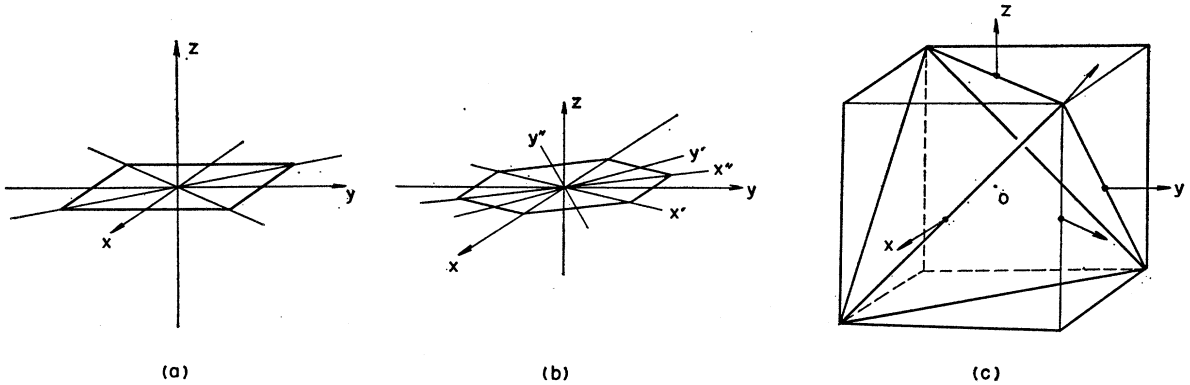

FIG. 1. Systems of the coordinate axes for the groups (a) D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h}, C_4, and S_4; (b) D_{6h}, C_{6h}, C_{6v}, D_{3d}, D_{3h}, D_6, C_6, D_3, C_3, C_{3v}, C_{3i}, and C_{3h}; (c) O_h, O, T_d, T_h, and T.

TABLE III. Effective Hamiltonian linear and quadratic in magnetic and electric fields.

