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Theoretical studies of EPR parameters and defect structures for Ni^{2+} ions in corundum

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ABSTRACT

In this paper, fourth-order perturbation formulae of zero-field splitting (ZFS) parameter D and g-factors $g_{//}$, $g_\perp$ for ground state $^3A_{2g}$ of $3d^8$ ions in the trigonal crystal field (CF) have been derived by perturbation theory method (PTM), and the complete energy matrices (45×45) including low symmetry ligand field (C_{3v}), Coulomb interactions and spin-orbital (SO) coupling interaction for $3d^8$ ions have been constructed, in the strong-field scheme. In these formulae, both the contributions from the SO of the central 3d ion and the ligands taken into account by using the two SO coupling parameter model, and the contributions to the ZFS from all excited states are included. These PTM formulae and complete energy matrices are applied to investigate the EPR parameters D and g-factors for Ni^{2+} ions in Al_2O_3 crystals unifiedly, and the calculated results of PTM and complete diagonalization method (CDM) are not only close to each other but also in good agreement with the experimental data, and the local structure of $[NiO_6]^{10-}$ cluster is determined quantitatively. Furthermore, the validities of the present formulae are tested further by the comparison of calculated results of the formula and these of CDM based on intermediate –CF scheme, and the comparison shows that the calculated results with these two different methods are in mutually good agreement with each other in all different trigonal crystal environments, which also suggest that these fourth-order perturbation formulae are suitable for explaining both D and g-factors for $3d^8$ ions in trigonally distorted octahedral field.

1. Introduction

Doped-Al_2O_3 crystals with Ni^{2+} ions have been experimentally studied by EPR [1,2] and optical spectroscopy [3] and theoretically explained with PTM [4,5] and CDM [6,7]. The calculated results by perturbation method [4] show that it is unsuccessful to explain the experimental data of ZFS D and g-factors $g_{//}$, $g_\perp$ using second-order [8] perturbation formulae which take only the nearest excited $^3T_2$ level into account. Later, 'quasi-fourth-order' perturbation formulae [5] are presented and used to explain D and g-factors $g_{//}$, $g_\perp$ of $3d^8$ ions in trigonally distorted octahedral field. However, the validities of those 'quasi-fourth-order' perturbation formulae which omit contributions from some excited states are checked by CDM recently [6], and the investigations indicate that the 'quasi-fourth-order' perturbation formulae [5] work well for the g-factors ($g_{//}$, $g_\perp$), but not for the ZFS D parameters [6]. In addition, the PTM mentioned above are established on conventional ionic model and the electron transfer between the transition metal (TM) and ligand is ignored, thus, only the contribution from SO coupling of the central TM ion is included, and the covalence effect can only be introduced phenomenally. In fact, both the contributions from the TM and ligands, and the mechanism of the covalence effect to the D and g-factors $g_{//}$, $g_\perp$ are important [9] and can be included naturally, if the two SO coupling parameter model are used in the molecular orbital scheme, as showed below.

2. Theory and calculation

When the Ni^{2+} ions are doped into Al_2O_3 crystals, it usually replaces Al^{3+} ions and the clusters of[$NiO_6]^{10-}$ with C_{3v} point group symmetry are formed. The CF potential of trigonal symmetry can be expressed as [10]

$$H_{CF} = [B_{43}^{\mathrm{Cubic}}(\sqrt{7/10}C_0^{(4)} + (C_3^{(4)} - C_{-3}^{(4)}))] + [B_{20}C_0^{(2)} + (B_{40} - \sqrt{7/10}B_{43})C_0^{(4)}] \tag{1}$$

in which, the first term is cubic part, and the second pare is trigonal part, respectively. the relationship between the conventional notations of CF parameters $D\sigma$, Dt and the Wybourne's notations are [11]

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$$-7D\sigma = B_{20},$$
$$-21D\tau = B_{40} - \sqrt{7/10}B_{43} \tag{2}$$

