Electrostatic theory and spin-Hamiltonian separation for $3d^3$ ions in orthorhombic and tetragonal centres

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Abstract. The spin-Hamiltonian parameters for the $3d^3$ ion in an orthorhombic centre are calculated within the framework of the electrostatic model. Expressions for the three components of the g tensor and the fine structure parameters b_2^0 and b_2^2 are given in terms of the crystalline field energies and spin–orbit coupling parameters. The calculations are performed including the contributions from the $^4T_2$ states in the ground term and the $^2T_2$ states in the excited terms. The relationship between $g_\parallel - g_\perp$ and b_2^0 is derived. The basis of the spin-Hamiltonian separation for the orthorhombic centre of $3d^3$ ions is shown by electrostatic theory. The proper coordinate system for the orthorhombic centre is also discussed.

1. Introduction

The magnetic impurity centres of $3d^3$ ions are of interest due to their applications in laser materials. In particular, in recent years, Cr^{3+} ions introduced into fluorides with an intermediate crystalline field have been investigated for potential uses in variable-wavelength solid state lasers (Henderson and Imbusch 1989). Electron paramagnetic resonance (EPR) is a powerful technique to investigate the electronic states and structures of the magnetic impurity centres formed in ionic crystals from the relationship between the spin-Hamiltonian parameters and the crystalline field of surrounding ions (Yamaga *et al* 1993). EPR results for the several Cr^{3+} centres with orthorhombic and tetragonal symmetries in the compounds of the layered perovskite-type crystals have been reported in previous papers (Takeuchi *et al* 1982, 1983, Arakawa *et al* 1986, 1988a, b). The spin Hamiltonians obtained from the EPR experiments reflect the distortions of the crystalline field from cubic symmetry. In this connection, we proposed the spin-Hamiltonian separation (SHS) analysis of the orthorhombic Cr^{3+} centres in the layered perovskite fluorides (Takeuchi *et al* 1982, 1983). The SHS method was first developed using the transformation properties of the second-rank Stevens operators for Cr^{3+} ions and successfully extended to the other Fe^{3+} and Gd^{3+} centres in several fluorides (Takeuchi *et al* 1987, 1991a, b). This method is useful for identifying the orthorhombic or monoclinic centres associated with some charge compensators and for investigating the relationships among the magnetic centres in different matrix crystals.

For the purpose of obtaining quantitative knowledge about the effects of the surrounding ions on the central magnetic ion, it may be essential to relate the spin-Hamiltonian parameters, i.e. the g tensor and the fine structure parameters b_n^m, to the true Hamiltonian that is composed of crystal–field, orbital–Zeeman, spin–Zeeman and spin–orbit interactions. In the traditional analyses (Abragam and Bleaney 1970, Pilbrow 1990) the fine structure

and the Zeeman terms in the spin Hamiltonian are explained within the ground ^4F term. However, in the octahedral ligand field with orthorhombic or tetragonal symmetry, the spin–orbit interaction admixes the doublet-excited $^2T_2$ states to the ground $^4A_2(^4F)$ state together with an admixture of the $^4T_2(^4F)$ state. The contributions from the doublet states should be examined in a detailed discussion of anisotropy of the spin-Hamiltonian parameters, and the SHS method should be based on the microscopic theory including the main contributions from the excited quartet and doublet states.

In section 2, we perform the electrostatic calculations of the three components of the **g** tensor and the second-rank fine structure parameters b_2^0 and b_2^2 for an orthorhombic centre using perturbation theory. From the expressions for the spin-Hamiltonian parameters given in terms of the true Hamiltonian parameters, we can derive in general the relationship, which is known empirically in fluorides (Patel *et al* 1976, Takeuchi *et al* 1982, 1983, Arakawa *et al* 1986, 1988a, b), between the axial parameters $g_\parallel - g_\perp$ and b_2^0.

In section 3, we discuss the SHS method by microscopic treatments within the framework of the electrostatic theory mentioned in section 2. The basis of the SHS analysis and the condition for application will be shown for the case of an orthorhombic centre.