$g_{\|\|}\beta H_z\sigma_z$	D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h}, C_4, S_4; D_{6h}, C_{6h}, C_{6v}, D_{3d}, D_{3h}, D_6, C_6, D_3, C_3, C_{3v}, C_{3i}, C_{3h}
$RE_z\sigma_y$	D_{2d}
$RE_z\sigma_y-R'E_z\sigma_x$	S_4
$R'(E_x\sigma_y+E_y\sigma_x)$	D_3
$R(E_x\sigma_x-E_y\sigma_y)$	D_{3h}, C_{3v}
$R(E_x\sigma_x-E_y\sigma_y)+R'(E_x\sigma_y+E_y\sigma_x)$	C_{3h}, C_3
$G_1(H_x^2-H_y^2)\sigma_x+2G_2H_xH_y\sigma_y$	D_{4h}, D_4, C_{4v}, D_{2d}
$G_1(H_x^2-H_y^2)\sigma_x+2G_2H_xH_y\sigma_y+G_1'(H_x^2-H_y^2)\sigma_y-2G_2'H_xH_y\sigma_x$	C_{4h}, C_4, S_4
$G_1[(H_x^2-H_y^2)\sigma_x+2H_xH_y\sigma_y]$	D_{6h}, D_6, C_{6v}, D_{3h}
$G_1[(H_x^2-H_y^2)\sigma_x+2H_xH_y\sigma_y]+G_2H_z(H_x\sigma_x-H_y\sigma_y)$	D_{3d}, D_3, C_{3v}
$G_1[(H_x^2-H_y^2)\sigma_x+2H_xH_y\sigma_y]+G_1'[(H_x^2-H_y^2)\sigma_y-2H_xH_y\sigma_x]$	C_{6h}, C_6, C_{3h}
$G_1[(H_x^2-H_y^2)\sigma_x+2H_xH_y\sigma_y]+G_1'[(H_x^2-H_y^2)\sigma_y-2H_xH_y\sigma_x]+G_2H_z(H_x\sigma_x-H_y\sigma_y)+G_2'H_z(H_x\sigma_y+H_y\sigma_x)$	C_{3i}, C_3
$G_1[(1/\sqrt{3})(H_x^2+H_y^2-2H_z^2)\sigma_x+(H_x^2-H_y^2)\sigma_y]$	O_h, O, T_d
$G_1[(1/\sqrt{3})(H_x^2+H_y^2-2H_z^2)\sigma_x+(H_x^2-H_y^2)\sigma_y]+G_1'[(1/\sqrt{3})(H_x^2+H_y^2-2H_z^2)\sigma_y-(H_x^2-H_y^2)\sigma_x]$	T_h, T
$\bar{G}_1(E_x^2-E_y^2)\sigma_x+2\bar{G}_2E_xE_y\sigma_y$	D_{4h}, D_4, C_{4v}, D_{2d}
$\bar{G}_1(E_x^2-E_y^2)\sigma_x+2\bar{G}_2E_xE_y\sigma_y+\bar{G}_1'(E_x^2-E_y^2)\sigma_y-2\bar{G}_2'E_xE_y\sigma_x$	C_{4h}, C_4, S_4
$\bar{G}_1[(E_x^2-E_y^2)\sigma_x+2E_xE_y\sigma_y]$	D_{6h}, D_6, C_{6v}, D_{3h}
$\bar{G}_1[(E_x^2-E_y^2)\sigma_x+2E_xE_y\sigma_y]+\bar{G}_2E_z(E_x\sigma_x-E_y\sigma_y)$	D_{3d}, D_3, C_{3v}
$\bar{G}_1[(E_x^2-E_y^2)\sigma_x+2E_xE_y\sigma_y]+\bar{G}_1'[(E_x^2-E_y^2)\sigma_y-2E_xE_y\sigma_x]$	C_{6h}, C_6, C_{3h}
$\bar{G}_1[(E_x^2-E_y^2)\sigma_x+2E_xE_y\sigma_y]+\bar{G}_1'[(E_x^2-E_y^2)\sigma_y-2E_xE_y\sigma_x]+\bar{G}_2E_z(E_x\sigma_x-E_y\sigma_y)+\bar{G}_2'E_z(E_x\sigma_y+E_y\sigma_x)$	C_{3i}, C_3
$\bar{G}_1[(1/\sqrt{3})(E_x^2+E_y^2-2E_z^2)\sigma_x+(E_x^2-E_y^2)\sigma_y]$	O_h, O, T_d
$\bar{G}_1[(1/\sqrt{3})(E_x^2+E_y^2-2E_z^2)\sigma_x+(E_x^2-E_y^2)\sigma_y]+\bar{G}_1'[(1/\sqrt{3})(E_x^2+E_y^2-2E_z^2)\sigma_y-(E_x^2-E_y^2)\sigma_x]$	T_h, T
$\bar{g}_{\|\|}\beta H_zE_z\sigma_z$	C_{4v}, C_4; C_{6v}, C_6, C_{3v}, C_3
$K(H_xE_x+H_yE_y)\sigma_z$	C_{4v}; C_{6v}, C_6, C_{3v}, C_3
$K(H_xE_y-H_yE_x)\sigma_z$	D_4; D_6, C_6, D_3, C_3
$K_1(H_xE_x+H_yE_y)\sigma_z+K_2(H_xE_y-H_yE_x)\sigma_z$	C_4
$K(H_xE_y+H_yE_x)\sigma_z$	D_{2d}
$K_1(H_xE_x-H_yE_y)\sigma_z+K_2(H_xE_y+H_yE_x)\sigma_z$	S_4
$K(H_xE_x+H_yE_y+H_zE_z)\sigma_z$	T_d, T
$M_1H_z^2\mathbf{1}+M_2(H_x^2+H_y^2)\mathbf{1}$	D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h}, C_4, S_4; D_{6h}, D_6, C_{6h}, C_{6v}, D_{3d}, D_{3h}, C_6, D_3, C_3, C_{3v}, C_{3i}, C_{3h}
$M_0(H_x^2+H_y^2+H_z^2)\mathbf{1}$	O_h, O, T_d, T_h, T
$\bar{M}_1E_z^2\mathbf{1}+\bar{M}_2(E_x^2+E_y^2)\mathbf{1}$	D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h}, C_4, S_4; D_{6h}, D_6, C_{6h}, C_{6v}, D_{3d}, D_{3h}, C_6, D_3, C_3, C_{3v} C_{3i}, C_{3h}
$\bar{M}_0(E_x^2+E_y^2+E_z^2)\mathbf{1}$	O_h, O, T_d, T_h, T

TABLE IV. Effective Hamiltonian of hyperfine interaction.

