

# HIGHER-ORDER OPERATORS IN THE THEORY OF IONS IN CRYSTALS

## ELECTRONIC SPIN-SPIN COUPLING CONTRIBUTIONS TO SPIN HAMILTONIAN TENSORS

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Recoupling formalism is applied for a direct transformation of higher-order operators of the type  $(\hat{A} \cdot \hat{B})^n$  to the form of scalar products  $(\tilde{O}_A^{(k)} \cdot \tilde{O}_B^{(k)})$ . A brief review of examples of these operators in the literature is given. As a special case, a very simple form for electronic spin-spin coupling  $\hat{\mathcal{H}}_{ss}$  inside an  $LS$  term is derived. By extending the perturbational approach developed previously, general expressions for the contributions to spin Hamiltonians tensors from  $\hat{\mathcal{H}}_{ss}$  alone, as well as from  $\hat{\mathcal{H}}_{ss}$  and spin-orbit coupling jointly, are derived up to the fourth order in spin variables. The results are applied to the case of  $\text{Co}^{3+}(3d^6)$  ions in tetrahedral symmetry. A quantitative discussion yields good agreement with experiment for the parameter  $a$ , and confirms our earlier conclusion on the importance of the fourth order axial term  $F$ .

### 1. Introduction

In the past decade, there has been a tendency by numerous authors to introduce, into Hamiltonians for single ions in crystals or magnetically ordered systems, various higher-order terms of the type  $(\hat{A} \cdot \hat{B})^n$ , where  $n$  is an integer. The vectorial operators  $\hat{A}$  and  $\hat{B}$  can represent the orbital angular momentum operator  $\hat{L}$  or the spin operator  $\hat{S}$ , as the case may be.

At present, in crystal field and related theories, operator equivalents of the spherical harmonics  $\tilde{O}^{(k)}$ 's are widely used for single-ion problems because of their convenient transformation properties and the availability of Tables of their matrix elements.

Recently Thorpe [1], instead of  $(\hat{S}_i \cdot \hat{S}_j)^n$ , used spin equivalents of the spherical harmonics and defined an inner product  $C_i(\hat{S}_i \cdot \hat{S}_j)$  of spin operators at sites  $i$  and  $j$ . Any product  $C_i(\hat{S}_i \cdot \hat{S}_j)^n$ , can be expressed by means of products  $(\hat{S}_i \cdot \hat{S}_j)^n$ , and consists of a sum of the latter for  $n = 0, 1, \dots, l$ . Thereby, the relations of [1] are of the nature of a definition.

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In Section 2, on the basis of irreducible tensor algebra, we discuss a direct transformation of the products  $(\hat{A} \cdot \hat{B})^n$  to the form  $(\hat{O}_A^{(k)} \cdot \hat{O}_B^{(k)})$ . In Section 2, moreover, we give a brief review of examples of these higher-order operators found in the literature. Also, a very simple form of electronic spin-spin coupling  $\hat{\mathcal{H}}_{SS}$  within a given multiplet  $LS$  is derived.

For some transition metal ions, the contributions from  $\hat{\mathcal{H}}_{SS}$  to spin Hamiltonian tensors can be of a magnitude comparable with the contributions arising from spin-orbit coupling  $\hat{\mathcal{H}}_{SO}$  alone, because the former arise in lower orders of perturbation theory [2]. Therefore, in Section 3, by extending the perturbational approach developed in [3], relevant contributions from  $\hat{\mathcal{H}}_{SS}$  alone, as well as from  $\hat{\mathcal{H}}_{SS}$  and  $\hat{\mathcal{H}}_{SO}$  jointly, are derived. The resulting expressions, which are applicable to any symmetry of the crystalline environment and to any  $3d^n$  ion with orbitally nondegenerate ground state, have hitherto not been reported in the literature.

In Section 4, we apply the general expressions to the case of  $\text{Co}^{3+}(3d^6)$  ion in tetrahedral symmetry site. The present calculations confirm our earlier conclusion [4] on the importance of the fourth order axial term  $F$  and yield better agreement with the experimental value of  $|a|$ .

Section 5 contains a discussion of the parallel method of Wybourne [5] for deriving an effective Hamiltonian, in comparison with our method.

## 2. Higher-order operators

We consider the  $n$ -th power of a scalar product  $(\hat{A} \cdot \hat{B})^n$ . In other words,  $(\hat{A} \cdot \hat{B})^n$  is the  $n$ -multiple product of single invariant products  $(\hat{A} \cdot \hat{B})$ . Hence, we can apply recoupling procedure and change the coupling scheme to that desired in any particular case [6].

The recoupling scheme most suitable to our aims is illustrated by the graphical methods of Jucys and Bandzaitis [7] in Fig. 1.

