ON PARAMETERS OF SPIN HAMILTONIAN FOR $3d^n$ IONS. Co³⁺ IONS IN TETRAHEDRAL SYMMETRY

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An extension of the previously given model for perturbation treatment of spin Hamiltonian parameters is discussed. Contributions to the parameters for $3d^6$ ions in tetrahedral symmetry are derived. Quantitative results for Co³⁺ ions in garnets reveal the importance of the fourth order axial term F.

1. Introduction

In an ealier paper (to be referred to as I) we derived general expressions for spin Hamiltonian parameters adopting a new technique based on tensor algebra [1].

We used, in I, a "model" Hamiltonian of the form:

$$\hat{\mathscr{H}} = \hat{\mathscr{H}}_0 + \lambda \hat{\vec{L}} \cdot \hat{\vec{S}} + \mu_B (\hat{\vec{L}} + 2\hat{\vec{S}}) \cdot \vec{H}, \qquad (1)$$

where

$$\hat{\mathscr{H}}_0 = \hat{\mathscr{H}}_{\text{f.i.}} + \hat{\mathscr{H}}_{CF}. \qquad (2)$$

By using in (1) a simplified form of spin-orbit coupling, we limited our considerations to a space Ω od states arising from the lowest free-ion (f.i.) term ^{2S+1}L.

In the present paper we discuss an extension and application of the results of I. In Section 2 we discuss the effect of "mixing of states" in relation to the formalism of 1. In Section 3 we derive the relevant expressions for a $3d^6$ ion in a tetrahedral symmetry site. Expressions for the fourth order parameters have hitherto not been given in the literature.

2. Effect of mixing of states

$3d^n$ ions fall into one of the two following groups:
a) ones possessing the ground term ^{2S+1}D ($n = 1, 4, 6, 9$) and no higher term with the same spin multiplicity $(2S+1)$,

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b) ones possessing the ground term ^{2S+1}F ($n = 2, 3, 7, 8$) and one ^{2S+1}P term with the same S among the higher terms.

An exception from the above are the $3d^5$ ions being ^6S-state ions.

A crystal field Hamiltonian $\hat{\mathscr{H}}_{CF}$ in (2), when treated as a perturbation to $\hat{\mathscr{H}}_{f.i.}$, can mix only those zero-order states $|_v^{2S+1}\Gamma_{\alpha\mu}]$ of $\hat{\mathscr{H}}_{f.i.}$ which transform according to the same representation Γ_α and have the same S-number [2].

Thus, for ions (a), the zero-order states can be mixed by $\hat{\mathscr{H}}_{CF}$ only inside a manifold of states arising from a given term. The diagonalization of $\hat{\mathscr{H}}_0$ is then relatively simple. If this is the case the proper states of $\hat{\mathscr{H}}_0$ will be linear combinations of states $|^{2S+1}\Gamma_{\alpha\mu}(L)]$ with L and S fixed only.

When limiting considerations to the space Ω, the results of I apply directly to this case.

For ions (b), the exact diagonalization leads, among others, to linear combinations of states arising from different terms, as *e.g.*

$$|^{2S+1}\Gamma_{\alpha\mu}(F)] \quad \text{and} \quad |^{2S+1}\Gamma_{\beta\nu}(P)]. \tag{3}$$

An approximate method of diagonalization of the relevant secular determinants is developed in [3]. The above procedure leads to so-called "mixing of states" [4].

The extension of the space Ω to include states arising from the higher ^{2S+1}P term should improve the results. But then we have to take the perturbation operator in the modified form:

$$\hat{V} = (\lambda_F \hat{\vec{L}} + \lambda_P \hat{\vec{L}'}) \cdot \hat{\vec{S}} + \mu_B[(\hat{\vec{L}} + \hat{\vec{L}'}) + 2\hat{\vec{S}}] \cdot \vec{H}, \tag{4}$$

where λ_F and λ_P are spin-orbit coupling constants for the F and P term, respectively. The operator $\hat{\vec{L}}$ operates only on states $|\Gamma_{\alpha\mu}(F)]$, while $\hat{\vec{L}'}$ acts only on $|\Gamma_{\beta\nu}(P)]$.

The form of Eq. (4) ensures that matrix elements of $\hat{V}$ inside the basis of orbital states will still take the form of a scalar product like $(\hat{\vec{A}} \cdot \hat{\vec{S}})$. Thus, the formalism of I based on tensor algebra can be directly used in this case. The sense of the vectors $\vec{L}_{ij}$ changes, while the structure of the final expressions remains the same. Only the constants λ has to be omitted from the expressions in question, as it is now absorbed into $\hat{\vec{L}}_{eff}$.

The inclusion into our considerations of other higher terms $^{2S'+1}L'$ with different spin multiplicity is possible when using the exact form of spin-orbit coupling. This has been attempted for the second order parameter D with regard to V^{3+} ions in Al_2O_3 [5].