$A_{\|\|}I_z\sigma_z+P\{3I_z^2-I(I+1)\}\cdot 1$	D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h}, C_4, S_4; D_{6h}, D_6, C_{6h}, C_{6v}, D_{3d}, D_{3h}, C_6, D_3, C_3, C_{3v}, C_{3i}, C_{3h}
$B_1(I_x^2-I_y^2)\sigma_x+B_2(I_xI_y+I_yI_x)\sigma_y$	D_{4h}, D_4, C_{4v}, D_{2d}
$B_1(I_x^2-I_y^2)\sigma_x+B_2(I_xI_y+I_yI_x)\sigma_y+B_1'(I_x^2-I_y^2)\sigma_y-B_2'(I_xI_y+I_yI_x)\sigma_x$	C_{4h}, C_4, S_4
$B_1[(I_x^2-I_y^2)\sigma_x+(I_xI_y+I_yI_x)\sigma_y]$	D_{6h}, D_6, C_{6v}, D_{3h}
$B_1[(I_x^2-I_y^2)\sigma_x+(I_xI_y+I_yI_x)\sigma_y]+B_2[(I_zI_x+I_xI_z)\sigma_x-(I_yI_z+I_zI_y)\sigma_y]$	D_{3d}, D_3, C_{3v}
$B_1[(I_x^2-I_y^2)\sigma_x+(I_xI_y+I_yI_x)\sigma_y]+B_1'[(I_x^2-I_y^2)\sigma_y-(I_xI_y+I_yI_x)\sigma_x]$	C_{6h}, C_6, C_{3h}
$B_1[(I_x^2-I_y^2)\sigma_x+(I_xI_y+I_yI_x)\sigma_y]+B_1'[(I_x^2-I_y^2)\sigma_y-(I_xI_y+I_yI_x)\sigma_x]$ $+B_2[(I_zI_x+I_xI_z)\sigma_x-(I_yI_z+I_zI_y)\sigma_y]+B_2'[(I_zI_x+I_xI_z)\sigma_y+(I_yI_z+I_zI_y)\sigma_x]$	C_{3i}, C_3
$B_1\{(1/\sqrt{3})[3I_z^2-I(I+1)]\sigma_x-(I_x^2-I_y^2)\sigma_y\}$	O_h, O, T_d
$B_1\{(1/\sqrt{3})[3I_z^2-I(I+1)]\sigma_x-(I_x^2-I_y^2)\sigma_y\}+B_1'\{(1/\sqrt{3})\{3I_z^2-I(I+1)]\sigma_y+(I_x^2-I_y^2)\sigma_x\}$	T_h, T

we have used the Clebsch-Gordan coefficients for the O_h, D_{6h}, and D_{4h} groups given by Koster, Dimmock, Wheeler, and Statz.[7] In the same way, we can obtain the effective Hamiltonian for the non-Kramers doublets of all the symmetry groups shown in Table I. The results are given in Table III. In Table III, the matrices of the tensor operators given in Table II are, for convenience, replaced by the Pauli spin matrices as follows:

$$V(\Gamma_1^+)=\mathbf{1},\quad T(\Gamma_2^+)=\sigma_z,\quad V(\Gamma_3^+)=\sigma_x,\quad V(\Gamma_4^+)=\sigma_y$$
for the D_{4h} group,

$$V(\Gamma_1^+)=\mathbf{1},\quad T(\Gamma_2^+)=\sigma_z,\quad V_x(\Gamma_6^+)=\sigma_y,\quad V_y(\Gamma_6^+)=\sigma_x$$
for the D_{6h} group,

and

$$V(\Gamma_1^+)=\mathbf{1},\quad T(\Gamma_2^+)=\sigma_z,\quad V_1(\Gamma_3^+)=\sigma_x,\quad V_2(\Gamma_3^+)=-\sigma_y$$
for the O_h group.

It should be noted that σ_x, σ_y, and σ_z do not mean the spin–angular-momentum operators.

The effective Hamiltonian for the hyperfine interaction can be constructed in the same way as that for the ^{2S+1}E cubic terms is constructed.[8] We replace an electron spin S by a nuclear spin I in the treatment of ^{2S+1}E cubic term. The $2(2I+1)\times 2(2I+1)$ secular matrix can be represented as the linear combination of matrices of the products $I_q^{(k)}X_{\gamma_0}(\Gamma_0)$ $(0\leq k\leq 2I,\ \Gamma\times\Gamma=\Sigma\Gamma_0)$ with the basis $\tilde{\Phi}(I\Gamma,I_z\gamma)$, where $I_q^{(k)}$ is the irreducible nuclear-spin–tensor operator of the degree k. The effective Hamiltonian of the hyperfine interaction is, thus, given by

$$\mathcal{H}_{\rm eff}^{\rm hf}=\sum_{kq\Gamma_0\gamma_0}A_q{}^k(\Gamma_0\gamma_0)I_q{}^{(k)}X_{\gamma_0}(\Gamma_0). \tag{20}$$