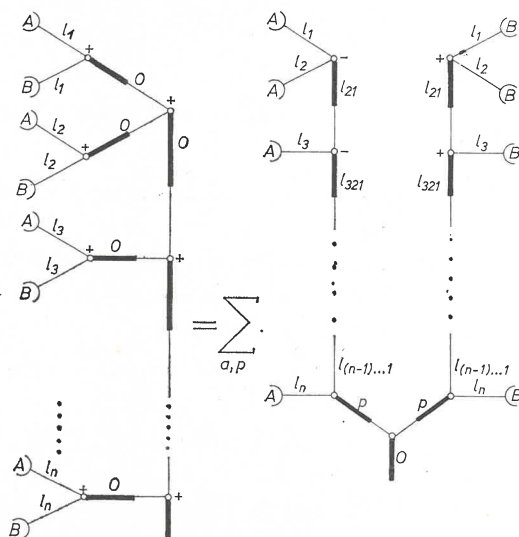


Fig. 1. Graphical representation of the recoupling procedure

The corresponding expression is written as follows:

$$\begin{aligned} & (A^{(l_n)} \cdot B^{(l_n)}) \dots (A^{(l_3)} \cdot B^{(l_3)}) (A^{(l_2)} \cdot B^{(l_2)}) (A^{(l_1)} \cdot B^{(l_1)}) = \\ & = \sum_{a,p} [A^{(l_n)} \times \dots \times [A^{(l_3)} \times [A^{(l_2)} \times A^{(l_1)}]^{(l_{21})}]^{(l_{321})} \dots]^{(l_{(n-1) \dots 321})} ]^{(p)}, \\ & \cdot [B^{(l_n)} \times \dots \times [B^{(l_3)} \times [B^{(l_2)} \times B^{(l_1)}]^{(l_{21})}]^{(l_{321})} \dots]^{(l_{(n-1) \dots 321})} ]^{(p)} \end{aligned} \quad (1)$$

where  $\Sigma_a$  denotes a sum over all intermediate  $\{l_{i\dots j}\}$ .

In the case under consideration, all  $l_i = 1$ , and  $p$  runs over  $\{0, 1, \dots, n\}$ . Eq. (1) expresses the direct transformation of  $(\hat{A} \cdot \hat{B})^n$  to a sum of products of  $p$ -th rank tensor operators  $\hat{Q}^{(p)} = [ \quad ]^{(p)}$ . Any single operator  $[A \times \dots \times [A \times A]^{(l)}]^{(p)} = \hat{Q}_A^{(p)}$  is at the same time a spherical tensor operator of the variables  $(\hat{A}_0, \hat{A}_{\pm 1})$ , where  $\hat{A}_i$  are the spherical components of a vector operator  $\hat{A}$ . (In this paper, we adopt the basic definitions of tensor algebra in accordance with Ref. [7].)

Hence, using commutation relations, we can transform the  $\hat{Q}^{(p)}$ 's to other angular momentum tensor operators, as done by us in an earlier paper [3]. We had chosen, among others, the operators  $O_q^{(k)}$  ( $j_z, j_{\pm}$ ) tabulated in [8]. In order to maintain the same phase factor as in [7], we introduced new operators  $\tilde{O}^{(k)}$ , defined as:

$$\tilde{O}_q^{(k)} = i^k O_q^{(k)}. \quad (2)$$

We established [3] the following transformation relations for single particle operator products:

$$\begin{aligned} \hat{Q}^{(p)} &= [X^{(1)} \times X^{(1)}]^{(p)} = \alpha_p \tilde{O}_X^{(p)} \\ \alpha_0 &= \frac{1}{\sqrt{3}} X^*; \quad \alpha_1 = -\frac{1}{\sqrt{2}} i; \quad \alpha_2 = \sqrt{\frac{2}{3}} \end{aligned} \quad (3)$$

and

$$\begin{aligned} \hat{Q}'^{(p)} &\equiv [X^{(1)} \times \hat{Q}^{(2)}]^{(p)} = \beta_p \tilde{O}_X^{(p)} \\ \beta_1 &= \frac{1}{2 \cdot \sqrt{15}} [4X^* - 1]; \quad \beta_2 = -i; \quad \beta_3 = \sqrt{\frac{2}{5}}, \end{aligned} \quad (4)$$

where  $X$  now stands for  $A$  or  $B$ , and  $X^* = X(X+1)$ , while  $\tilde{Q}_X^{(1)} \equiv \hat{X}$ .