In section 4, we discuss the spin-Hamiltonian parameters in the special case of $3d^3$ complexes in layered-perovskite crystals, where the crystalline field is assumed to come mainly from contributions from the six ligands, since the crystalline field contribution from far ions in this type of crystal is almost cubic and therefore negligible. Furthermore, the proper coordinate system with $|b_2^2/b_2^0| < 1$ for the orthorhombic centre will be discussed in terms of the metal–ligand distances.

2. Electrostatic calculations of spin-Hamiltonian parameters for orthorhombic and tetragonal Cr^{3+} centres

The EPR spectrum from the Cr^{3+} ion in an orthorhombic centre can be described by the following spin Hamiltonian with effective spin $S = \frac{3}{2}$:

$$\mathcal{H}_s = g_x \beta S_x H_x + g_y \beta S_y H_y + g_z \beta S_z H_z + \frac{1}{3}(b_2^0 O_2^0 + b_2^2 O_2^2). \tag{1}$$

The spin-Hamiltonian parameters, i.e. the fine structure parameters $b_2^m (m = 0, 2)$ and the three components of the **g** tensor, are determined experimentally by fitting the spectrum to the spin Hamiltonian in (1).

Here, we attempt to derive the expressions for these parameters on the basis of electrostatic theory. We follow the notation of Griffith (1961). Most of the electrostatic calculations for $3d^3$ ions were performed by collecting the contributions only from the quartet-excited state $^4T_2(t_2^2(^3T_1)e)$. However, the spin–orbit interaction also admixes the doublet-excited $^2T_2$ states to the ground $^4A_2(t_2^3)$ state. For a $3d^3$ ion in a cubic crystalline field, there exist five $^2T_2$ multiplets, i.e. $^2T_{2a}(t_2^3)$, $^2T_{2b}(t_2^2(^3T_1)e)$, $^2T_{2c}(t_2^2(^1T_2)e)$, $^2T_{2d}(t_2e^2(^1E))$ and $^2T_{2e}(t_2e^2(^1A_1))$ in increasing order of energy (Griffith 1961). We should therefore calculate the contributions to b_2^m and the **g** tensor from the quartet and doublet T_2 states, in order to examine these parameters more accurately than is possible with traditional formulae.

In perturbation theory the total true Hamiltonian $\mathcal{H}_t$ is the sum of the unperturbed Hamiltonian $\mathcal{H}_0$ and the perturbation Hamiltonian $\mathcal{H}'$. The total crystalline potential energy is the sum of the electrostatic interaction energies V_i of the ith 3d electron with the crystalline field, and decomposes into the cubic component $\sum_{i=1}^3 V_{0i}$ and the orthorhombic component

$\sum_{i=1}^{3} V_i'$, where V_i' is the electrostatic interaction of the ith 3d electron with the orthorhombic component of the crystalline field at the central magnetic ion. We select the unperturbed Hamiltonian $\mathcal{H}_0$ to include the electrostatic interaction which determines the ground $3d^3$ electronic configuration of a free ion and the cubic component of the electrostatic potential of the crystalline field. The perturbation Hamiltonian $\mathcal{H}'$ is selected as

$$\mathcal{H}' = \sum_{i=1}^{3} V_i' + \beta H \cdot \sum_{i=1}^{3} (l_i + g_f s_i) + \sum_{i=1}^{3} \zeta l_i \cdot s_i \qquad (2)$$

by neglecting small contributions from the spin–spin, spin–other-orbit, hyperfine interactions, and so on. The l_i and the s_i are respectively the one-electron orbital and spin angular momenta, $g_f (= 2.0023)$ is the free-electron g value and ζ is the spin–orbit coupling parameter of a 3d electron.