The real Hamiltonian of the hyperfine interaction[9] is given by

$$\mathcal{H}_{\rm hf}=(2\beta\beta_N\mu_N/I)\sum_i \mathbf{N}_i\cdot\mathbf{I}/r_i^3, \tag{21}$$

where

$$\mathbf{N}_i=\mathbf{l}_i-\mathbf{s}_i+3\mathbf{r}_i(\mathbf{r}_i\cdot\mathbf{s}_i)/r_i^3.$$

This Hamiltonian is invariant under the symmetry operations of the spatial and the time-reversal operations acting on both an electron system and a nucleon system. We can, thus, obtain the effective Hamiltonian for the non-Kramers doublets by constructing the invariants under the symmetry operations of the system in question. However, without doing this process, we can also obtain the effective Hamiltonian by the use of the fact that the nuclear-spin I transforms as the magnetic-field $\mathbf{H}$: The effective Hamiltonian of the hyperfine interaction can easily be obtained from that of the Zeeman term by replacing the magnetic field $\mathbf{H}$ by the nuclear spin I. For example, for the D_{3h} symmetry group, it is given by

$$\mathcal{H}_{\rm eff}^{\rm hf}=A_{\|}I_zT(\Gamma_2^+)+P[3I_z^2-I(I+1)]V(\Gamma_1^+)$$
$$+B_1[(I_x^2-I_y^2)V_y(\Gamma_6^+)+(I_xI_y+I_yI_x)V_x(\Gamma_6^+)]. \tag{22}$$

It should be noted that $2H_xH_y$ must be replaced by $(I_xI_y+I_yI_x)$ to make the effective Hamiltonian Hermitian. The term $[3I_z^2-I(I+1)]V(\Gamma_1^+)$ is included in Eq. (22), which splits the states with $I>\frac{1}{2}$. The effective Hamiltonian of the hyperfine interaction for all the non-Kramers doublets are given in Table IV.

The effects of the nuclear Zeeman interactions can also be treated in a similar way. The effective Hamiltonians for these interactions to the first order are shown in Table V.

IV. DISCUSSION

A. Remarks on Effective Hamiltonian

As the basis of our effective Hamiltonian, we have chosen function $\tilde{\varphi}_i$ which transforms in the same way as the unperturbed wave function φ_i of the Γ state for both symmetry operations R of group G and the time reversal: These operations leave the unperturbed system invariant. Therefore, if one has one-to-one correspondence between φ_i and the perturbed wave function ψ_i, the association of $\tilde{\varphi}_i$ with ψ_i is unique. As shown in Eq. (4), such a correspondence between φ_i and ψ_i exists if the same irreducible representation does not appear more than once in the distorted systems. This is certainly the case in our problem as shown in Table I. Here, Zeeman and Stark terms are not considered to

[9] B. R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill Book Co., New York, 1963), p. 85.

TABLE V. Effective Hamiltonian involving magnetic field and nuclear spin.

$C_1(H_xI_x-H_yI_y)\sigma_x+C_2(H_xI_y+H_yI_x)\sigma_y$	D_{4h}, D_4, C_{4v}, D_{2d}
$C_1(H_xI_x-H_yI_y)\sigma_x+C_2(H_xI_y+H_yI_x)\sigma_y+C_1'(H_xI_x-H_yI_y)\sigma_y-C_2'(H_xI_y+H_yI_x)\sigma_x$	C_{4h}, C_4, S_4
$C_1[(H_xI_x-H_yI_y)\sigma_x+(H_xI_y+H_yI_x)\sigma_y]$	D_{6h}, D_6, C_{6v}, D_{3h}
$C_1[(H_xI_x-H_yI_y)\sigma_x+(H_xI_y+H_yI_x)\sigma_y]+C_2H_z(I_x\sigma_x-I_y\sigma_y)+C_3I_z(H_x\sigma_x-H_y\sigma_y)$	D_{3d}, D_3, C_{3v}
$C_1[(H_xI_x-H_yI_y)\sigma_x+(H_xI_y+H_yI_x)\sigma_y]+C_1'[(H_xI_x-H_yI_y)\sigma_y-(H_xI_y+H_yI_x)\sigma_x]$	C_{6h}, C_6, C_{3h}
$C_1[(H_xI_x-H_yI_y)\sigma_x+(H_xI_y+H_yI_x)\sigma_y]+C_1'[(H_xI_x-H_yI_y)\sigma_y-(H_xI_y+H_yI_x)\sigma_x]$ $+C_2H_z(I_x\sigma_x-I_y\sigma_y)+C_3I_z(H_x\sigma_x-H_y\sigma_y)+C_2'H_z(I_x\sigma_y+I_y\sigma_x)+C_3'I_z(H_x\sigma_y+H_y\sigma_x)$	C_{3i}, C_3
$C_1[(1/\sqrt{3})(H_xI_x+H_yI_y-2H_zI_z)\sigma_x+(H_xI_x-H_yI_y)\sigma_y]$	O_h, O, T_d
$C_1[(1/\sqrt{3})(H_xI_x+H_yI_y-2H_zI_z)\sigma_x+(H_xI_x-H_yI_y)\sigma_y]+C_1'[(1/\sqrt{3})(H_xI_x+H_yI_y-2H_zI_z)\sigma_y-(H_xI_x-H_yI_y)\sigma_x]$	T_h, T
$D_1H_zI_z\mathbf{1}+D_2(H_xI_x+H_yI_y)\mathbf{1}$	D_{4h}, D_4, C_{4v}, D_{2d}; D_{6h}, D_6, C_{6v}, D_{3d}, D_{3h}, D_3, C_{3v}
$D_1H_zI_z\mathbf{1}+D_2(H_xI_x+H_yI_y)\mathbf{1}+D_3(H_xI_y-H_yI_x)\mathbf{1}$	C_{4h}, C_4, S_4; C_{6h}, C_6, C_{3i}, C_{3h}, C_3
$D_1(H_xI_x+H_yI_y+H_zI_z)\mathbf{1}$	O_h, O, T_d, T_h, T