Using Eq. (3) and (4), we obtain from the general expression (1) the desired direct transformation formulas as follows:

$$(\hat{A} \cdot \hat{B})^2 = \frac{1}{3} A^* B^* - \frac{1}{2} \tilde{O}_A^{(1)} \cdot \tilde{O}_B^{(1)} + \frac{2}{3} \tilde{O}_A^{(2)} \cdot \tilde{O}_B^{(2)}, \quad (5)$$

$$\begin{aligned} (\hat{A} \cdot \hat{B})^3 &= -\frac{1}{6} A^* B^* + \frac{1}{5} [3A^* B^* - A^* - B^* + 2] \tilde{O}_A^{(1)} \cdot \tilde{O}_B^{(1)} - \\ &\quad - \frac{4}{3} \tilde{O}_A^{(2)} \cdot \tilde{O}_B^{(2)} + \frac{2}{5} \tilde{O}_A^{(3)} \cdot \tilde{O}_B^{(3)}. \end{aligned} \quad (6)$$

Terms of powers higher than 3 are rarely found in the literature.

The higher-order operators of the type under consideration fall into the following two groups:

1. Isotropic exchange interactions,
  2. Terms  $(\hat{L} \cdot \hat{S})^n$ , like spin-orbit coupling.
1. The most general isotropic exchange interaction given by Thorpe [1] is:

$$\hat{\mathcal{H}} = \frac{1}{2} \sum_{ijm} J_{ij}^{(n)} C_n(\hat{S}_i \cdot \hat{S}_j). \quad (7)$$

On comparing our Eq. (5) and the corresponding one of [1], it is clear that  $\tilde{O}_A^{(2)} \cdot \tilde{O}_B^{(2)}$  identifies with  $C_2(\hat{S} \cdot \hat{S})$  and the conveniently defined spin spherical harmonics  $C_{l,m}(\hat{S})$  equal our  $\tilde{O}_q^{(k)}$ 's.

In the literature, one finds three different approaches to higher-order exchange interaction terms. Some authors simply incorporate the biquadratic exchange term  $j(\hat{S} \cdot \hat{S})^2$  into the Hamiltonian [1] [9]. Others have attempted to explain the existence of these higher-order terms by perturbation theory calculations on assuming the usual exchange  $J(\hat{S} \cdot \hat{S})$  to be the zero-order term [10].

Others have treated the  $n$ -th order exchange terms as allowed by symmetry [11], or on the basis of Schrödinger's generalization of the Dirac permutation operator  $P_{ij}$  for spin  $S = \frac{1}{2}$  to cases of arbitrary spin  $S$  [12].

2. Terms  $(\hat{L} \cdot \hat{S})^n$  like spin-orbit coupling occur in the literature in the three following problems:

a) For the description of the spin-orbit splitting inside an orbital triplet  $T_2$  of a  $3d^n$  ion [13].

b) Similarly to case (a), Karayanis [14] introduced for the description of the ground term of a  $4f^n$  ion an effective spin-orbit Hamiltonian  $H_E = \sum_n \lambda_n (\hat{L} \cdot \hat{S})^n$ , with  $1 \leq n \leq 2S$ .

c) The effective electronic spin-spin coupling inside a given  $LS$  term, as is well known, can be written as [15] [3] [16]:

$$\hat{\mathcal{H}}_{SS} = -\varrho [(\hat{L} \cdot \hat{S})^2 + \frac{1}{2} (\hat{L} \cdot \hat{S}) - \frac{1}{3} L^* S^*]. \quad (8)$$

On inserting Eq. (5) into Eq. (8), we obtain:

$$\hat{\mathcal{H}}_{SS} \equiv -\frac{2}{3} \varrho \tilde{O}_L^{(1)} \cdot \tilde{O}_S^{(2)}. \quad (9)$$

The resulting expression (9) is very simple in form and obviously more convenient for further calculations than Eq. (8). In the same way, one can simplify the quadrupole interaction term in atomic spectroscopy [16] [17].

### 3. Electronic spin-spin coupling contributions to spin Hamiltonian tensors

We introduce the following brief notation for the matrix elements of orbital angular momentum operators:

$$L_{\alpha\beta}^{(2)} \equiv [\alpha | \tilde{O}_L^{(2)} | \beta] \quad \text{and} \quad L_{\alpha\beta}^{(1)} \equiv [\alpha | \tilde{O}_L^{(1)} | \beta], \quad (10)$$

where  $\tilde{O}_L^{(1)}$  equals  $\hat{L}$  if the operator  $\hat{L}$  is written in spherical coordinates [7].

For details of the perturbation theory formalism and the mathematical techniques, we refer to [18] and [3] respectively.