The doublet states first contribute to the spin-Hamiltonian parameters in the third order of perturbation theory. All spin-Hamiltonian parameters were calculated up to third order in the perturbation Hamiltonian $\mathcal{H}'$. Matrix elements of the true Hamiltonian terms in (2) were calculated by computer at the Computation Centre of Nagoya University, using software written by us. It was found from these results that only the $^4T_2$, $^2T_{2a}$ and $^2T_{2b}$ states contribute to the spin-Hamiltonian parameters. We define the cubic field energies E_1, E_2, E_3 relative to the ground $^4A_2$ state for the $^4T_2$, $^2T_{2a}$, $^2T_{2b}$ multiplets, respectively, as follows:

$$E_1 = E(^4T_2) - E(^4A_2) \qquad E_2 = E(^2T_{2a}) - E(^4A_2) \qquad E_3 = E(^2T_{2b}) - E(^4A_2) \qquad (3)$$

and the orthorhombic field splittings Δ_ξ, Δ_η, Δ_ζ of the $^4T_2$ states, as follows:

$$\Delta_\xi = \left\langle {}^4T_2 \tfrac{3}{2} \xi \left| \sum_{i=1}^{3} V_i \right| {}^4T_2 \tfrac{3}{2} \xi \right\rangle - E(^4T_2)$$

$$\Delta_\eta = \left\langle {}^4T_2 \tfrac{3}{2} \eta \left| \sum_{i=1}^{3} V_i \right| {}^4T_2 \tfrac{3}{2} \eta \right\rangle - E(^4T_2) \qquad (4)$$

$$\Delta_\zeta = \left\langle {}^4T_2 \tfrac{3}{2} \zeta \left| \sum_{i=1}^{3} V_i \right| {}^4T_2 \tfrac{3}{2} \zeta \right\rangle - E(^4T_2).$$

The following expressions for the spin-Hamiltonian parameters are then obtained:

$$b_2^0 = \tfrac{4}{9} \zeta^2 \left(\frac{1}{E_1^2} - \frac{1}{E_3^2} \right) [\Delta_\zeta - \tfrac{1}{2}(\Delta_\xi + \Delta_\eta)] \qquad (5a)$$

$$b_2^2 = \tfrac{2}{3} \zeta^2 \left(\frac{1}{E_1^2} - \frac{1}{E_3^2} \right) (\Delta_\xi - \Delta_\eta) \qquad (5b)$$

$$g_x = g_f - \frac{8\zeta}{3E_1} + g^{(3)} + \frac{8\zeta}{3E_1^2} \Delta_\xi \qquad (5c)$$

$$g_y = g_f - \frac{8\zeta}{3E_1} + g^{(3)} + \frac{8\zeta}{3E_1^2} \Delta_\eta \qquad (5d)$$

$$g_z = g_f - \frac{8\zeta}{3E_1} + g^{(3)} + \frac{8\zeta}{3E_1^2} \Delta_\zeta \qquad (5e)$$

where

$$g^{(3)} = -\frac{2\zeta^2}{9E_1^2}(2g_f + 1) - \frac{2\zeta^2}{3E_2^2}(g_f + 1) - \frac{4\zeta^2}{9E_3^2}(2g_f - 1) - \frac{4\zeta^2}{3E_1E_2} + \frac{4\zeta^2}{3E_2E_3} + \frac{4\zeta^2}{9E_1E_3}. \quad (6)$$

For the tetragonal case about the z axis, where $\Delta_\xi = \Delta_\eta$, equations (5a) and (5b) become

$$b_2^0 = \tfrac{4}{9}\zeta^2\left(\frac{1}{E_1^2} - \frac{1}{E_3^2}\right)(\Delta_\zeta - \Delta_\xi) \qquad b_2^2 = 0. \quad (7)$$