3. The case of $3d^5$ ions in tetrahedral symmetry

Recently, Sturge *et al.* [6] have investigated Co ions doped into YGaG and YIG compounds. The spin Hamiltonian used by them included $g_\perp$, $g_{\parallel}$, D and $a/6$ conventional terms. A fourth order axial term $F/180$ was neglected. The following expressions for D and a were given by them:

$$D = -\lambda^2 \left[\frac{4}{\Delta_B} - \frac{1}{\Delta_E} \right] - \lambda^2 \frac{4}{\Delta_T}, \tag{5}$$

$$a = -4D^2/\Delta_A + \text{terms of order } \lambda^4/\Delta^3. \tag{6}$$

The appropriate energy level diagram for a Co^{3+} ion in a tetrahedral symmetry site is shown in Fig. 1.

From the optical data [7], it is known that $\Delta_T = 9\,200$ cm^{-1}, $\Delta_D = 8\,300$ cm^{-1}, $\Delta_B = 5\,200$ cm^{-1}. The value of Δ_A is not known for Co^{3+} ions but was believed [6] to be in the range $1\,000$ cm^{-1} to $2\,000$ cm^{-1}.

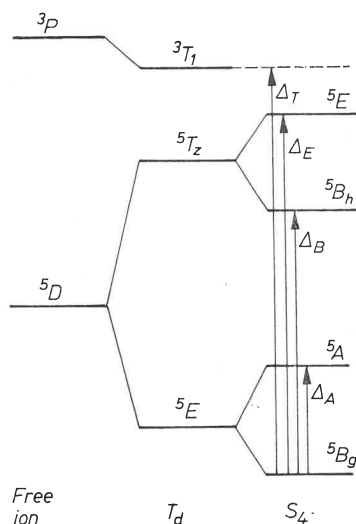The merely tentative Eq. (6) was used for a crude estimation of Δ_A as about $1\,200$ cm^{-1} [6].

Fig. 1. Energy level diagram for tetrahedral Co^{3+} in garnets (not to scale)

Since the Co^{3+} ion $(3d^6)$ belongs to group (a) of $3d^n$ ions, we can afford to carry out a more detailed analysis.

General formulas for spin-Hamiltonian parameters applicable to any symmetry are derived in I and will not be given here. Using moreover the equations of Appendix B in I and taking into consideration the relevant energy-level diagram of an ion, one can directly obtain any desired contribution to the parameters.

In this paper, the zero-order wave functions are taken from [8] and a secular determinant for the ground B_g and higher B_h states is diagonalized (see Appendix A). Matrix elements $\vec{L}_{ij}$ of the operator $\hat{\vec{L}}$ inside a manifold of states arising from the ^5D term are evaluated in Appendix B.

Along these lines, we obtain for $g_\perp$, $g_\parallel$ and D the same expressions as in [6] (except for the term $4\lambda^2/\Delta_T$ in (5)).

The third order contribution to D is obtained by us as:

$$D_3 = -(3 + \sqrt{3})\lambda^3 \frac{1}{\Delta_B \Delta_E}. \tag{7}$$

Using $\lambda = -110$ cm^{-1} [6], we obtain $D_3 \approx +0.15$ cm^{-1}, while D from the second order expressions is estimated as 7.8 cm^{-1} (without including the term $4\lambda^2/\Delta_T$). This ensures that a fourth order correction to D is completely negligible.

We obtain the third order corrections to the g-tensor as:

$$(g_3^a)_{\|} = -\frac{4\lambda^2}{\Delta_E \Delta_B} \qquad\qquad (g_3^a)_{\perp} = 0$$

$$(g_3^b)_{\|} = -\frac{2\lambda^2}{\Delta_E^2} \qquad\qquad (g_3^b)_{\perp} = -\lambda^2 \left(\frac{4}{\Delta_B^2} + \frac{1}{\Delta_E^2} \right). \tag{8}$$

Eq. (8) gives for both $g_{\|}$ and $g_{\perp}$ a value of -0.002, comparable with current experimental error for $g_{\|}$ and $g_{\perp}$. This ensures that a fourth order contribution to the g-tensor is irrelevant too.

The fourth order parameters $B_q^{(4)}$ of spin-Hamiltonian were defined in (I) as:

$$\mathscr{H}^{(4)} = \sum_q (-1)^{4-q} B_q^{(4)} \tilde{O}_{-q}^{(4)} \tag{9}$$

where the $\tilde{O}_q^{(4)}$'s were components of an operator equivalent (for definition, see I).

From our general formulas, the following expressions are found for the $B_q^{(4)}$'s:

$$B_0^{(4)} = \frac{8}{35\sqrt{10}} \lambda^4 \left[\frac{32}{\Delta_B^3} + \frac{2}{\Delta_E^3} - \frac{8}{\Delta_B \Delta_E^2} - \frac{3}{\Delta_A \Delta_E} \right]$$

$$B_{+4}^{(4)} = -\frac{12}{5\sqrt{7}} \lambda^4 \frac{1}{\Delta_A \Delta_E^2} u^2$$

$$B_{-4}^{(4)} = -\frac{12}{5\sqrt{7}} \lambda^4 \frac{1}{\Delta_A \Delta_E^2} v^2, \tag{10}$$

where u and v describe a mixing of $|B_g^0]$ and $|B_h^0]$ states by the crystal field $\hat{\mathscr{H}}_{CF}$ (see Appendix A).