On recoupling the scalar products occurring in the crude perturbation expressions and applying the symmetry predictions [3], we obtain the relevant terms arising from the consecutive orders of perturbation theory. We write the general spin Hamiltonian derived in this manner in the following form:

$$\hat{\mathcal{H}} = B^{(2)} \cdot \tilde{O}_S^{(2)} + B^{(4)} \cdot \tilde{O}_S^{(4)}. \quad (11)$$

Below, we derive expressions for the contributions under consideration to the tensors  $B^{(2)}$  and  $B^{(4)}$ .

### A. Contributions from $\hat{\mathcal{H}}_{SS}$ alone

#### 1. First order of perturbation theory:

$${}^1B^{(2)} = -\frac{2}{3} \varrho L_{00}^{(2)} \quad (12)$$

#### 2. Second order:

$${}^2B^{(2)} = -\frac{4}{9} \gamma_2 \varrho^2 \sum_{\alpha} \frac{1}{\Delta_{\alpha}} T_{\alpha}^{(2)}, \quad (13)$$

$${}^2B^{(4)} = -\frac{4}{9} \gamma_4 \varrho^2 \sum_{\alpha} \frac{1}{\Delta_{\alpha}} T_{\alpha}^{(4)}, \quad (14)$$

where

$$T_{\alpha}^{(k)} = [L_{0\alpha}^{(2)} \times L_{\alpha 0}^{(2)}]^{(k)}. \quad (15)$$

The values of the coefficients  $\gamma_k$  are given in Appendix A. The explicit formulas for the components of the tensors  $T_{\alpha}^{(k)}$  are straightforwardly obtainable from the Tables of [19] for decomposition of the product  $D^{(2)} \otimes D^{(2)}$ .

Using the rough values  $(\lambda/\varrho) \approx 10^2$  and  $\Delta \approx 10^3 \div 10^4 \text{ cm}^{-1}$  [2], one can predict that the contribution  ${}^2B^{(2)}$  is negligibly small in comparison with the usual  $B^{(2)}$  of order  $(\lambda^2/\Delta)$ . On the other hand,  ${}^2B^{(4)}$  can be, at the most, comparable to the usual  $B^{(4)}$ , which is of order  $(\lambda^4/\Delta^3)$ . For this reason, no higher contributions of the type A will be considered.

### B. Contributions from $\hat{\mathcal{H}}_{SS}$ and $\hat{\mathcal{H}}_{S0}$ jointly

#### 1. Second order of perturbation theory:

$${}^2B'^{(2)} = \frac{2}{3} \delta_2 \varrho \lambda \sum_{\alpha} \frac{1}{\Delta_{\alpha}} \{U_{\alpha}^{(2)} + U'_{\alpha}{}^{(2)}\}, \quad (16)$$

where

$$U_{\alpha}^{(2)} = [L_{0\alpha}^{(1)} \times L_{\alpha 0}^{(2)}]^{(2)}; \quad U'_{\alpha}{}^{(2)} = [L_{0\alpha}^{(2)} \times L_{\alpha 0}^{(1)}]^{(2)}. \quad (17)$$

For the definition of the coefficient  $\delta_2$ , see Appendix A. The contribution  ${}^2B^{(2)}$  is about one hundredth of  $B^{(2)}$ .

## 2. Third order:

We consider only the terms of order  $(\rho\lambda^2/\Delta^2)$ , as only they can be of a magnitude comparable with  $B^{(4)} \sim (\lambda^4/\Delta^3)$ .

We obtain, among others, the following term:

$$\begin{aligned} \sum_{\alpha,\beta} \frac{1}{\Delta_\alpha \Delta_\beta} \{ & (L_{0\alpha}^{(1)} \cdot \tilde{O}^{(1)}) (L_{\alpha\beta}^{(1)} \cdot \tilde{O}^{(1)}) (L_{\beta 0}^{(2)} \cdot \tilde{O}^{(2)}) + \\ & + (L_{0\alpha}^{(1)} \cdot \tilde{O}^{(1)}) (L_{\alpha\beta}^{(2)} \cdot \tilde{O}^{(2)}) (L_{\beta 0}^{(1)} \cdot \tilde{O}^{(1)}) + \\ & + (L_{0\alpha}^{(2)} \cdot \tilde{O}^{(2)}) (L_{\alpha\beta}^{(1)} \cdot \tilde{O}^{(1)}) (L_{\beta 0}^{(1)} \cdot \tilde{O}^{(1)}) \}. \end{aligned} \quad (18)$$

Any of the terms in Eq. (18) can contribute to  $B^{(2)}$ , but this part is irrelevant for our purposes, since it is negligibly small. On applying the commutation relations for spin tensor operators [20] to a single product from Eq. (18), for example to  $(A^{(2)} \cdot \tilde{O}^{(2)}) (B^{(1)} \cdot \tilde{O}^{(1)})$ , one obtains a product with inverted sequence  $(B^{(1)} \cdot \tilde{O}^{(1)}) (A^{(2)} \cdot \tilde{O}^{(2)})$  plus a term linked with the operator  $\tilde{O}^{(2)}$  alone. The part  $\tilde{O}^{(2)}$ , inserted into a triple product in Eq. (18), cannot lead to any term of fourth order in spin variables, *e. g.* to a term linked with  $\tilde{O}^{(4)}$ . Thus, one is justified in changing the sequence in any triple product in order to obtain a more convenient form of Eq. (18). We choose a form like (1) (1) (2).