As seen from (5c)–(5e), the anisotropic part of the **g** tensor is determined by the orthorhombic splitting of the $^4T_2$ multiplet. On the other hand, the fine structure parameters b_2^0 and b_2^2 are ascribed to the orthorhombic splittings of both the $^4T_2$ and $^2T_{2b}$ multiplets. If we define the axial parameter

$$g_\parallel - g_\perp = g_z - \tfrac{1}{2}(g_x + g_y)$$

we obtain its expression and its relation to b_2^0 as follows:

$$g_\parallel - g_\perp = \frac{8\zeta^2}{3E_1^2}[\Delta_\zeta - \tfrac{1}{2}(\Delta_\xi + \Delta_\eta)] = b_2^0\frac{6}{\zeta[1 - (E_1/E_3)^2]}. \quad (8)$$

From table A28 of Griffith (1961) the energy separations of $^4T_2$ and $^2T_{2b}$ from the $^4A_2$ state are expressed as

$$E_1 = 10Dq \qquad E_3 \simeq 9B + 3C + 10Dq \quad (9)$$

where $10Dq$ is the cubic field parameter and B and C are the Racah parameters. The $g_\parallel - g_\perp$ term in an orthorhombic centre is dependent on the cubic field parameter $10Dq$ and is proportional to the orthorhombic splitting of the $^4T_2$ multiplet. We may therefore expect from the relationship $E_1 < E_3$ that the anisotropy $g_\parallel - g_\perp$ has the same sign as the sign of b_2^0 which is dependent on the Racah parameters B and C. If $E_3 = 2E_1$, for example, the magnitude of b_2^0 becomes 25% smaller than that with only the $^4T_2$ contribution.

3. Spin-Hamiltonian separation analysis for orthorhombic centres

From (7) we can obtain the following expressions of the uniaxial parameters $b_{2(1)}^0$ and $b_{2(2)}^0$ for the respective tetragonal centres about the y and x axes:

$$b_{2(1)}^0 = \tfrac{4}{9}\zeta^2\left(\frac{1}{E_1^2} - \frac{1}{E_3^2}\right)(\Delta_\eta - \Delta_\zeta) \quad (10a)$$

$$b_{2(2)}^0 = \tfrac{4}{9}\zeta^2\left(\frac{1}{E_1^2} - \frac{1}{E_3^2}\right)(\Delta_\xi - \Delta_\zeta). \quad (10b)$$

By comparing the expressions in (5a), (5b), (10a) and (10b), we obtain the relationships between b_2^0, b_2^2 and $b_{2(1)}^0$, $b_{2(2)}^0$ as follows:

$$b_{2(1)}^0 = -b_2^0 - \tfrac{1}{3}b_2^2 \qquad b_{2(2)}^0 = -b_2^0 + \tfrac{1}{3}b_2^2. \quad (11)$$

Under the conditions in (11) we can write the following equation from the SHS analysis:

$$b^0_{2(1)}[3S^2_y - S(S+1)] + b^0_{2(2)}[3S^2_x - S(S+1)] = b^0_2[3S^2_z - S(S+1)] + b^2_2(S^2_x - S^2_y). \quad (12)$$

From the above discussions, the terms in $b^0_{2(1)}$ and $b^0_{2(2)}$ are regarded as the uniaxial fine structure terms of the tetragonal centres about the y and x axes, respectively, with the fine structure parameters $b^0_{2(1)}$ and $b^0_{2(2)}$ (Takeuchi and Arakawa 1983). Each uniaxial term can therefore be compared with other tetragonal centres having almost the same cubic field energy splittings, E_1 and E_3, as those of the orthorhombic centre.

The basis of the spin-Hamiltonian separation analysis has thus been shown for the orthorhombic centre of the $3d^3$ ions within the framework of the electrostatic model using perturbation theory including the $^4T_2$ and $^2T_2$ contributions.

