

Investigations of the electron paramagnetic resonance spectra of VO^{2+} in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system

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Abstract. The EPR spectra for VO^{2+} in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ system are calculated using complete diagonalization method (CDM) and perturbation theory method (PTM). The calculated results are in good agreement with the observed values. By comparing the calculated results by CDM and PTM in a wide range of crystal field parameters, the validity of the PTM formulas has been studied. It is shown that, the PTM formulas are reasonable and reliable in a wide range of CF parameters.

Keywords. $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$; electron paramagnetic resonance spectra; $3d^1$ ions.

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1. Introduction

In past decades, the structure, properties and compositions of $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramic have been studied theoretically and experimentally [1–4]. Electron paramagnetic resonance (EPR) technique yields information about the environmental symmetry and electric fields around paramagnetic ions doped to diamagnetic structures. The VO^{2+} (or V^{4+}) ions were used extensively as a dopant material in various systems [5,6]. Farah [7] has revealed V^{4+} coordination in quenched sodium silicate melts and examined V^{4+} in calcium silicate and complex metallurgical slags. V^{4+} has been found as a tetragonally distorted octahedral VO^{2+} complex which tends to become less distorted than octahedral symmetry. There are no theoretical investigations of EPR spectra of transition metal ions in $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ glass-ceramic system until now. In the present paper, the EPR spectra of VO^{2+} ions

in CaO–Al₂O₃–SiO₂ system have been studied, and the validity of perturbation theory method (PTM) formulas have been checked.

2. Theory

2.1 CDM method

The energy matrices for the d¹ configuration ion with tetragonal symmetry have been established based on the following Hamiltonian:

$$H = H_f + H_{CF}(B_{kq}) + H_{SO}(\zeta), \quad (1)$$

where H_f and H_{SO} are the free-ion term and spin-orbit coupling interaction, respectively and ζ is the spin-orbit coupling constant. The crystal field interaction term can be written as

$$H_{CF} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}C_4^{(4)} + B_{4-4}C_{-4}^{(4)}, \quad (2)$$

where $C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}}Y_{kq}$ are the normalized spherical harmonics and B_{kq} are crystal field (CF) parameters with $B_{4-4} = B_{44}$. For V⁴⁺ in CaO–Al₂O₃–SiO₂ system, by fitting the experimental EPR parameters, we take $B_{20} = 18,900 \text{ cm}^{-1}$, $B_{40} = 20,100 \text{ cm}^{-1}$, $B_{44} = 18,700 \text{ cm}^{-1}$.

V⁴⁺ is of the 3d¹ type. There is only one term for free 3d¹ ions, i.e. ²D term. ²D term is split by an octahedron CF (O_h) into ²E_g and ²T_{2g} terms. If the octahedron is distorted along the tetragonal axis, the symmetry is lowered. Then the ²E_g term splits to ²A₁ and ²B₁, the ²T_{2g} splits to ²B₂ and ²E. In compressed tetragonal octahedral symmetry, the ground state is ²B₂ [8]. Thus, the Hamiltonian matrix is a 10 × 10 matrix. By diagonalizing the complete energy matrix, the optical spectra and the eigenvectors can be obtained.

For 3d¹ ions in tetragonal CF the effective spin-Hamiltonian (SH) is given as

$$H_S = g_{\parallel}\mu_B B_z S_z + g_{\perp}\mu_B (B_x S_x + B_y S_y) + A_{\parallel}I_z S_z + A_{\perp}(I_x S_x + I_y S_y). \quad (3)$$

The symbols appearing in eq. (3) have their usual meanings. g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the g -tensor. According to SH theory, the g factors can be expressed as

$$g_{\parallel} = 2\langle\psi_+|kL_z + g_e S_z|\psi_+\rangle, \quad (4)$$

$$g_{\perp} = 2\langle\psi_+|kL_x + g_e S_x|\psi_-\rangle, \quad (5)$$

where g_e is the free-spin g value of 2.0023 and k is the orbital-reduction factor (we take it as 0.7 here). $|\psi_+\rangle$ and $|\psi_-\rangle$ express the two full configuration eigenfunctions of eigenstates ²B₂. A_{\parallel} and A_{\perp} are the parallel and perpendicular components of hyperfine tensor, and can be expressed as [9,10]

Table 1. The EPR parameters for VO^{2+} in $CaO-Al_2O_3-SiO_2$ system.