Finally, we obtain the following expression for the third-order contribution to the tensor  $B^{(4)}$ :

$$\begin{aligned} {}^3B^{(4)} = & + \frac{2}{3} \alpha_2 \gamma_4 \rho \lambda^2 \left\{ \sum_{\alpha} \frac{1}{\Delta_\alpha^2} ([L_{0\alpha}^{(1)}, L_{\alpha 0}^{(1)}, L_{00}^{(2)}]^{(4)} - [L_{0\alpha}^{(1)}, L_{\alpha 0}^{(1)}, L_{\alpha\alpha}^{(2)}]^{(4)}) - \right. \\ & \left. - \sum_{\alpha \neq \beta} \frac{1}{\Delta_\alpha \Delta_\beta} ([L_{0\alpha}^{(1)}, L_{\alpha\beta}^{(1)}, L_{\beta 0}^{(2)}]^{(4)} + [L_{0\alpha}^{(1)}, L_{\beta 0}^{(1)}, L_{\alpha\beta}^{(2)}]^{(4)} + [L_{\alpha\beta}^{(1)}, L_{\beta 0}^{(1)}, L_{0\alpha}^{(2)}]^{(4)}) \right\} \end{aligned} \quad (19)$$

where the symbol  $[ , , ]^{(4)}$  has the following meaning:

$$V^{(4)} \equiv [L_i^{(1)}, L_j^{(1)}, L_k^{(2)}]^{(4)} \equiv [[L_i^{(1)} \times L_j^{(1)}]^{(2)} \times L_k^{(2)}]^{(4)}. \quad (20)$$

The coefficient  $\alpha_2$  is given by Eq. (3). The explicit formulas for components of the tensors  $V^{(4)}$  are to be obtained by a stepwise procedure  $((D^{(1)} \otimes D^{(1)}) \otimes D^{(2)})$  from the Tables of Ref. [19]. In Appendix A, we give only the tensor components  $V_0^{(4)}$  and  $V_{\pm 4}^{(4)}$  relevant for the cubic and tetragonal symmetries.

## 4. Application to $\text{Co}^{3+}$ ( $3d^6$ ) ions in tetrahedral symmetry

Previously, we derived general expressions for contributions to spin-Hamiltonian tensors from  $\hat{\mathcal{H}}_{SO}$  alone [3] and applied them to the case of  $\text{Co}^{3+}(3d^6)$  ion in garnet structure [4]. The conventional fourth-order axial term  $F$  was shown to be relevant, but only poor agreement with the experimental [21] value for the parameter  $a$  was achieved [4].

Below, the contributions to the tensors  $B^{(2)}$  and  $B^{(4)}$  from  $\hat{\mathcal{H}}_{SS}$ , as well as from  $\hat{\mathcal{H}}_{SS}$  and  $\hat{\mathcal{H}}_{SO}$  jointly, are derived in the explicit form for the case under consideration. The matrix elements  $L_{\alpha\beta}^{(1)}$  for  $\text{Co}^{3+}$  ion in  $S_4$  symmetry were evaluated in [4], whereas the  $L_{\alpha\beta}^{(2)}$  are evaluated in Appendix B of this paper. We illustrate the possible "transfer processes" in Fig. 2.

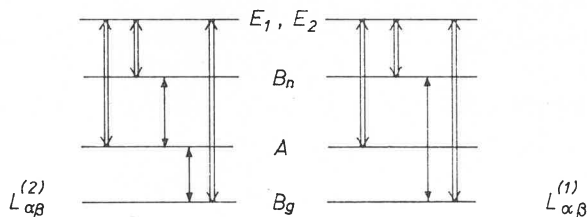


Fig. 2. The possible transfer processes within the states arising from a  ${}^5D$  term in tetrahedral symmetry