4. Octahedral crystalline fields in perovskite-type compounds

The explicit forms of Δ_ξ, Δ_η, Δ_ζ in terms of the one-electron matrix elements (Takeuchi 1993) are given as

$$\Delta_\xi = \tfrac{1}{3}(-2\langle\xi|V_i|\xi\rangle + \langle\eta|V_i|\eta\rangle + \langle\zeta|V_i|\zeta\rangle) - \tfrac{1}{4}(\langle\epsilon|V_i|\epsilon\rangle - \langle\theta|V_i|\theta\rangle) + \tfrac{\sqrt{3}}{2}\langle\epsilon|V_i|\theta\rangle \quad (13a)$$

$$\Delta_\eta = \tfrac{1}{3}(\langle\xi|V_i|\xi\rangle - 2\langle\eta|V_i|\eta\rangle + \langle\zeta|V_i|\zeta\rangle) - \tfrac{1}{4}(\langle\epsilon|V_i|\epsilon\rangle - \langle\theta|V_i|\theta\rangle) - \tfrac{\sqrt{3}}{2}\langle\epsilon|V_i|\theta\rangle \quad (13b)$$

$$\Delta_\zeta = \tfrac{1}{3}(\langle\xi|V_i|\xi\rangle + \langle\eta|V_i|\eta\rangle - 2\langle\zeta|V_i|\zeta\rangle) + \tfrac{1}{2}(\langle\epsilon|V_i|\epsilon\rangle - \langle\theta|V_i|\theta\rangle). \quad (13c)$$

As the crystalline field from far-neighbour ions in perovskite-like crystals is considered to be small and approximately cubic, we assume that the crystalline field at the central magnetic ion is mainly determined by the six ligands. Here, we try to calculate b^0_2 and b^2_2 for an orthorhombic centre in the special case of the octahedrally coordinated $3d^3$ ion in perovskite-like crystals. The ligand configuration is shown in figure 1(a), where the xyz coordinate system is defined. A negative point charge $-e$ is assumed on each ligand. The metal–ligand distances are R_1 for the ligands 1 and 4, R_2 for the ligands 2 and 5, and R_3 for the ligands 3 and 6. From equations (5) and (13), and tables 4 and 6 in Takeuchi (1993), the following expressions are obtained:

$$b^0_2 = \tfrac{1}{2}F\left[\left(\frac{1}{R^5_1} - \frac{1}{R^5_3}\right) + \left(\frac{1}{R^5_2} - \frac{1}{R^5_3}\right)\right] \quad (14a)$$

$$b^2_2 = \tfrac{3}{2}F\left(\frac{1}{R^5_2} - \frac{1}{R^5_1}\right) \quad (14b)$$

where

$$F = \tfrac{10}{27}e^2\langle r^4\rangle\zeta^2\left(\frac{1}{E^2_1} - \frac{1}{E^2_3}\right). \quad (15)$$

For a Cr^{3+} ion, $\langle r^4\rangle = 4.35\,au$ (Freeman and Watson 1965), $\zeta = 273\,cm^{-1}$ (Griffith 1961), and $e = 1.602 \times 10^{-19}\,C$.

If we use the condition $R_1 = R_2$, the expressions for a tetragonal centre about the z axis become

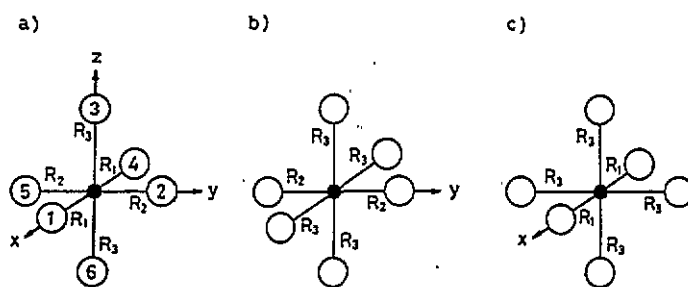$$b^0_2 = F\left(\frac{1}{R^5_1} - \frac{1}{R^5_3}\right) \qquad b^2_2 = 0. \quad (16)$$

Figure 1. Configurations of ligand ions in (*a*) an orthorhombic centre, (*b*) a tetragonal centre about the *y* axis and (*c*) a tetragonal centre about the *x* axis.