And, the trigonal CF parameters v and v' can be expressed as [11]

$$\begin{aligned} v &= -3D\sigma - \frac{20}{3}D\tau \\ &= \frac{3}{7}B_{20} + \frac{20}{63}(B_{40} - \sqrt{7/10}B_{43}) \end{aligned} \tag{3}$$

$$\begin{aligned} v' &= \sqrt{2}\left(D\sigma - \frac{5}{3}D\tau\right) \\ &= -\frac{\sqrt{2}}{7}B_{20} + \frac{5\sqrt{2}}{63}(B_{40} - \sqrt{7/10}B_{43})\Big] \end{aligned} \tag{4}$$

The physical Hamiltonian for trigonally distorted octahedral field can be expressed as

$$\begin{aligned} \hat{H} &= \hat{H}_1(10Dq) + \hat{H}_2\,(B,\,C) + \hat{H}_3\,(D\sigma,\,D\tau) + \hat{H}_4(\xi,\zeta') + \hat{H}_{Ze} \\ &= [\hat{H}_1(10Dq) + \hat{H}_2^{a}(B,\,C)] + [\hat{H}_2^{b}(B,\,C) + \hat{H}_3\,(D\sigma,\,D\tau) \\ &\quad + \hat{H}_4(\zeta,\zeta') + \hat{H}_{Zee} \end{aligned} \tag{5}$$

Where $\hat{H}_1(10Dq)$ is the cubic CF, $\hat{H}_2^{a}(B,\,C)$ and $\hat{H}_2^{\mathrm{b}}(B,\,C)$ are diagonal part and non-diagonal part of the Coulomb interaction $\hat{H}_2(B,\,C)$ term, respectively, B and C are the Racah parameters in crystal, and $\hat{H}_3(D\sigma,\,D\tau)$ is the trigonal CF, $\hat{H}_4(\zeta,\zeta')$ is spin-orbit term, and $\hat{H}_{Zee}$ is Zeeman term. Using Macfarlane's strong field perturbation method [12,13], fourth-order perturbation formulae of zero-field splitting (ZFS) parameter D and g-factors $g_{//}$, $g_{\perp}$ are derived as

$$\begin{aligned} D^{'} = {} & \frac{3\sqrt{2}\xi\zeta' v'}{2}\left(\frac{1}{E_7E_{10}} - \frac{1}{E_7E_8}\right) - \frac{\zeta'^2 v}{2}\left(\frac{1}{{E_{10}}^2} - \frac{1}{{E_8}^2}\right) \\ & + 6\sqrt{2}Bv'\zeta'^2\left(\frac{1}{E_6{E_{10}}^2} + \frac{1}{E_6E_7E_{10}} - \frac{3}{E_5E_7E_8} - \frac{3}{E_5E_7E_{10}}\right) \end{aligned} \tag{6}$$

