Studies of EPR *g*-factors on Rutile (TiO$_2$) with Co^{2+} Ion

Shao-Yi Wu[a,b] and Wen-Chen Zheng[a,b,c]

[a] Department of Material Science, Sichuan University, Chengdu 610064, P. R. China
[b] International Centre for Materials Physics, Chinese Academy of Sciences,
   Shenyang 110016, P. R. China
[c] Key Laboratory for Radiation Physics and Technology of Ministry of Education,
   P. R. China (in Sichuan University)

Reprint requests to S.-Y. W.; E-mail: wushaoyi.netease.com

The anisotropic g-factors g_X, g_Y, and g_Z for Co^{2+} in rutile crystal are studied from the second-order perturbation formulas based on the cluster approach. In the studies, the contributions due to covalency effects, the configuration interaction and the rhombic crystal field are taken into account. The calculated values are close to the observed ones. The small discrepancy between calculation and experiment is discussed.

Key words: Electron Paramagnetic Resonance; Crystal- and Ligand-field Theory; Co^{2+}; Rutile.

Introduction

Rutile (TiO$_2$) is a useful material for applications in optical communication, solid-state maser and in photoelectrolysis of water [1 - 3]. Many EPR experiments of transition-metal (3d^n) ions in rutile have been made. Among them, the anisotropic g factors g_X, g_Y, and g_Z for Co^{2+}-doped rutile were reported by various researchers [4 - 5], however few theoretical studies for these EPR parameters have been made. In order to explain satisfactorily these EPR data, reasonable and quantitative calculations for 3d^7 (Co^{2+}) in rhombic octahedral crystals are required. Tinkham [6] gave the first-order and Robbroeck et al. [7] developed second-order perturbation formulas of g_i ($i = X, Y, Z$) for the 3d^7 ion in rhombic octahedra. In these formulas, although the covalency effect is considered, the configuration interaction due to the admixture among the ground and excited orbital states is omitted and the treatments of the contributions from covalency effect and rhombic crystal field are oversimplified. On the other hand, considering the configuration interaction, Osaki and Uryu [8] extended the Abragam and Pryce theory [9] to rhombic symmetry and gave implicit formulas of g_i. Unfortunately the covalency effect and the fourth-order rhombic potential part were neglected, and for the configuration interaction only the admixture of the excited triplet ^{4}T$_2$(F) to the ground state ^{4}T$_1$(F) was considered. In addition, several parameters related to covalency effect, the configuration interaction and rhombic crystal-field are adjustable. So, the above formulas are incomplete and unsatisfactory, and they cannot yield quantitative and reasonable explanations of g_i for Co^{2+} in rhombic crystals. For overcoming the weakness of [10], we present now a cluster approach to the calculation of g_i for 3d^7 (Co^{2+}) in rhombic octahedra. In these formulas, the contributions of the covalency effect, the configuration interaction and the rhombic field are considered and the parameters related to the three important contributions can be estimated from the optical spectra and the structural data of the crystal under study. Based on these formulas, the anisotropic g-factors g_X, g_Y, and g_Z for Co^{2+} ion in rutile are calculated and the results are discussed.

Calculation

The EPR spectra of Co^{2+} in octahedra are typical of an effective spin $S' = \frac{1}{2}$, which arises from the splitting of the ^{4}F ground term into six Kramers doublets by the spin-orbit interaction and low symmetry crystal field. The EPR response comes from the lowest lying doublet and yields anisotropic g factors [11]. Because of the large spin-orbit coupling coefficient of Co^{2+}, the Jahn-Teller effect is not important and can be neglected for Co^{2+} in octahedra [11 - 12], as done in many previous papers [6 - 9]. Thus from the

cluster approach, the microscopic formulas of g factors for 3d^7 (Co^{2+}) ions in rhombic octahedral clusters are derived by using the following perturbation method [11]:

$$g_X = \frac{4\left[\left(\frac{\alpha}{\alpha'}\right)^2 \frac{2k\alpha}{x+2}\frac{\alpha'}{\alpha''} + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha'}\right)^2 \nu_{4X} + \frac{8\nu_5}{(x+2)^2} + \frac{12\nu_6}{x(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4\nu_{7X}}{x+2}}{\frac{\alpha^2}{\alpha'\alpha''} + \frac{6}{x^2} + \frac{8}{(x+2)^2}},$$