### A. Contributions from $\hat{\mathcal{H}}_{SS}$ alone

$$1. \quad {}^1B_0^{(2)} = +2\varrho \quad (21)$$

$$2. \quad {}^2B_0^{(2)} = -\frac{9}{14} \varrho^2 \left( \frac{4}{\Delta_A} - \frac{3}{\Delta_E} \right) \quad (22)$$

$$3. \quad {}^2B_0^{(4)} = \frac{12}{35} \varrho^2 \left( \frac{6}{\Delta_E} - \frac{1}{\Delta_A} \right)$$

$${}^2B_{+4}^{(4)} = -\frac{12}{\sqrt{70}} \varrho^2 v^2 \frac{1}{\Delta_A}$$

$${}^2B_{-4}^{(4)} = -\frac{12}{\sqrt{70}} \varrho^2 u^2 \frac{1}{\Delta_A} \quad (23)$$

where  $\Delta_i = E_i - E_{Bg}$ , and  $u, v$  are coefficients arising by diagonalization of  $\hat{\mathcal{H}}_{CF}$  of  $S_4$  symmetry within  $B_g^0$  and  $B_n^0$  states [4].

### B. Contributions from $\hat{\mathcal{H}}_{SS}$ and $\hat{\mathcal{H}}_{SO}$ jointly

$$1. \quad {}^2B_0^{(2)} = \varrho \lambda \frac{6}{\Delta_E} \quad (24)$$

$$2. \quad {}^3B_0^{(4)} = \frac{12}{35} \varrho \lambda^2 \left( \frac{12}{\Delta_B \Delta_E} + \frac{1}{\Delta_B^2} - \frac{2}{\Delta_A \Delta_E} - \frac{3}{\Delta_E^2} \right)$$

$${}^3B_{+4}^{(4)} = -6 \sqrt{\frac{2}{35}} \varrho \lambda^2 v^2 \left( \frac{2}{\Delta_A \Delta_E} + \frac{1}{\Delta_E^2} \right)$$

$${}^3B_{-4}^{(4)} = -6 \sqrt{\frac{2}{35}} \varrho \lambda^2 u^2 \left( \frac{2}{\Delta_A \Delta_E} + \frac{1}{\Delta_E^2} \right). \quad (25)$$

All the other components of the tensors  $B^{(2)}$  and  $B^{(4)}$  vanish identically, since they are not allowed by the symmetry  $S_4$ .

From the optical data of [22], the following values were taken [21] [4]:

$\Delta_E = 8.300 \text{ cm}^{-1}$ ;  $\Delta_B = 5.200 \text{ cm}^{-1}$ ;  $\Delta_A = 1000 \div 2000 \text{ cm}^{-1}$ , while  $\lambda = -110 \text{ cm}^{-1}$  and  $\Delta_A = 1.200$  were assumed for numerical discussion [4].

For a lack of  $\rho$ -value for  $\text{Co}^{3+}$  ion, the value  $\rho = +1 \text{ cm}^{-1}$  is taken as for the isoelectronic  $\text{Fe}^{2+}(3d^6, ^5D)$  ion [15] [16]. The relations between our  $B_q^{(k)}$ 's and the conventional spin Hamiltonian parameters are to be found in [3].

The most important contribution to the second-order parameter  $B_0^{(2)}$  is  ${}^1B_0^{(2)} = +2 \text{ cm}^{-1}$ , which is equivalent to  $D = -3 \text{ cm}^{-1}$ . The remaining  ${}^iB_0^{(2)}$  are negligibly small.

TABLE I  
Improved values of the parameters  $B_0^{(4)}$ ,  $B_4^{(4)}$  and  $a$ ,  $F$  (in  $\text{cm}^{-1}$ ) for  $\text{Co}^{3+}$  ion in garnets

$\Delta_A \text{ cm}^{-1}$	1.000	1.200	2.000
${}^2B_0^{(4)}(\rho^2)$	-0.00010	-0.00004	+0.00007
${}^3B_0^{(4)}(\rho\lambda^2)$	+0.00051	+0.00068	+0.00101
$B_0^{(4)}$	+0.00041	+0.00064	+0.00108
${}^2B_4^{(4)}(\rho^2)$	-0.00143	-0.00119	-0.00071
${}^3B_4^{(4)}(\rho\lambda^2)$	-0.00443	-0.00372	-0.00234
$B_4^{(4)}$	-0.00586	-0.00491	-0.00305
$a_{ss} + a_{ss-so}$	-0.147	-0.123	-0.076
$a_{so}$	-0.048	-0.040	-0.025 <sup>1</sup>
$a$	-0.195	-0.163	-0.101
$F_{ss} + F_{ss-so}$	+0.230	+0.199	+0.139
$F_{so}$	+0.113	+0.103	+0.084 <sup>1</sup>
$F$	+0.343	+0.302	+0.223

<sup>1</sup> Values from Ref. [4].