$$\begin{aligned} D^{''} = {} & \frac{v'\zeta^2}{8}\left(\frac{1}{{E_7}^3} + \frac{3}{E_7{E_{10}}^2} - \frac{3}{E_8{E_7}^2} - \frac{3}{E_9{E_7}^2}\right) \\ & - \frac{vv'\zeta\zeta'}{2\sqrt{2}}\left(\frac{1}{E_7{E_{10}}^2} + \frac{2}{E_{10}{E_7}^2} - \frac{1}{E_7{E_8}^2} - \frac{1}{E_8{E_7}^2} - \frac{1}{E_7E_9E_{10}}\right) \\ & \frac{3v'\zeta^2\zeta'}{4\sqrt{2}}\left(\frac{1}{E_{10}{E_7}^2} + \frac{1}{E_7{E_8}^2} - \frac{1}{E_8{E_7}^2} - \frac{1}{E_7E_8E_{10}}\right) \\ & + \frac{v^2\zeta'^2}{12}\left(\frac{1}{{E_{10}}^3} - \frac{1}{{E_8}^3} + \frac{3}{E_7{E_8}^2} - \frac{3}{E_9{E_{10}}^2}\right) \\ & + \frac{v'\zeta'^2}{6}\left(\frac{12}{E_1{E_{10}}^2} - \frac{6}{E_2{E_{10}}^2} + \frac{8}{E_3{E_{10}}^2} - \frac{8}{E_4{E_{10}}^2}\right. \\ & + \frac{3}{E_6{E_{10}}^2} + \frac{12}{E_1{E_7}^2} - \frac{6}{E_2{E_7}^2} + \frac{8}{E_3{E_7}^2} - \frac{8}{E_4{E_7}^2} \\ & + \frac{3}{E_5{E_7}^2} + \frac{3}{E_6{E_7}^2} + \frac{24}{E_1E_7E_{10}} + \frac{12}{E_2E_7E_{10}} + \frac{16}{E_3E_7E_{10}} \\ & \left. - \frac{16}{E_4E_7E_{10}} + \frac{36}{E_5E_7E_{10}} + \frac{6}{E_6E_7E_{10}} + \frac{42}{E_5E_7E_8} + \frac{12}{E_5{E_8}^2}\right) \\ & - \frac{v\zeta\zeta'^2}{4}\left(\frac{1}{{E_8}^3} + \frac{1}{E_{10}{E_8}^2} - \frac{3}{E_7{E_8}^2} - \frac{2}{E_8{E_{10}}^2} - \frac{3}{E_7E_8E_{10}}\right) \\ & + \frac{3v'\zeta'^3}{\sqrt{2}}\left(\frac{1}{E_5E_7E_{10}} + \frac{1}{E_5E_8E_{10}} - \frac{2}{E_6E_8E_{10}} + \frac{1}{E_5E_7E_8} - \frac{2}{E_6E_7E_8}\right. \\ & \left. + \frac{1}{E_5{E_8}^2}\right) \end{aligned} \tag{7}$$

$$\begin{aligned} g_{//} = {} & \mathrm{g_e} + \frac{4k'\zeta'}{E_8} + \frac{2\sqrt{2}v'(k'\xi + k_F\zeta')}{E_7E_8} - \frac{4k'\upsilon\zeta'}{3{E_8}^2} - \frac{k'\xi\zeta'}{{E_8}^2} - \frac{(g_e - k/2)\zeta'^2}{{E_8}^2} \\ & - \frac{(g_e - k/2)\zeta'^2}{{E_{10}}^2} - \frac{k'\xi\zeta'}{E_8E_{10}} + \left(\frac{48\sqrt{2}Bk'\zeta'v'}{E_5E_7E_8} - \frac{12Bk'\zeta'^2}{E_6E_8E_{10}} - \frac{12Bk'\zeta'^2}{E_6{E_{10}}^2}\right) \end{aligned} \tag{8}$$

$$g_{\perp} = g_{//} - \frac{3\sqrt{2}v'(k'\zeta + k\zeta')}{E_1E_3} + \frac{2k'v\zeta'}{{E_1}^2} - \frac{72\sqrt{2}Bk'\zeta'v'}{E_5E_7E_8} \tag{9}$$

In the above formulae, $D = D^{'} + D^{''}$, and $D^{''}$ is the term omitted before [5]. If the $k^{'} = k$ and $\zeta^{'} = \zeta$ are taken in the above formulae, the corresponding formula are equal to those 'quasi-fourth-order' in Ref. [5], except for the coefficient of the last term of $g_{//}$ in Eq. (3) of Ref. [4] in which 12 is misprinted as 6, in addition, the zero energy for the ground state W_5 in Ref. [4] in which 9B is misprinted as 2B obviously. E_{i} are the zeroth-order energy denominations denoting the energy difference between the ground and the excited states, and have following form

