

Investigations of the EPR and Optical Spectra for VO²⁺ in C₃H₇NO₂ Powders

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(Received December 31, 2009; in final form April 19, 2010)

The EPR and optical spectra for VO²⁺ in C₃H₇NO₂ powders are calculated from complete diagonalization method and perturbation theory method, respectively. The calculated results are in good agreement with observed values. The negative signs of hyperfine structure constants A_{\parallel} and A_{\perp} for VO²⁺ in C₃H₇NO₂ powders are also suggested from the calculations.

PACS numbers: 76.30Fc, 71.70Ch, 78.50Ec, 71.55Ht

1. Introduction

The VO²⁺ (or V⁴⁺) ions were used extensively as a dopant material in various systems [1–9]. Recently, VO²⁺ doped C₃H₇NO₂ powders have been examined by electron paramagnetic resonance (EPR) and optical absorption spectroscopy [5]. The experimental values of g factors are $g_{\parallel} = 1.932$ and $g_{\perp} = 1.999$. As known, an octahedral site with a tetragonal compression would give the value of $g_{\parallel} < g_{\perp} < g_e$, where g_e is the free-spin g value of 2.0023. The observed values of the spin Hamiltonian parameters agree with the relation. That is to say, VO²⁺ complexes in C₃H₇NO₂ powders are tetragonally distorted octahedral symmetry. Until now, no satisfactory theoretical explanations for the optical and EPR parameters have been made. In this paper, the optical and EPR spectra have been theoretical explained by using perturbation theory method (PTM) and complete diagonalization method (CDM), respectively. And the crystal field (CF) parameters Dq , Ds and Dt are obtained.

2. Calculations

2.1. Perturbation theory method

V⁴⁺ is of the $3d^1$ type. There is only one term for free $3d^1$ 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 2A_1 and 2B_1 , the ${}^2T_{2g}$ splits to 2B_2 and 2E . In compressed tetragonal octahedral symmetry, the ground state is 2B_2 . Thus, the energy

intervals can be expressed as:

$$E_1 = E({}^2E) - E({}^2B_2) = -3Ds + 5Dt, \quad (1)$$

$$E_2 = E({}^2B_1) - E({}^2B_2) = 10Dq, \quad (2)$$

$$E_3 = E({}^2A_1) - E({}^2B_2) = 10Dq - 4Ds - 5Dt, \quad (3)$$

where Dq is the cubic crystal field parameter, Ds and Dt are the tetragonal crystal field parameters.

For $3d^1$ ions in tetragonal CF the effective spin-Hamiltonian (SH) is given as [3]:

$$H_S = g_{\parallel}\mu_B B_z S_z + g_{\perp}\mu_B (B_x S_x + B_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y). \quad (4)$$

The symbols appearing in Eq. (4) have their usual meanings. g_{\parallel} and g_{\perp} are the parallel and perpendicular components of the g -tensor. A_{\parallel} and A_{\perp} are the parallel and perpendicular components of the hyperfine tensor. The third-order perturbation formulas of spin-Hamiltonian parameters for $3d^1$ ions in tetragonal symmetry with the ground state 2B_2 can be derived from the perturbation theory as [9]:

$$g_{\parallel} = g_e - \frac{8k\zeta}{E_2} - \frac{(k + g_e)\zeta^2}{E_1^2} - \frac{4k\zeta^2}{E_1 E_2}, \quad (5)$$

$$g_{\perp} = g_e - \frac{2k\zeta}{E_1} + \frac{(k - g_e)\zeta^2}{E_1^2} - \frac{2g_e\zeta^2}{E_2^2}, \quad (6)$$

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

$$A_{\perp} = P \left[-\kappa + \frac{2}{7} + \frac{11}{14}(g_{\perp} - g_e) \right], \quad (8)$$

where k is the orbital-reduction factor, we take it as 0.7 here. E_1 and E_2 are the energy intervals given in Eqs. (1) and (2). κ 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

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for VO²⁺ in crystals. Considering the covalence reduction effect, ζ and P can be calculated from the relations [9–11]:

$$\zeta \approx k\zeta_0, P \approx kP_0, \quad (9)$$

here $\zeta_0 = 248 \text{ cm}^{-1}$ [12] and $P_0 = 172 \times 10^{-4} \text{ cm}^{-1}$ [13] are the values of ζ and P of V⁴⁺ in free state. By fitting the observed EPR and optical spectra, we obtained the value of CF parameters are: $Dq = 1466 \text{ cm}^{-1}$, $Ds = -2804 \text{ cm}^{-1}$, $Dt = 637 \text{ cm}^{-1}$. Substituting these CF parameters into above formulas, the energy levels and EPR parameters can be calculated. The calculated results are listed in the Table.