	Calculated results using PTM	Calculated results using CDM	Observed value [7]
g_{\parallel}	1.9358	1.9359	1.936
g_{\perp}	1.9788	1.9791	1.979
A_{\parallel}	-168.3	-168.3	162.1
A_{\perp}	-58.1	-58.1	60.6

$$A_{\parallel} = P \left[-\kappa - \frac{4}{7} + (g_{\parallel} - g_e) + \frac{3}{7}(g_{\perp} - g_e) \right], \quad (6)$$

$$A_{\perp} = P \left[-\kappa + \frac{2}{7} + \frac{11}{14}(g_{\perp} - g_e) \right], \quad (7)$$

where $\kappa = 0.84$ [10] is the core polarization constant which indicates the contribution to the A_{\parallel} and A_{\perp} by the unpaired s -electron. P is the dipolar hyperfine structure constant for VO^{2+} in crystals. Considering the covalence reduction effect, ζ and P can be calculated from the relations

$$\zeta \approx k\zeta_0, \quad P \approx kP_0. \quad (8)$$

Here $\zeta_0 = 248 \text{ cm}^{-1}$ [11] and $P_0 = 172 \times 10^{-4} \text{ cm}^{-1}$ [12] are the values of ζ and P for V^{4+} in free state. By diagonalizing the complete energy matrix, the values of g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} can be obtained using eqs (4)–(7). The calculated results are listed in table 1.

2.2 PTM method

Recently, Wang *et al* derived the third-order perturbation formulas of spin-Hamiltonian parameters for $3d^1$ ions in tetragonal symmetry with the ground state 2B_2 as [10]

$$g_{\parallel} = g_e - \frac{8k\zeta}{E_2} - \frac{(k + g_e)\zeta^2}{E_1^2} - \frac{4k\zeta^2}{E_1E_2} \quad (9)$$

$$g_{\perp} = g_e - \frac{2k\zeta}{E_1} + \frac{(k - g_e)\zeta^2}{E_1^2} - \frac{2g_e\zeta^2}{E_2^2} \quad (10)$$

with

$$E_1 = E({}^2E) - E({}^2B_2) = \frac{3}{7}B_{20} - \frac{5}{21}B_{40} + \frac{\sqrt{70}}{21}B_{44} \quad (11)$$

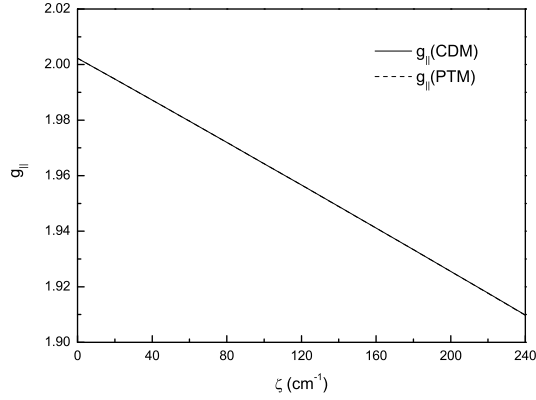


Figure 1. g_{\parallel} vs. ζ for $3d^1$ ions in compressed tetragonal CF.