induce distortions, as they are invariant to any generalized symmetry operations introduced in Sec. II. Summarizing the argument given here, we remark that there is no freedom in the association of $\tilde{\varphi}_i$ with ψ_i.

Now let us discuss the problem related to the phase of $\tilde{\varphi}_i$. In Tables III–V, some terms are given with primed parameters. The matrix of the term with a primed parameter can be obtained from that of the corresponding term with an unprimed parameter by replacing the unprimed parameter in the upper-right nondiagonal element by the primed parameter times $-i$ and that in the lower left by the primed parameter times i. For example, the linear terms in an electric field for C_{3h} and C_3 are given in Table III as

$$R(E_x\sigma_x-E_y\sigma_y)+R'(E_x\sigma_y+E_y\sigma_x). \tag{23}$$

The matrix of the first term with parameter R is calculated as

$$\begin{matrix}\tilde{\varphi}_+\\ \tilde{\varphi}_-\end{matrix}\begin{bmatrix} 0 & R(E_x+iE_y) \\ R(E_x-iE_y) & 0 \end{bmatrix}. \tag{24}$$

Then, replacing R in the upper-right element in (24) by $-iR'$ and R in the lower left by iR', one obtains

$$\begin{matrix}\tilde{\varphi}_+\\ \tilde{\varphi}_-\end{matrix}\begin{bmatrix} 0 & -iR'(E_x+iE_y) \\ iR'(E_x-iE_y) & 0 \end{bmatrix} \tag{25}$$

for the second term with R' in (23). From (24) and (25), the matrix of the terms in (23) is finally given as

$$\begin{matrix}\tilde{\varphi}_+\\ \tilde{\varphi}_-\end{matrix}\begin{bmatrix} 0 & R_0e^{i\alpha}(E_x+iE_y) \\ R_0e^{-i\alpha}(E_x-iE_y) & 0 \end{bmatrix}, \tag{26}$$

where R_0 and α are real and given by

$$R_0e^{i\alpha}=R-iR'. \tag{27}$$

Now, it is easy to see that parameter α can be eliminated by choosing $e^{i\alpha/2}\tilde{\varphi}_+$ and $e^{-i\alpha/2}\tilde{\varphi}_-$ as the basis in place of $\tilde{\varphi}_+$ and $\tilde{\varphi}_-$, respectively.

The above-mentioned argument shows that, if one has a pair of primed and unprimed terms, one may neglect one of them by choosing appropriate phase for the basis set. However, one cannot do so for additional pairs. For example, Table III shows that for C_{3h} we have an additional pair, $\bar{G}_1$ and $\bar{G}_1'$, in the quadratic terms in an electric field. In this case, we cannot eliminate, say, both R' and $\bar{G}_1'$, at the same time by choosing appropriate phase for the bases. Considering this fact, we have listed all the primed and unprimed terms in the tables without neglecting any of them. Mathematically, the primed and unprimed terms are independent invariants in the sense that the matrix of one term cannot be given by that of another.