The parameter F is positive, since $E_1 < E_3$, which can be seen from (9). We therefore obtain $b_2^0 < 0$ for the tetragonal compression of the ligand octahedron ($R_3 < R_1$) and $b_2^0 > 0$ for the tetragonal elongation ($R_3 > R_1$). Experimental values of b_2^0 for the several tetragonal Cr^{3+} centres (centre I) in K_2NiF_4-type fluorides are listed in table 1. All the b_2^0 values are negative, so that tetragonal compression may happen in these centres in a similar fashion to the compressed octahedra of the matrix crystals (Yamaguchi 1972, Takeuchi *et al* 1982). The axial parameters $g_\parallel - g_\perp$ are also negative, and are consistent with the relationship in (8).

Table 1. Values of the axial parameters ($g_\parallel - g_\perp$, b_2^0) of the Cr^{3+} centres and the metal–ligand distances ($a/2$) along the a axes in matrices for the A_2MF_4- and AMF_3-type perovskite crystals. (b_2^0, $b_{2(1)}$, $b_{2(2)}$ are in units of $10^{-4} \, cm^{-1}$.)

Matrix	K_2MgF_4	K_2ZnF_4	Rb_2MgF_4	Rb_2ZnF_4	Rb_2CdF_4	Cs_2CdF_4
$a/2$ (Å)	1.984[a]	2.030[a]	2.0292[b]	2.0682[b]	2.2009[b]	——
Centre III						
$g_\parallel - g_\perp$	+0.0030[c]	+0.0018[c]	+0.0030[d]	+0.0023[e]	+0.0023[e]	+0.0026[e]
b_2^0	+504[c]	+413[c]	+580.7[d]	+401.5[e]	+554.0[e]	+622.0[e]
$b_{2(1)}^0$	−443[d]	−402[c]	−577.6[d]	−394.7[e]	−665.4[e]	−740.9[e]
$b_{2(2)}^0$	−565[d]	−424.0[c]	−583.8[d]	−408.3[e]	−442.6[e]	−503.1[e]
Centre I						
$g_\parallel - g_\perp$	−0.0017[d]	−0.0007[c]	−0.0022[d]	−0.0024[e]	−0.0032[e]	−0.0022[e]
b_2^0	−421.5[d]	−381[c]	−526.1[d]	−369.0[e]	−666.4[e]	−702.0[e]

Matrix	$KMgF_3$	$KZnF_3$		$RbZnF_3$	$RbCdF_3$	$CsCdF_3$
$a/2$ (Å)	1.9947[f]	2.026[g]		2.066[g]	2.200[g]	2.230[g]
Cr^{3+}–V_M centre						
b_2^0	——	−542.1[h]		−535.0[i]	−569.3[h]	−629.3[h]

[a] Yamaguchi (1972).
[b] Schrama (1973).
[c] Takeuchi *et al* (1982).
[d] Arakawa *et al* (1988a).
[e] Arakawa *et al* (1986).
[f] Davies and Horai (1971).
[g] Rousseau *et al* (1978).
[h] Takeuchi and Arakawa (1984).
[i] Arakawa and Takeuchi (1994).

From (11) and (14), the expressions for the parameters $b^0_{2(1)}$ and $b^0_{2(2)}$ are obtained as follows:

$$b^0_{2(1)} = F\left(\frac{1}{R^5_3} - \frac{1}{R^5_2}\right) \qquad b^0_{2(2)} = F\left(\frac{1}{R^5_3} - \frac{1}{R^5_1}\right). \tag{17}$$