$$g_Y = \frac{4\left[\left(\frac{\alpha}{\alpha''}\right)^2 \frac{2k\alpha}{x+2}\frac{\alpha''}{\alpha'} + \frac{12}{x(x+2)}\right] + \left(\frac{\alpha}{\alpha''}\right)^2 \nu_{4Y} + \frac{8\nu_5}{(x+2)^2} + \frac{12\nu_6}{x(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}}\frac{4\nu_{7Y}}{x+2}}{\frac{\alpha^2}{\alpha'\alpha''} + \frac{6}{x^2} + \frac{8}{(x+2)^2}}, \tag{1}$$

$$g_Z = 2 + \frac{4(k\alpha+2)\left[\frac{3}{x^2} - \frac{4}{(x+2)^2}\right] + \left[\frac{9}{x^2} - \frac{4}{(x+2)^2}\right](\nu_{1X} + \nu_{1Y}) - \frac{\alpha}{(\alpha'\alpha'')^{1/2}}\left(\frac{3}{x} - \frac{4}{x+2}\right)(\nu_{3X} + \nu_{3Y})}{\frac{\alpha^2}{\alpha'\alpha''} + \frac{6}{x^2} + \frac{8}{(x+2)^2}},$$

where x can be determined from the rhombic energy level splittings Δ $(= E\{^4\mathrm{B}_1[^4\mathrm{T}_1(\mathrm{F})]\}$ $- E\{^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{F})]\})$ and δ $(= E\{^4\mathrm{B}_2[^4\mathrm{T}_1(\mathrm{F})]\}$ $- E\{^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{F})]\})$ of the $^4\mathrm{T}_1$ ground state using the expression

$$\Delta = \frac{\zeta\alpha'\alpha''}{3}\left[\frac{3}{\alpha x} + \frac{4\zeta}{\alpha\zeta(x+2)+6\delta}\right] - \frac{\zeta\alpha}{6}(x+3). \tag{2}$$

The ν_{ij} are defined as

$$\nu_{1X} = \frac{k'\zeta'}{3}\left[\frac{15f_{1X}^2}{2E_{1X}} + \frac{2q_{1X}^2}{E_{2X}}\right],$$

$$\nu_{1Y} = \frac{k'\zeta'}{3}\left[\frac{15f_{1Y}^2}{2E_{1Y}} + \frac{2q_{1Y}^2}{E_{2Y}}\right],$$

$$\nu_{3X} = \frac{k'\zeta'}{3}\left[\frac{15f_{1X}f_{2X}}{2E_{1X}} - \frac{2q_{1X}q_{2X}}{E_{2X}}\right],$$

$$\nu_{3Y} = \frac{k'\zeta'}{3}\left[\frac{15f_{1Y}f_{2Y}}{2E_{1Y}} - \frac{2q_{1Y}q_{2Y}}{E_{2Y}}\right],$$

$$\nu_{4X} = \frac{k'\zeta'}{3}\left[\frac{15f_{2X}^2}{2E_{1Y}} + \frac{4q_{2X}^2}{E_{2Y}}\right],$$

$$\nu_{4Y} = \frac{k'\zeta'}{3}\left[\frac{15f_{2Y}^2}{2E_{1X}} + \frac{4q_{2Y}^2}{E_{2X}}\right],$$

$$\nu_5 = \frac{4k'\zeta'q_3^2}{3E_{2Z}},$$

$$\nu_6 = \frac{k'\zeta'}{3}\left[\frac{15f_3^2}{2E_{1Z}} + \frac{2q_3^2}{E_{2Z}} + \frac{2(\rho_X + \rho_Y)^2}{E_3}\right],$$