For a quantitative discussion of the parameters  $B_q^{(4)}$ , we neglect the mixing of states  $B_g^0$  and  $B_n^0$ . Then,  $u = v = 1$  and  $B_{+4}^{(4)} = B_{-4}^{(4)} = B_4^{(4)}$  [4]. The values of the fourth-order parameters are listed in Table I. They permit the following conclusions:

1. The terms of order  $(\rho\lambda^2)$  arising from the third order of perturbation theory contribute more strongly to the  $B_0^{(4)}$  and  $B_4^{(4)}$  than the terms  $(\rho^2)$  from second order of theory.
2.  $\hat{\mathcal{H}}_{SS}$  coupling alone, as well as  $\hat{\mathcal{H}}_{SS}$  and  $\hat{\mathcal{H}}_{SO}$  jointly, contribute more strongly to  $B_4^{(4)}$  but rather slightly to  $B_0^{(4)}$ .
3. The contributions of both types considered in this paper are considerably larger than those arising from  $\hat{\mathcal{H}}_{SO}$  alone. Hence, the present calculations provide a reasonable refinement of our earlier work [4].



4. Our theoretical value  $a = -0.163$  for  $\Delta_A = 1.200 \text{ cm}^{-1}$  is now of the same order of magnitude as  $|a| = 0.66 \text{ cm}^{-1}$  obtained from EPR [21]. Agreement between the two values is now better.

5. The present calculations confirm the importance of the fourth-order axial term  $F$  and show that the omission by previous authors [21] of the  $F$  term when fitting the spin-Hamiltonian to experiment was, at the least, unjustified.

### 5. Remarks on the method

Recently, Wybourne [5] developed a general theory of effective operators based on perturbation theory and tensor operator algebra. It may be worth while to compare the two methods.

In our method [3], we deal with the recoupling of products of orbital operator matrix elements (which are tensors) and spin tensor operators. The occurrence of such products was due to the implicit structure of the perturbation problem considered, without a necessity for any additional assumptions.

On the other hand, instead of the "real" perturbation operator  $\hat{V}$ , Wybourne [5] introduced by definition certain effective perturbing potentials  $\hat{V}_{AB}$ 's. Any  $\hat{V}_{AB}$  was restricted to act only between given zero-order states  $\langle Aa|$  and  $|Bb\rangle$ . Hence, Wybourne was able to apply the closure theorem for a complete set of states to the numerators in the perturbation expressions. That, in turn, led to a product of operators  $\hat{V}_{AB}\hat{V}_{BC}\dots\hat{V}_{ZA}$  alone, playing the role of an effective interaction within the zero-order states  $\{|Aa\rangle\}$  of the ground energy level. It was only at this stage of the theory that Wybourne used the recoupling formalism for transforming the product operator  $\hat{V}_{AB}\hat{V}_{BC}\dots\hat{V}_{ZA}$  to a simpler form.

Thus, our method is not a special case of the more general method of Wybourne, despite the similar mathematical techniques applied in both.

### 6. Conclusions

We have considered, firstly, a direct transformation of higher order operators. Then, with the form obtained for spin-spin coupling  $\hat{\mathcal{H}}_{SS}$ , we derived general expressions for the contributions to spin Hamiltonian tensors involving  $\hat{\mathcal{H}}_{SS}$ . The utility of this extension of our previous calculations [3] [4] is proven by the quantitative results derived for a  $\text{Co}^{3+}$  ion in garnets.

However, further extension of our method suggest themselves. The following appear to be the most relevant:

1. Consideration of higher-order Zeeman terms of the type  $(HS^3)$  which can be of importance in the interpretation of EPR and ENDOR spectra in some cases [24].

2. Modification of the model to treat ions with orbitally degenerate ground states. This should lead to a two-; or three-dimensional spin Hamiltonian for  $E_g$  and  $T_{2g}$  ground states, respectively [18] [25].

We intend to deal with these problems in future papers.

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## APPENDIX A

1. We establish only the relevant coefficients needed in Eqs (13) and (14)

$$[\tilde{O}^{(2)} \times \tilde{O}^{(2)}]^{(k)} = \gamma_k \tilde{O}^{(k)}$$

$$\gamma_2 = \frac{1}{2\sqrt{14}}(4j(j+1)-15); \quad \gamma_4 = \frac{6}{\sqrt{70}}. \quad (\text{A1})$$

In Eq. (A1), we proceed as described in Section 2 of this paper. Application of the isomorphism of the solid harmonics  $C^{(k)}$  and  $O^{(k)}$  [8] by using the expression Eq. (4-5) in [33] for  $[C^{(k)} \times C^{(k)}]^{(K)} = a_K C^{(K)}$  is not allowed because the  $C^{(k)}$ 's do not obey the usual relations for the spin operators:

$$\hat{S} \cdot \hat{S} \rightarrow S(S+1) \quad \text{and} \quad \hat{S} \times \hat{S} = i\hat{S}.$$

2. In Eq. (16), we need:

$$[\tilde{O}^{(2)} \times \tilde{O}^{(1)}]^{(2)} = \delta_2 \tilde{O}^{(2)} \quad \text{and} \quad [\tilde{O}^{(1)} \times \tilde{O}^{(2)}]^{(2)} = \delta'_2 \tilde{O}^{(2)}. \quad (\text{A2})$$

$\delta'_2$  is expressed as the combination:

$$\delta'_2 = \frac{1}{\alpha_2} \beta_2 = -i \sqrt{\frac{3}{2}}, \quad (\text{A3})$$

whereas  $\delta_2$  was calculated separately, and we found that  $\delta_2 = \delta'_2$ .