These expressions are the same as those of the uniaxial parameters b^0_2 for the tetragonal centres about the y and x axes, respectively, shown in figure 1(b) and 1(c). In table 1 the separated parameters $b^0_{2(1)}$ and $b^0_{2(2)}$ are listed for the orthorhombic Cr^{3+} centres (centre III) in the K_2NiF_4-type fluorides, together with b^0_2 for the Cr^{3+} centres associated with the nearest divalent-metal vacancies in the $KNiF_3$-type fluorides. Each value of $b^0_{2(1)}$ is close to b^0_2 in the centre I, and $b^0_{2(2)}$ is close to b^0_2 for the Cr^{3+}–V_M centre. As seen from table 1, the metal–ligand distances $a/2$ of the matrix crystals in the c plane are almost the same for the $KNiF_3$-type crystal and the corresponding K_2NiF_4-type crystals. We can therefore expect that the cubic field splittings are approximately the same for both types of crystal. Moreover, the signs of $g_\parallel - g_\perp$ and b^0_2 are positive for each centre III and therefore consistent with the relationship in (8). For $KMgF_3$ doped with Cr^{3+} ions Patel *et al* (1976) reported two tetragonal centres with the fine structure parameters $b^0_2 = -2167 \times 10^{-4}\,\mathrm{cm^{-1}}$ and $-24\,000 \times 10^{-4}\,\mathrm{cm^{-1}}$. The value $b^0_2 \simeq -700 \times 10^{-4}\,\mathrm{cm^{-1}}$ is expected for the Cr^{3+}–V_{Mg} tetragonal centre from the trend of b^0_2 for the Cr^{3+}–V_M centres in AMF_3 and $b^0_{2(2)}$ for the centre III in A_2MF_4. It is therefore confirmed by systematic SHS analysis that the above two tetragonal centres observed in $KMgF_3$ are not the Cr^{3+}–V_{Mg} centre. It has been our experience that the Cr^{3+}–V_{Mg} centre is difficult to form in the as-grown $KMgF_3$ crystal, although the centre III can be easily formed in the K_2MgF_4 crystal.

In general, the EPR spectrum can be described in any coordinate system relative to the crystalline axes. However, for the purpose of comparing it with other centres, it may be proper to describe the spectrum in the coordinate system where the z axis is parallel to the direction in which the spectrum shows the maximum fine structure splitting. In this proper coordinate system the condition $|b^2_2/b^0_2| < 1$ holds. If the distances R_1, R_2 and R_3 are in a narrow range where the variation of R^{-5} is regarded as linear in R, the proper coordinate system is characterized by the condition

$$|R_3 - \tfrac{1}{2}(R_1 + R_2)| > \tfrac{3}{2}|R_1 - R_2| \tag{18}$$

as seen from (14). Considering the metal–ligand distances R_α, R_β, R_γ respectively along the α, β, γ axes in the order $R_\alpha < R_\beta < R_\gamma$, we find the following two cases in the proper coordinate system:

(case A) positive b^0_2 with $z \parallel \gamma$ where $R_\gamma - R_\beta > R_\beta - R_\alpha$, and
(case B) negative b^0_2 with $z \parallel \alpha$ where $R_\gamma - R_\beta < R_\beta - R_\alpha$.

Since b^0_2 are positive for the orthorhombic Cr^{3+} centres III, case A may hold where the γ axis is parallel to the a axis and the M^{2+} vacancy is on the b axis. For the tetragonal centre I, case B may hold with the α axis parallel to the c axis because of the negative value of b^0_2.

5. Conclusions

The expressions for the spin-Hamiltonian parameters **g** and b^m_2 ($m = 0, 2$) are calculated by perturbation theory on the basis of the electrostatic model. The doublet $^2T_{2a}$ and $^2T_{2b}$ states

contribute to $\mathbf{g}$ and the $^2T_{2b}$ states contribute to b_2^m together with contributions from the $^4T_2$ states. It is found that the axial parameters $g_\| - g_\perp$ have the same signs as those of the b_2^0 parameter in the electrostatic model including the doublet T_2 contributions. When the excited $^2T_{2b}$ state becomes close to the $^4T_2$ state, the magnitude of b_2^0 decreases significantly from the value calculated within the ^4F term. The formula of the spin-Hamiltonian separation has been shown for the orthorhombic centre of the $3d^3$ ion on the basis of electrostatic theory. In the special case of the octahedrally coordinated centres with an almost cubic crystalline field from far ions, the relative metal–ligand distances along the three crystalline axes determine the direction of the main principal axis and the sign of the b_2^0 parameter.

Acknowledgments

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