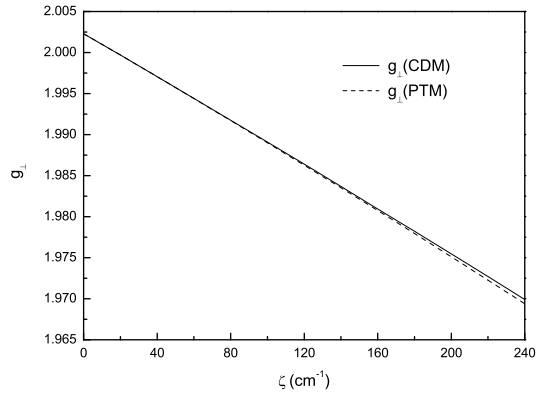


Figure 2. g_{\perp} vs. ζ for $3d^1$ ions in compressed tetragonal CF.

$$E_2 = E(^2B_1) - E(^2B_2) = \frac{2\sqrt{70}}{21} B_{44} \quad (12)$$

$$E_3 = E(^2A_1) - E(^2B_2) = \frac{4}{7} B_{20} + \frac{5}{21} B_{40} + \frac{\sqrt{70}}{21} B_{44}. \quad (13)$$

3. Calculation

From table 1, one can see that, the calculated results by CDM are in good agreement with the observed values. Thus, the EPR spectra of VO^{2+} in $CaO-Al_2O_3-SiO_2$ system are explained theoretically. Using eqs (6)–(13), one can obtain the EPR parameters. The calculated results are also listed in table 1. It should be noted that, the observed values of A_{\parallel} and A_{\perp} are actually the absolute values. So in table 1, the observed values of A_{\parallel} and A_{\perp} are positive. From the above calculations, the

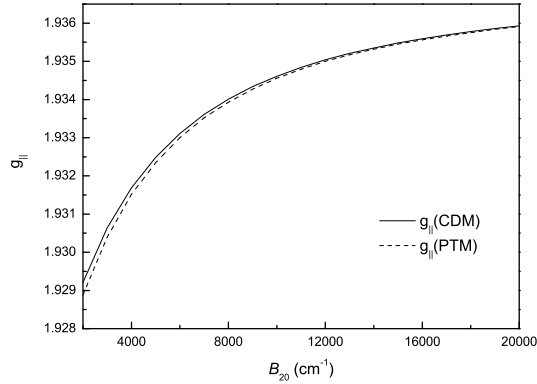


Figure 3. g_{\parallel} vs. B_{20} for $3d^1$ ions in compressed tetragonal CF.

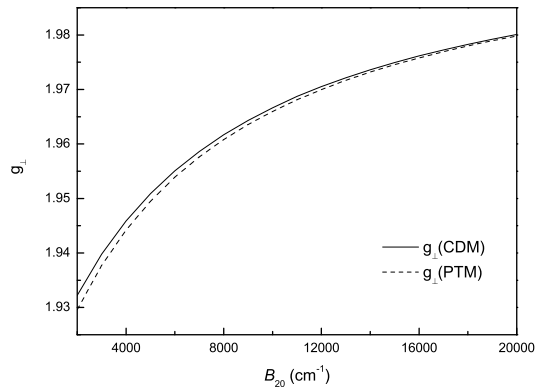


Figure 4. g_{\perp} vs. B_{20} for $3d^1$ ions in compressed tetragonal CF.

values of A_{\parallel} and A_{\perp} should be negative. This is coincident with the results in ref. [10]. From table 1, one can see that, the results calculated by PTM agree well with CDM. That is to say, both theoretical methods are effective in the calculations of EPR spectral parameters for $3d^1$ ions in crystals.

4. The validity of PTM formulas

To study the validity of PTM formulas further, we compared the calculations using the two approaches in a wide range of CF parameters. The ranges of B_{20} , B_{40} , B_{44} are 2000–20,000 cm^{-1} and that of ζ are 0–240 cm^{-1} , respectively.

The calculated results are shown in figures 1–8. In these figures, the solid lines are for the calculated results using CDM and dashed lines are for the calculated results using eqs (9)–(13). From these figures one can see that, the results calculated using CDM and PTM agree well with each other in a wide range of CF parameters and spin-orbit coupling parameters. This shows that the PTM formulas can be used generally. From figures 1 and 2, one can see that, the values of g factors

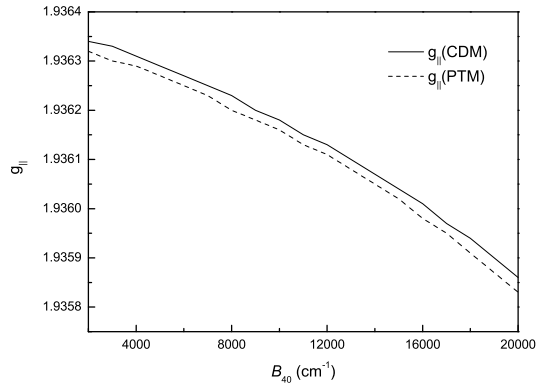


Figure 5. g_{\parallel} vs. B_{40} for $3d^1$ ions in compressed tetragonal CF.