$$\begin{aligned} E_1 &= E(\mathrm{a}^1\mathrm{A}_{1g}) - E(^3\mathrm{A}_{2g}) = 16B + 4C; \\ E_2 &= E(\mathrm{a}^1E_g) - E(^3\mathrm{A}_{2g}) = 8B + 2C; \\ E_3 &= E(\mathrm{b}^1\mathrm{A}_{1g}) - E(^3\mathrm{A}_{2g}) = 18B + 5C + 20D\mathrm{q}; \\ E_4 &= E(\mathrm{b}^1E_g) - E(^3\mathrm{A}_{2g}) = 8B + 2C + 20D\mathrm{q}; \\ E_5 &= E(\mathrm{a}^3\mathrm{T}_{1g}) - E(^3\mathrm{A}_{2g}) = 3B + 20D\mathrm{q}; \\ E_6 &= E(\mathrm{a}^1\mathrm{T}_{2g}) - E(^3\mathrm{A}_{2g}) = 9B + 2C + 20D\mathrm{q}; \\ E_7 &= E(\mathrm{b}^3\mathrm{T}_{1g}) - E(^3\mathrm{A}_{2g}) = 12B + 10D\mathrm{q}; \\ E_8 &= E(^3\mathrm{T}_{2g}) - E(^3\mathrm{A}_{2g}) = 10D\mathrm{q}; \\ E_9 &= E(^1\mathrm{T}_{1g}) - E(^3\mathrm{A}_{2g}) = 12B + 2C + 10D\mathrm{q}; \\ E_{10} &= E(\mathrm{b}^1\mathrm{T}_{2g})) - \mathrm{E}(^3\mathrm{A}_{2g}) = 8B + 2C + 10D\mathrm{q}; \end{aligned} \tag{10}$$

The molecular orbital (MO) of a single ion in the crystal system are [14]

$$\begin{aligned} \psi_t^a &= (N_t^a)^{-1/2}(\varphi_t - \lambda_\pi\chi_\pi) \\ \psi_e^a &= (N_e^a)^{-1/2}(\varphi_e - \lambda_s\chi_s - \lambda_\sigma\chi_\sigma) \end{aligned} \tag{11}$$

and the corresponding SO coupling parameters ζ, ζ', and orbital reduction factors k, $k^{'}$ can be expressed as [14]

$$\begin{aligned} \zeta &= (N_t^a)^{-1}[\zeta_d + (\lambda_\pi)^2\zeta_p/2] \\ \zeta' &= ({N_t}^aN_e^a)^{-1/2}[\zeta_d - \lambda_\pi\lambda_\sigma\zeta_p/2] \\ k &= (N_t^a)^{-1}[1 - 2\lambda_tS_\pi + (\lambda_\pi)^2/2] \\ k' &= (N_t^aN_e^a)^{-1/2}[1 - \lambda_sS_s - \lambda_\sigma S_\sigma - \lambda_\pi S_\pi - \lambda_\pi(\lambda_\sigma + A\lambda_s)/2] \end{aligned} \tag{12}$$

in which, ζ_d, ζ_p are SO parameters of TM and ligand in free state, respectively.

For Al_2O_3:Ni^{2+}, ζ_d (Ni^{2+}) ≈ 649 cm^{-1} [15] and $\zeta_{\mathrm{p}}(O^-)$ ≈ 150 cm^{-1} [9]. The two SO coupling interaction matrices of ζ, ζ' within the trigonal basis can be written as

$$\begin{array}{c|cccc} & {x_+}^{+} & {x_-}^{-} & {u_+}^{+} & {u_-}^{-} \\ \hline {x_+}^{+} & -\zeta/2 & 0 & -\sqrt{2}/2\,\zeta' & -\zeta' \\ {x_-}^{-} & 0 & -\zeta/2 & \zeta' & -\sqrt{2}/2\,\zeta' \\ {u_+}^{+} & -\sqrt{2}/2\,\zeta' & \zeta & 0 & 0 \\ {u_-}^{-} & -\zeta' & -\sqrt{2}/2\,\zeta' & 0 & 0 \end{array} \tag{13}$$