As pointed out in Sec. II, one of the merits of our method is that the physical origin of each term in the effective Hamiltonian can be understood easily. This enables us to estimate the order of magnitude of undetermined parameters. For example, let us consider the first-order terms of the electric field in the effective Hamiltonian of the C_{3h} symmetry group. In terms of irreducible tensor operators, they are given as

$$R[E_xV_y(\Gamma_6^+)-E_yV_x(\Gamma_6^+)] +R'[E_xV_x(\Gamma_6^+)+E_yV_y(\Gamma_6^+)]. \tag{28}$$

These terms are expected to be given by the second-order perturbation involving an odd-parity potential and a Stark term, such as

$$[\langle\varphi(\Gamma_5^+,+)|V_{\text{odd}}\mathcal{H}_s|\varphi(\Gamma_5^+,-)\rangle+\text{c.c.}]/\Delta E. \tag{29}$$

In the above expression, the summations over all the intermediate states have been performed by making the approximation of replacing the energy denominators by a single average denominator ΔE. For the C_{3h} symmetry group, the odd terms in the crystal field potential are given by

$$V_{\text{odd}}=aV(\Gamma_3^-)+bV(\Gamma_4^-), \tag{30}$$

TABLE VI. Selection rules for the transitions between the magnetic- and the electric-field spilt levels of the non-Kramers doublets.

Static field	Oscillating field	Site symmetries
$\mathbf{H}\parallel z$	$\mathbf{E}_{osc}\parallel z$	S_4, D_{2d}
	$\mathbf{E}_{osc}\perp z$	D_{3h}, D_3, C_{3h}, C_{3v}, C_3
$\mathbf{H}\perp z$	$\mathbf{H}_{osc}\parallel z$	D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h} C_4, S_4; D_{6h}, D_6, C_{6h}, C_{6v}, D_{3d}, D_{3h}, C_6, D_3, C_3, C_{3i}, C_{3v}, C_{3h}
	$\mathbf{E}_{osc}\parallel z$	S_4, D_{2d}
	$\mathbf{E}_{osc}\perp z$	D_{3h}, D_3, C_{3h}, C_{3v}, C_3
$\mathbf{E}\parallel z$	$\mathbf{H}_{osc}\parallel z$	S_4, D_{2d}
	$\mathbf{E}_{osc}\parallel z$[a]	S_4, D_{2d}
$\mathbf{E}\perp z$	$\mathbf{H}_{osc}\parallel z$	D_{4h}, D_4, C_{4v}, D_{2d}, C_{4h} C_4, S_4; D_{6h}, D_6, C_{6h}, C_{6v}, D_{3d}, D_{3h}, C_6, D_3, C_3, C_{3i}, C_{3v}, C_{3h}
	$\mathbf{E}_{osc}\parallel z$	S_4, D_{2d}
	$\mathbf{E}_{osc}\perp z$	D_{3h}, D_3, C_{3h}, C_{3v}, C_3

[a] This is allowed if the static-field terms of the third order are taken into account.

where

$$V(\Gamma_3^-)=\sum_{t=\text{odd}} iA_3{}^t(C_3{}^{(t)}+C_{-3}{}^{(t)}),$$

$$V(\Gamma_4^-)=\sum_{t=\text{odd}} B_3{}^t(C_3{}^{(t)}-C_{-3}{}^{(t)}),$$

and the $C_p{}^{(t)}$ is defined by $C_p{}^{(t)}=[4\pi/(2t+1)]^{1/2}Y_{tp}$: Y_{tp} is the spherical harmonic function. The Stark term $\mathcal{H}_s$ for $\mathbf{E}\perp z$ is as follows:

$$\mathcal{H}_s=e[V_+(\Gamma_5^-)E_-+V_-(\Gamma_5^-)E_+], \tag{31}$$

where $V_\pm(\Gamma_5^-)=\mp(i/\sqrt{2})(x\pm iy)$ and $E_\pm=\mp(i/\sqrt{2})\times(E_x\pm iE_y)$. By using the table of the Clebsch-Gordan coefficients,[7] one obtains

$$\begin{aligned}V_{\text{odd}}\mathcal{H}_s&=(ae/\Delta E)V(\Gamma_3^-)[V_+(\Gamma_5^-)E_-+V_-(\Gamma_5^-)E_+]\\&\quad+(be/\Delta E)V(\Gamma_4^-)[V_+(\Gamma_5^-)E_-+V_-(\Gamma_5^-)E_+]\\&=(ae/\Delta E)[E_xV_x(\Gamma_6^+)+E_yV_y(\Gamma_6^+)]\\&\quad+(be/\Delta E)[E_xV_y(\Gamma_6^+)-E_yV_x(\Gamma_6^+)],\end{aligned} \tag{32}$$

where $V_\pm(\Gamma_6^+)=\mp(i/\sqrt{2})[V_x(\Gamma_6^+)\pm iV_y(\Gamma_6^+)]$. Comparing (32) with (28), one sees that R and R' are given as

$$\begin{aligned}R&=2i(be/\Delta E)\langle\varphi(\Gamma_5^+,+)|\,V(\Gamma_4^-)V_-(\Gamma_5^-)|\,\varphi(\Gamma_5^+,-)\rangle,\\R'&=2(ae/\Delta E)\langle\varphi(\Gamma_5^+,+)|\,V(\Gamma_3^-)V_-(\Gamma_5^-)|\,\varphi(\Gamma_5^+,-)\rangle,\end{aligned} \tag{33}$$