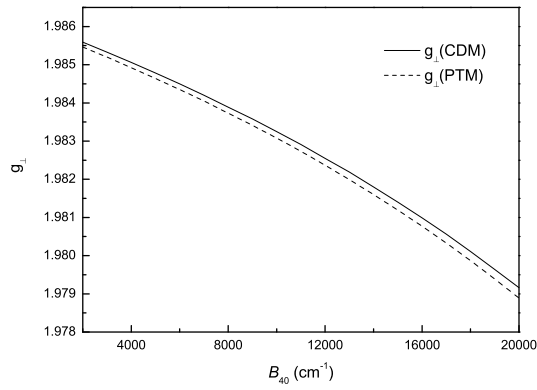


Figure 6. g_{\perp} vs. B_{40} for $3d^1$ ions in compressed tetragonal CF.

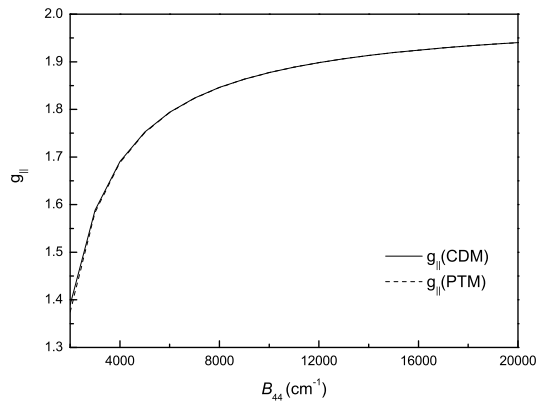


Figure 7. g_{\parallel} vs. B_{44} for $3d^1$ ions in compressed tetragonal CF.

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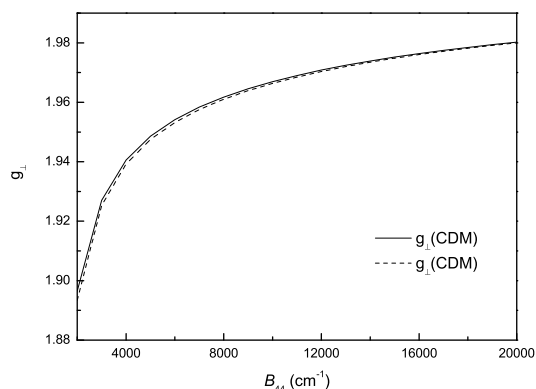


Figure 8. g_{\perp} vs. B_{44} for $3d^1$ ions in compressed tetragonal CF.

are almost linear to ζ . But from eqs (9) and (10), the relations between g factors and ζ are square relation. This shows that the linear terms in eqs (9) and (10) are the dominant part of g factors. In eqs (9) and (10), the first term is g_e , the second term is the second-order perturbation term, the third and the fourth terms are third-order perturbation terms. For g_{\parallel} and g_{\perp} , the values of the second-order perturbation terms are -0.06524 and -0.02258 , respectively. The values of the third-order perturbation terms are -0.00123 and -0.00088 , respectively. One can see that the contributions to g factors from the third-order perturbation terms are far less than that of the second-order perturbation terms. Thus, the detailed calculations verified our analysis above.

5. Summary

The EPR spectra of VO^{2+} in $CaO-Al_2O_3-SiO_2$ system are investigated by CDM and PTM. The validity of the PTM formulas are studied. It is shown that, the PTM formulas are reasonable and reliable in a wide range of CF parameters.

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