$$\nu_{7X} = \frac{\nu_{3X}}{2}, \quad \nu_{7Y} = \frac{\nu_{3Y}}{2}, \tag{3}$$

where E_{1X}, E_{1Y}, E_{1Z}, E_{2X}, E_{2Y}, E_{2Z}, and E_3 are the energy differences between the ground state $^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{F})]$ and the excited states $^4\mathrm{B}_3[^4\mathrm{T}_2(\mathrm{F})]$, $^4\mathrm{B}_2[^4\mathrm{T}_2(\mathrm{F})]$, $^4\mathrm{B}_1[^4\mathrm{T}_2(\mathrm{F})]$, $^4\mathrm{B}_3[^4\mathrm{T}_1(\mathrm{P})]$, $^4\mathrm{B}_2[^4\mathrm{T}_1(\mathrm{P})]$, $^4\mathrm{B}_1[^4\mathrm{T}_1(\mathrm{P})]$, and $^4\mathrm{A}[^4\mathrm{A}_2(\mathrm{F})]$, respectively. E_{ij}, Δ and δ can be calculated from the d-d transition energy matrices for the 3d^7 ion in rhombic symmetry. The parameters f_{ij}, q_{ij}, ρ_i and α^i are related to the configuration interactions due to the admixture among the ground and excited states in rhombic symmetry and so the rhombic crystal parameters D_s, D_t, D_ξ, and D_η are included in the expressions of these configuration interaction parameters [10] (for saving space, these expressions, which can be seen in [10], are not written here). ζ and ζ' are the spin-orbit coupling coefficients. k and k' are the orbital reduction factors. From the cluster approximation, they are [10, 13, 14]

$$\zeta = N_\mathrm{t}(\zeta_\mathrm{d}^0 + \lambda_\mathrm{t}^2\zeta_\mathrm{p}^0/2), \ \zeta' = \sqrt{N_\mathrm{t}N_\mathrm{e}}(\zeta_\mathrm{d}^0 - \lambda_\mathrm{t}\lambda_\mathrm{e}\zeta_\mathrm{p}^0/2),$$

$$k = N_\mathrm{t}(1 + \lambda_\mathrm{t}^2/2), \ k' = \sqrt{N_\mathrm{t}N_\mathrm{e}}(1 - \lambda_\mathrm{t}\lambda_\mathrm{e}/2), \tag{4}$$

where ζ_d^0 and ζ_p^0 are, respectively, the spin-orbit coupling coefficient of the 3d^7 ion and that of the ligand in free state. For TiO$_2$:Co^{2+} we have $\zeta_\mathrm{d}^0 \approx 533$ cm^{-1} [15] and $\zeta_\mathrm{p}^0 \approx 136$ cm^{-1} [16]. The normalization factors N_γ and the orbital mixing coefficients λ_γ can be estimated from a semiempirical LCAO method [10, 13, 14]. According to this method we have the normalization condition

$$N_\gamma(1 - 2\lambda_\gamma S_\mathrm{dp}(\gamma) + \lambda_\gamma^2) = 1 \tag{5}$$

and the approximate relationship

$$f_\gamma N_\gamma^2[1 + \lambda_\gamma^2 S_\mathrm{dp}^2(\gamma) - 2\lambda_\gamma S_\mathrm{dp}(\gamma)], \tag{6}$$

where $S_{dp}(\gamma)$ are the group overlap integrals. From the Slater-type SCF functions [17, 18] and the average metal-ligand distance of rutile [19], we obtain for TiO$_2$:Co^{2+}, $S_{dp}(t_{2g}) \approx 0.0170$, $S_{dp}(e_g) \approx 0.0517$. f_γ [$\approx (B/B_0 + C/C_0)/2$] is the ratio of the Racah parameters for a 3d^n ion in a crystal to those of a free ion. For free Co^{2+} [15], $B_0 \approx 1115$ cm^{-1} and $C_0 \approx 4366$ cm^{-1}. Since the optical spectra of TiO$_2$:Co^{2+} were not reported, we estimate reasonably the optical spectral parameters (Racah parameters and the cubic crystal field parameter D_q) from the optical spectra of a similar crystal. From the optical spectra of MgO:Co^{2+} [20, 21] and in consideration of the average metal-ligand distance in TiO$_2$ being smaller than that of MgO, we estimate for TiO$_2$:Co^{2+}

$$D_q \approx 1220 \, \text{cm}^{-1}, \; B \approx 680 \, \text{cm}^{-1}, \; C \approx 3460 \, \text{cm}^{-1}. \tag{7}$$

Thus f_γ and hence N_γ, λ_γ can be calculated from (5) and (6). By using these parameters, we obtain $\zeta \approx 461$ cm^{-1}, $\zeta' \approx 442$ cm^{-1}, $k \approx 0.928$ and $k' \approx 0.763$ for Co^{2+} in TO$_2$ from (4).