The presence of two terms $R[E_xV_y(\Gamma_6^+)-E_yV_x(\Gamma_6^+)]$ and $R'[E_xV_x(\Gamma_6^+)+E_yV_y(\Gamma_6^+)]$ for the C_{3h} symmetry corresponds to that there are two independent odd terms $V(\Gamma_3^-)$ and $V(\Gamma_4^-)$ in the crystal field potential. For the D_{3h} symmetry, the odd term in the crystal field potential is only $V(\Gamma_4^-)$, so that only the first unprimed terms is present in the effective Hamiltonian as shown in Table III.

B. Selection Rules

Selection rules for paraelectric and paramagnetic resonance in the non-Kramers doublets are easily derived from our effective Hamiltonian, when some of the applied fields in the linear terms are regarded as oscillating fields of radiation. If static-field terms have diagonal elements and oscillating-field terms have nondiagonal ones, or vice versa, the oscillating field may induce transitions between the split levels. Some caution is necessary when both static and oscillating fields appear in the nondiagonal. For example, let us consider the case in which both the static electric field $\mathbf{E}$ and oscillating electric field $\mathbf{E}_{\text{osc}}$ are parallel to the z axis. Table III shows that the splitting linear to E_z is expected for D_{2d} and S_4 from the terms $RE_z\sigma_y$ and $RE_z\sigma_y-R'E_z\sigma_x$, respectively. We also have the terms proportional to $E_{\text{osc},z}$ of the same origin for these systems. In this case, it is clear that for the basis set, for which the E_z terms are diagonal, the $E_{\text{osc},z}$ terms are also diagonal inducing no transition between the split levels. However, if one takes into account the higher-order static-field terms, the third-order terms in the present example, one may expect nonvanishing terms linear to $E_{\text{osc},z}$ in the nondiagonal for the basis set for which all the static-field terms are diagonal. Thus, the electric-dipole transitions polarized along the z axis become allowed for D_{2d} and S_4 with $\mathbf{E}\|z$.

The selection rules derived in this way are listed in Table VI. The table can also be used for the case in which both static electric and magnetic fields are applied simultaneously. According to our careful examination, the transition in this case is allowed if it is allowed for either one of the static fields.

Selection rules for circularly polarized radiation can easily be derived in a similar way by reexpressing the effective Hamiltonian in terms of

$$E_{\text{osc},\pm}=\mp(i/\sqrt{2})(E_{\text{osc},x}\pm iE_{\text{osc},y})$$

and

$$H_{\text{osc},\pm}=\mp(1/\sqrt{2})(H_{\text{osc},x}\pm iH_{\text{osc},y}).$$

For example, in D_3, D_{3h}, C_{3v}, C_{3h}, and C_3, the electric-dipole transition is circularly polarized when $\mathbf{H}\|z$, as shown in (26). The sense of the polarization depends on the sign of g_{II}.

It should be remarked that any transition is forbidden for the cubic groups, O_h, O, T_d, T_h, and T. To discuss the selection rules for transitions between the hyperfine-split components, the selection rule $\Delta m=0$ has to be applied to nuclear states with nuclear magnetic quantum number $m(m=I, I-1,\cdots,-I)$, as the orientation of the nuclear spin does not change during electronic transitions.

In concluding this subsection, let us compare some of our results with those obtained by the perturbation theory and experiments. As an example, we consider praseodymium ethylsulphate. The ground state of the free Pr^{3+} ion is $^3H_4(4f^2)$, which, under the action of a