3. In Eq. (18) we need:

$$[[\tilde{O}^{(1)} \times \tilde{O}^{(1)}]^{(2)} \times \tilde{O}^{(2)}]^{(4)} = \alpha_2 \gamma_4 \tilde{O}^{(4)}. \quad (\text{A4})$$

4. With the tensor  $V^{(4)}$  defined as follows:

$$V_q^{(4)} = [[X^{(1)} \times Y^{(1)}]^{(2)} \times L^{(2)}]_q^{(4)}, \quad (\text{A5})$$

its components relevant for cubic and tetrahedral symmetry are given explicitly as:

$$V_0^{(4)} = \frac{1}{\sqrt{70}} \{X_{+1}Y_{+1}L_{-2} + X_{-1}Y_{-1}L_{+2} + \sqrt{6}(X_0Y_0 + X_{-1}Y_{+1} + X_{+1}Y_{-1})L_0 +$$

$$+ 2\sqrt{2}((X_{+1}Y_0 + X_0Y_{+1})L_{-1} + (X_{-1}Y_0 + X_0Y_{-1})L_{+1})\},$$

$$V_{\pm 4}^{(4)} = X_{\pm 1}Y_{\pm 1}L_{\pm 2}. \quad (\text{A6})$$

## APPENDIX B

The following definition for a tensor orbital operator is adopted:  $\tilde{O}_L^{(2)} = \sum_q \hat{O}_q^{(2)} e_q^{[2]}$  and its matrix elements  $L_{\alpha\beta}^{(2)}$  are evaluated using Eq. (2) and Tables [26] [27] within the states arising from  ${}^5D$  term in tetrahedral symmetry (Table II).

TABLE II

	$B_g$	$A$	$B_n$	$E_1$	$E_2$
$B_g$	$-3\vec{e}_0^{[2]}$	$-\frac{3}{\sqrt{2}}(\alpha\vec{e}_{-2}^{[2]} + \beta\vec{e}_{+2}^{[2]})$	0	$-\frac{3}{2}\sqrt{3}\beta\vec{e}_1^{[2]}$	$+\frac{3}{2}\sqrt{3}\alpha\vec{e}_{-1}^{[2]}$
$A$	$-\frac{3}{\sqrt{2}}(\alpha\vec{e}_{-2}^{[2]} + \beta\vec{e}_{+2}^{[2]})$	$+3\vec{e}_0^{[2]}$	$-\frac{3i}{\sqrt{2}}(\alpha\vec{e}_{-2}^{[2]} - \beta\vec{e}_{+2}^{[2]})$	$+\frac{3}{2}\vec{e}_{-1}^{[2]}$	$-\frac{3}{2}\vec{e}_1^{[2]}$
$B_n$	0	$-\frac{3i}{\sqrt{2}}(\alpha\vec{e}_{-2}^{[2]} - \beta\vec{e}_{+2}^{[2]})$	$-3\vec{e}_0^{[2]}$	$+i\frac{3}{2}\sqrt{3}\beta\vec{e}_1^{[2]}$	$+i\frac{3}{2}\sqrt{3}\alpha\vec{e}_{-1}^{[2]}$
$E_1$	$\frac{3}{2}\sqrt{3}\alpha\vec{e}_{-1}^{[2]}$	$-\frac{3}{2}\vec{e}_1^{[2]}$	$i\frac{3}{2}\sqrt{3}\alpha\vec{e}_{-1}^{[2]}$	$\frac{3}{2}\vec{e}_0^{[2]}$	$\frac{3}{2}\sqrt{6}\vec{e}_2^{[2]}$
$E_2$	$-\frac{3}{2}\sqrt{3}\beta\vec{e}_1^{[2]}$	$+\frac{3}{2}\vec{e}_{-1}^{[2]}$	$i\frac{3}{2}\sqrt{3}\beta\vec{e}_1^{[2]}$	$+\frac{3}{2}\sqrt{6}\vec{e}_{-2}^{[2]}$	$+\frac{3}{2}\vec{e}_0^{[2]}$

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