TABLE

The EPR and optical spectra for VO²⁺ in C₃H₇NO₂ powders. (The units of optical spectra are in cm⁻¹, the units of A_{||} and A_⊥ are in 10⁻⁴ cm⁻¹.)

	Calculated by PTM	Calculated by CDM	Observed value [5]
² B ₂ → ² E	11597	11510 11684	11595
² B ₂ → ² B ₁	14660	14670	14658
² B ₂ → ² A ₁	22691	22698	22696
g	1.9349	1.9349	1.932
g _⊥	1.9805	1.9807	1.999
A	-182.8	-182.8	187.0
A _⊥	-72.4	-72.4	72.1

2.2. Complete diagonalization method

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

$$H = H_f + H_{CF}(Dq, Ds, Dt) + H_{SO}(\zeta) \quad (10)$$

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

$$H_{CF} = B_{20}C_0^{(2)} + B_{40}C_0^{(4)} + B_{44}C_4^{(4)} + B_{4-4}C_{-4}^{(4)} \quad (11)$$

where $C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}}Y_{kq}$ are normalized spherical harmonics, and B_{kq} are CF parameters with $B_{44} = B_{4-4}$. The CF parameter B_{kq} measure the strength of the interaction between the open-shell electrons of the paramagnetic ions and their surrounding crystalline environment. they can be expressed as:

$$B_{20} = -7Ds, \quad (12)$$

$$B_{40} = 21Dq - 21Dt, \quad (13)$$

$$B_{44} = 21\sqrt{\frac{5}{14}}Dq. \quad (14)$$

Our calculations for the Hamiltonian matrices are carried out in the intermediate crystal field coupling scheme [14]. In the intermediate crystal field coupling scheme, the

eigenfunctions have the form $|SLM_S M_L\rangle$. According to the group theory, one can obtain all the 10 eigenfunctions of d¹ ions in tetragonal symmetry. The matrix element of the crystal field H_{CF} and the spin-orbit coupling H_{SO} can be expressed as:

$$\begin{aligned} \langle d^1 SLM_S M_L | H_{CF} | d^1 S' L' M'_S M'_L \rangle &= \delta_{M_S M'_S} \delta_{S S'} \\ &\times \sum_{k,q} B_{kq} \langle d || C^{(k)} || d \rangle \begin{bmatrix} L & k & L' \\ -M_L & q & M'_L \end{bmatrix} \\ &\times \langle d^1 SL || U^{(k)} || d^1 S' L' \rangle, \quad (15) \\ \langle d^1 SLM_S M_L | H_{SO} | d^1 S' L' M'_S M'_L \rangle & \end{aligned}$$

$$\begin{aligned} &= \langle d || l^{(1)} || d \rangle \zeta \sum_{q=-1}^1 (-1)^{q+S+L-M_S-M_L} \\ &\times \begin{bmatrix} S & 1 & S' \\ -M_S & -q & M'_S \end{bmatrix} \begin{bmatrix} L & 1 & L' \\ -M_L & q & M'_L \end{bmatrix} \\ &\times \langle d^1 SL || V^{(11)} || d^1 S' L' \rangle, \quad (16) \end{aligned}$$

where the [] indicates 3j-symbols. The reduced matrix elements and the electrostatic matrix elements can be found in [15].

By means of the equivalence between the spin Hamiltonian and the Zeeman interaction, the g factors can be expressed as [9]:

$$g_{||} = 2\langle \psi_+ | kL_z + g_e S_z | \psi_+ \rangle, \quad (17)$$

$$g_{\perp} = 2\langle \psi_+ | kL_x + g_e S_x | \psi_- \rangle, \quad (18)$$

where $|\psi_+\rangle$ and $|\psi_-\rangle$ express the two full configuration eigenfunctions of eigenstates ²B₂, and the detailed expressions used in the present paper are listed in the appendix. The expressions of A_{||} and A_⊥ are the same as those in Eqs. (7) and (8).