On neglecting this mixing effect, $u = v \equiv 1$ and $B_{-4}^{(4)} = B_{+4}^{(4)} \equiv B_4^{(4)}$. For this case, the relations between our $B_q^{(4)}$'s and the conventional parameters a and F, as established in I, are:

$$a = 3\sqrt{70}\, B_4^{(4)}$$

$$F = \tfrac{9}{2} \left[5 B_0^{(4)} - \sqrt{70}\, B_4^{(4)} \right]. \tag{11}$$

From Eqs (10) and (11), we see that no contributions like $1/\Delta_B \Delta_A \Delta_E$ or $1/\Delta_A \Delta_B^2$ can enter into the expression for a.

On inserting into Eqs (10) the (above stated) values of Δ_i and λ, we find the values of a and F given in Table I.

Our calculations yield F larger than a, proving the former's real importance. The value of $|a| = 0.66$ cm^{-1} obtained by EPR [6] is by one order of magnitude larger than our result.

TABLE I

Values of parameters $B_0^{(4)}$, $B_4^{(4)}$ a and F (in cm^{-1})

Δ_A[cm^{-1}]	1.000	1.200	2.000
$B_0^{(4)}$	+0.0018	+0.0019	+0.0021
$B_4^{(4)}$	−0.0019	−0.0016	−0.0010
a	−0.048	−0.040	−0.025
F	+0.113	+0.103	+0.084

TABLE II

Parameters a and F for Fe^{3+} ions in (d) sites in some garnets (in cm^{-1})

Host	a	F	References
YAlG	0.0075	−0.0110	[9]
LuAlG	0.0084	−0.0104	[9]
LuGaG	0.0065	−0.0047	[9]
YGaG	0.0062	−0.0040	[10]

For comparison, we refer in Table II to some other experimental dates for Fe^{3+} ions in tetrahedral (d) sites of garnets [9], [10].

Although the data of Table II are not directly comparable with our results, they nevertheless confirm the fact that the relation $F > a$ is quite reasonable in the present case. Our detailed analysis shows that this is so for Co^{3+} ions.

In concluding, the exceptionally large value of a obtained in [6] can be attributed to the incorrect omission of the fourth order axial term F in the spin-Hamiltonian.

APPENDIX A

The basis of zero-order states for the B representations of the group S_4 is [8]:

$$|B_g^0] = \frac{1}{\sqrt{2}} (|2, 2] + |2, -2]),$$

$$|B_h^0] = \frac{i}{\sqrt{2}} (|2, 2] - |2, -2]). \tag{A.1}$$

The diagonalization of a secular determinant of $\hat{\mathscr{H}}_{CF}$ of symmetry S_4 yields:

$$|B_g] = \frac{1}{\sqrt{2}} (u|2, 2] + v|2, -2]),$$

$$|B_h] = \frac{i}{\sqrt{2}}\,(u|2,\,2] - v|2,\,-2]), \tag{A.2}$$

and $u = e^{-i\theta}$, $v = e^{+i\theta}$, where θ is determined as:

$$\tan 2\theta = \frac{2[B_g^0|\hat{\mathscr{H}}_{CF}|B_h^0]}{[B_g^0|\hat{\mathscr{H}}_{CF}|B_g^0] - [B_h^0|\hat{\mathscr{H}}_{CF}|B_h^0]}\,. \tag{A.3}$$

APPENDIX B

The following definition for a vector is adopted: $\vec{A} = \sum_q A_q^{(1)}\vec{e}_q^{[1]}$ and the matrix elements $\vec{L}_{ij}$ are evaluated in spherical coordinates [11]:

	B_g	A	B_h	E_1	E_2
B_g	·	·	$-2\vec{e}_0^{[1]}$	$+iv\vec{e}_{+1}^{[1]}$	$+iu\vec{e}_{-1}^{[1]}$
A	·	·	·	$-i\sqrt{3}\,\vec{e}_{-1}^{[1]}$	$-i\sqrt{3}\,\vec{e}_{+1}^{[1]}$
B_h	$+2\vec{e}_0^{[1]}$	·	·	$+v\vec{e}_{+1}^{[1]}$	$-u\vec{e}_{-1}^{[1]}$
E_1	$-iu\vec{e}_{-1}^{[1]}$	$+i\sqrt{3}\,\vec{e}_{+1}^{[1]}$	$+u\vec{e}_{-1}^{[1]}$	·	·
E_2	$-iv\vec{e}_{+1}^{[1]}$	$+i\sqrt{3}\,\vec{e}_{-1}^{[1]}$	$-v\vec{e}_{+1}^{[1]}$	·	·

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