According to the superposition model [22], the rhombic field parameters can be expressed as

$$D_s \approx (4/7)\overline{A}_2(R_0)[(R_0/R_\perp)^{t_2} - (R_0/R_\parallel)^{t_2}],$$

$$D_\xi \approx (4/7)\overline{A}_2(R_0)(R_0/R_\perp)^{t_2} \cos\theta,$$

$$D_t \approx -(4/21)\overline{A}_4(R_0) \tag{8}$$
$$\cdot [(7\cos 2\theta + 3)(R_0/R_\perp)^{t_4} + 4(R_0/R_\parallel)^{t_4}],$$

$$D_\eta \approx (20/21)\overline{A}_2(R_0)(R_0/R_\perp)^{t_4} \cos\theta,$$

where the power-law exponents $t_2 \approx 3$ and $t_4 \approx 5$ because of the ionic nature of bonds [10, 22]. $\overline{A}_2(R_0)$ and $\overline{A}_4(R_0)$ are the intrinsic parameters with the reference distance $R_0 (= \overline{R})$. For the 3d^n octahedral cluster, $\overline{A}_4(R_0) \approx (3/4)D_q$ [10, 22]. Since the ratio $\overline{A}_2(R_0)/\overline{A}_4(R_0)$ is in the range of 9 - 12 for 3d^n ions in many crystals [10, 23, 24], we take $\overline{A}_2(R_0) \approx 9.2\,\overline{A}_4(R_0)$ here. The structural parameter $R_\parallel$ ($\times 2$) denotes the apical metal-ligand distance, and $R_\perp$ ($\times 4$) the equatorial one. θ is the angle between two $R_\perp$ bonds. These parameters of rutile crystal are [19]

Table 1. Anisotropic g factors for rutile with Co^{2+}.

	g_X	g_Y	g_Z
Calculation	6.20 (2)	2.051 (5)	4.04 (2)
Experiment*	5.88 (2) [4]	2.190 (5) [4]	3.75 (1) [4]
	5.885 (1) [5]	2.079 (1) [5]	3.735 (5) [5]

* In the calculation, the axes are taken as $X \parallel [\overline{1}\,1\,0]$, $Y \parallel [0\,0\,1]$ and $Z \parallel [1\,1\,0]$, which are different from those of the EPR experiment coordination axes in [4, 5]. Therefore, we need a rotation of the axes of the experiment coordination so that the experimental values in [4, 5] can be compared with the theoretical results.

$$R_\parallel \approx 1.9800(9)\,\text{Å}, \; R_\perp \approx 1.9485(5)\,\text{Å}, \; \theta \approx 81.21(4)^\circ. \tag{9}$$

Substituting all these parameters into the above formulas, we have calculated the anisotropic g-factors for Co^{2+} in rutle. The results are close to the observed values (see Table 1). The small discrepancy between calculation and experiment may be due to the following points:

(i) Approximations occur in the above formulas, for example the small contributions due to the Jahn-Teller effects and the admixture among the lowest Kramers doublet $J' = 1/2$ and the higher $J' = 3/2$ and $J' = 5/2$ states are neglected (note: for the latter, Choi et al. [25] estimated that the contribution is smaller than 3 % for LiNbO$_3$:Co^{2+}).

(ii) The optical spectrum parameters are approximately estimated from those of similar crystal.

(iii) The structural data are taken as the host ones. Since the charge and size of Co^{2+} differ from those of the replaced Ti^{4+} ion [26], the local structural parameters in the vicinity of Co^{2+} should be unlike those of the host ones. Since the anisotropic g-factors are sensitive to the local structural parameters, the applications of the host structural data should result in calculation errors. In fact, for Co^{2+}-doped rutile, three other Co^{2+} defect centers attributed to the substitutional Co^{2+} ions combined with the nearest and the second neighbour oxygen vacancies were reported [6]. Their anisotropic g-factors are significantly different from those of the regular Co^{2+} center studied in this paper and from center to center [6], because of the different local structural parameters. So, the above small discrepancy can be understood.

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