crystalline field of C_{3h} symmetry, splits into a singlet and four doublets.[1] The lowest doublet may be written as $\psi_1=a|J_z=+4\rangle+b|J_z=-2\rangle$ and $\psi_2=a^*|J_z=-4\rangle+b^*|J_z=+2\rangle$, where $|a|^2+|b|^2=1$. With $\mathbf{H}$ parallel to the z axis, the eigenfunctions are simply ψ_1 and ψ_2. The electric-dipole transition between these states is parity forbidden. The matrix element of such parity-forbidden electric-dipole transition in rare-earth ions was derived by Judd[10] and Ofelt.[11] By using Eq. (13) in Ref. 10, we obtain the selection rule $J_z-J_z'=p+q$, where p is the azimuthal quantum number of the odd-parity terms of the crystalline-field potential ($p=\pm 3$ for C_{3h} symmetry) and $q=0$ and $q=\pm 1$ for the polarization $\mathbf{E}_{\rm osc}\|z$ and $\mathbf{E}_{\rm osc}\perp z$, respectively. The electric-dipole transition $\psi_1\rightleftharpoons\psi_2$ is, therefore, allowed for the polarization $\mathbf{E}_{\rm osc}\perp z$, since $J_z=+4,\ -2$, $J_z'=-4,\ +2$, and $q=\pm 1$ in this case. This agrees with our result. Recent EPR experiments on Pr^{3+} in ethylsulphate[12] and in the double nitrate salt[13] have shown that the transitions between the magnetic-field split levels of the non-Kramers doublet are mainly induced by the high-frequency electric field perpendicular to the trigonal axis. The selection rule obtained here is consistent with these experimental results.

C. Comparison with Other Methods

Mathematically, it is expected that our method gives the same results as those given by the spin-one formalism of Mueller, although the spin-one formalism starts with an expanded subspace. Comparing the results of both methods in detail, we have found that this expectation is true if the spin-one formalism is applied correctly, or if the following corrections are made in Mueller's Table II of Ref. 4:

(1) The term $(\frac{1}{2})T[E_xH_x+E_yH_y]S_z$ is not applicable to S_4, D_4, D_{2d}, D_3, D_{3h}, and D_6.

(2) The term $(H_xE_y-H_yE_x)S_z$ is applicable to D_4, C_4, D_6, C_6, D_3, and C_3; $(H_xE_x-H_yE_y)S_z$ to S_4; $(H_xE_y+H_yE_x)S_z$ to D_{2d} and S_4. All these terms are missing.

(3) The term $(\frac{1}{2})[G_1(H_x^2-H_y^2)(S_x^2-S_y^2)+2G_2H_xH_y\times(S_xS_y+S_yS_x)]$ is applicable to S_4, but $(\frac{1}{2})G[(H_x^2-H_y^2)(S_x^2-S_y^2)+2H_xH_y(S_xS_y+S_yS_x)]$ is not.

(4) The missing term $G_2H_z[H_x(S_x^2-S_y^2)-H_y(S_xS_y+S_yS_x)]$ is applicable to D_{3d}, D_3, C_{3v}, C_{3i}, and C_3.

All the terms corresponding to those with primed parameters in our effective Hamiltonian, which have been discussed in Sec. IV A, are not listed in Mueller's table in case they are accompanied by the corresponding unprimed terms. They are as follows:

(1)′ The term $E_z(S_x^2-S_y^2)$ is applicable to S_4.

(2)′ The term $[E_x(S_xS_y+S_yS_x)+E_y(S_x^2-S_y^2)]$ is applicable to C_{3h} and C_3.

(3)′ The term $G_1'(H_x^2-H_y^2)(S_xS_y+S_yS_x)+2G_2'H_x\times H_y(S_x^2-S_y^2)$ is applicable to C_{4h}, C_4, and S_4.

(4)′ The term $G_1'[(H_x^2-H_y^2)(S_xS_y+S_yS_x)-2H_xH_y\times(S_x^2-S_y^2)]$ is applicable to C_{6h}, C_6, C_{3h}, C_{3i}, and C_3.

(5)′ The term $G_2'H_z[H_x(S_xS_y+S_yS_x)+H_y(S_x^2-S_y^2)]$ is applicable to C_{3i} and C_3.

Koster and Statz[14] determined the general forms of the secular matrices of the perturbation Hamiltonian $\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})$ for the states which diagonalize the crystal field Hamiltonian, by using the first-order perturbation theory. These secular matrices for the non-Kramers doublets are the same as those of the linear magnetic-field terms in the effective Hamiltonian obtained in the present paper.

Recently, Murao, Spedding, and Good[15] studied, by the exhaustive use of group theory, the Zeeman effect for optical spectra of rare-earth ions in the crystal field with C_{3h} symmetry. The results obtained by them for an even number of electrons are as follows: (1) When $\mathbf{H}\|z$, non-Kramers doublets split in the first order; (2) when $\mathbf{H}\perp z$, non-Kramers doublets show no first-order effect and they shift and split in the second order. These results are consistent with the ones obtained in the present paper.

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