Substituting the CF parameters into Eqs. (10)–(16), one can obtain the 10 × 10 complete energy matrix, After diagonalizing the matrix, the energy levels and the eigenfunctions of ground state can be obtained. The eigenfunctions can be used to calculate the g factors. The calculated results are also listed in the Table.

3. Discussion and conclusion

(1) One can see from the Table, that results obtained by CDM and PTM are not only very close to each other, but also in good agreement with observed values. Thus, the EPR and optical spectra of VO²⁺ in C₃H₇NO₂ powders are explained theoretically. In CDM, all the microscopic states are considered, and the results calculated from CDM can be regarded as accurate results. On this basis, some PTM formulas are checked [16–18]. The validity of PTM formulas of g-factors for 3d¹ ions at tetragonal symmetry have been investigated in [16]. It is shown, that the PTM formulas are reasonable and reliable in a wide range of CF parameters. From Eqs. (1)–(3), (5) and (6), one can see, that only the highest energy level ²A₁ is omitted in these third-order

perturbation formulas. So the results calculated by PTM can agree well with those by CDM.

(2) It should be noted, that the signs of A_{\parallel} and A_{\perp} for $3d^n$ or $4f^n$ ions in crystals can not be determined from EPR spectra directly. So, the experimental values of A_{\parallel} and A_{\perp} are actually the absolute values. Muncaster and Parke [19] have proved that the signs of A_{\parallel} and A_{\perp} should be negative for VO^{2+} ions in hydrated salts and glasses. In this paper, we found, that the signs of A_{\parallel} and A_{\perp} for VO^{2+} in $\text{C}_3\text{H}_7\text{NO}_2$ powders also should be negative. This is coincident with the VO^{2+} in other crystals [9].

(3) The optical absorption spectrum shows three bands characteristic of VO^{2+} ions in tetragonal symmetry. The cubic crystal field parameter Dq and the tetragonal field parameters Ds and Dt were obtained. The values of CF parameters we obtained are: $Dq = 1466 \text{ cm}^{-1}$, $Ds = -2804 \text{ cm}^{-1}$, $Dt = 637 \text{ cm}^{-1}$. These values are similar as VO^{2+} in other crystals [20, 21]. So, the CF parameters we obtained in this paper are reliable.

Acknowledgments

This work was supported by the Education Committee Natural Science Foundation of Shaanxi Province (Grant No. 08JK216), a Baoji University of Arts and Sciences Key Research Grant (Grant No. ZK 0713), and HPC Lab, Shenzhen Institute of Advanced Technology, CAS, China.

Appendix

The two full configuration eigenfunctions of eigenstates 2B_2 , $|\psi_+\rangle$ and $|\psi_-\rangle$, are as follows:

$$\begin{aligned}
 |\psi_+\rangle &= 0.999866 \frac{1}{\sqrt{2}} \left(\left| 2, 2, \frac{1}{2}, \frac{1}{2} \right\rangle - \left| 2, -2, \frac{1}{2}, \frac{1}{2} \right\rangle \right) \\
 &\quad - 0.011741 \frac{1}{\sqrt{2}} \left(\left| 2, 2, \frac{1}{2}, \frac{1}{2} \right\rangle + \left| 2, -2, \frac{1}{2}, \frac{1}{2} \right\rangle \right) \\
 |\psi_-\rangle &= 0.999866 \frac{1}{\sqrt{2}} \left(\left| 2, 2, \frac{1}{2}, -\frac{1}{2} \right\rangle - \left| 2, -2, \frac{1}{2}, -\frac{1}{2} \right\rangle \right) \\
 &\quad + 0.011741 \frac{1}{\sqrt{2}} \left(\left| 2, 2, \frac{1}{2}, -\frac{1}{2} \right\rangle + \left| 2, -2, \frac{1}{2}, -\frac{1}{2} \right\rangle \right)
 \end{aligned}$$

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