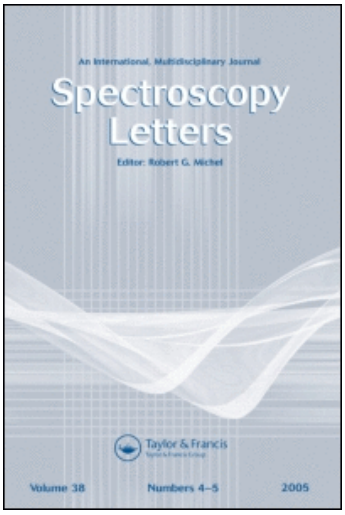

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Theoretical Studies of Optical Spectra and EPR Parameters for V^{4+} Impurity Ions in CoMTH

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ABSTRACT On the basis of the perturbation formulas and 10×10 complete energy matrices for a d^1 configuration ion in a tetragonal crystal field, for V^{4+} ions doped in cobalt maleate tetrahydrate (CoMTH) single crystals, the optical spectra and electron paramagnetic resonance (EPR) parameters (g factors $g_{//}, g_{\perp}$ and hyperfine structure constants $A_{//}$, $A_{\perp}$) of the octahedral $(VO_6)^{8-}$ clusters have been studied by two theoretical models. By simulating the calculated optical spectra and the EPR parameters to the observed values, the magnitude of orbital reduction factor k, core polarization constant κ and crystal field parameters B_k^q are determined. The calculated results are in reasonable agreement with the experimental values.

KEYWORDS CoMTH, crystal field theory, EPR, optical spectra, V^{4+}

1. INTRODUCTION

The electron paramagnetic resonance (EPR) technique may yield useful information about the immediate environment of paramagnetic centers in crystals. Optical absorption studies can provide the crystal field parameters and structure of energy levels of the transition-metal or rare-earth ions.[1–4] Therefore, EPR and optical spectrum technique are two powerful tools for studying point symmetry and dynamic properties of the transition-metal or rare-earth ions in the host crystals. VO^{2+} (or V^{4+}) ion is used extensively in impurity probe for EPR and optical studies. Vanadyl complexes have been the subject of investigation over resent years.[5–7] The EPR and optical absorption studies of VO^{2+} in CoMTH have been reported;[7] however, there is no theoretical investigation in literature on EPR and optical spectra studies of VO^{2+} in CoMTH single crystal to our knowledge. According to crystal field theory, the EPR parameters and optical spectra data for transition-metal ions in crystals can be computed and explained by two theoretical models,[8,9] i.e., the perturbation theory model (PTM) and the complete diagonalization energy matrix model (CDM). We have undertaken the present two theoretical models on the EPR and optical absorption investigations of VO^{2+} ions doped in CoMTH single crystals. The theoretical results of the two models both agree well with the observed values. It seems that the PTM and CDM are all effective to study the EPR and optical

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spectra data of d^1 electronic configuration. Moreover, the correlative parameters have been determined by the crystal field formulas.

2. MODELS OF CALCULATION

2.1. Model for the Construction of the PTM of a d^1 Configuration Ion in a Tetragonal Crystal Field

In a tetragonal field, the spin-Hamiltonian of a d^1 configuration ion can be given as[10]

$$H_s = \mu_B g_\perp (H_x S_x + H_y S_y) + \mu_B g_{//} j H_z S_z + A_{//} I_z S_z + A_\perp (I_x S_x + I_y S_y) \quad (1)$$

where g_i ($i = \perp, //$) indicates the components of the g factors, μ_B is the Bohr magneton, S_i and I_i ($i = x,y,z$) are electron and nuclear spin operators, and H_i ($i = x,y,z$) indicates the components of the magnetic field along the x-, y-, and z-axes. Using the high-order perturbation theory,[11,12] the g factors and hyperfine structure constants A can be calculated by the formulas

$$g_{//} = g_s - \frac{8k\lambda}{E_1} - \frac{(g_s + k)\lambda^2}{E_2^2} - \frac{4k\lambda^2}{E_1 E_2}$$
$$g_\perp = g_s - \frac{2k\lambda}{E_2} - \frac{(g_s/2 - k)\lambda^2}{E_2^2} - \frac{2g_s\lambda^2}{E_1^2} \quad (2)$$

$$A_{//} = P\left[-\kappa - \frac{4}{7} + (g_{//} - g_s) + \frac{3(g_\perp - g_s)}{7}\right]$$
$$A_\perp = P\left[\frac{2}{7} - \kappa + \frac{11}{14}(g_\perp - g_s)\right] \quad (3)$$

in which g_s (≈2.0023) is g value of the free electron; κ is the core polarization constant; k is the orbit reduction factor and λ is the spin-orbit coupling coefficient. The energy denominators are $E_2 = E(^2E_g) - E(^2B_{2g})$ and $E_1 = E(^2B_{1g}) - E(^2B_{2g})$. The energy level differences between exciting state ^2E_g, $^2B_{1g}$, $^2A_{1g}$ and ground state $^2B_{2g}$ are given by

$$E_1 = E(^2E_g) - E(^2B_{2g}) = \frac{3}{7}B_2^0 - \frac{5}{21}\left(B_4^0 - \frac{\sqrt{70}}{5}B_4^4\right)$$
$$E_2 = E(^2B_{1g}) - E(^2B_{2g}) = \frac{2\sqrt{70}}{21}B_4^4$$
$$E_3 = E(^2A_{1g}) - E(^2B_{2g}) = \frac{4}{7}B_2^0 + \frac{5}{21}B_4^0 + \frac{\sqrt{70}}{21}B_4^4 \quad (4)$$

TABLE 1 The Optical Absorption Spectra (in cm^{-1}) and EPR Parameters for VO^{2+} Ions in CoMTH Crystal

Variable	Calculation		Experiment[7]
	CDM	PTM	
$^2B_{2g} \rightarrow {}^2E_g$	13237	13328	13325
	13416		
$\rightarrow {}^2B_{1g}$	16067	16056	16060
$\rightarrow {}^2A_{1g}$	25435	25428	—
$g_{//}$	1.9364	1.9364	1.94(1)
$g_\perp$	1.9822	1.9822	1.98(1)
$A_{//}$ ($10^{-4}\,cm^{-1}$)	−187.79	−187.79	187(1)[a]
$A_\perp$ ($10^{-4}\,cm^{-1}$)	−73.58	−73.58	73(2)[a]

[a]The absolute values were given in the experiment.

where the crystal field parameters B_k^q are adjustable and can be determined from the optical spectra data of experiment. From Eq. (4), one can obtain the theoretical optical spectrum bands of PTM.

Considering the covalence reduction effect for $3d^n$ ions in many crystals,[2,3,6–9] we obtain

$$\lambda = k\lambda_0, \quad P = kP_0, \quad (5)$$

λ_0 and P_0 are the corresponding parameters for $3d^n$ ions in free ion state. For free V^{4+} ion, we have $\lambda_0 \approx 248\,cm^{-1}$[13] and $P_0 \approx 172 \times 10^{-4}\,cm^{-1}$.[14] The unknown parameters k, κ, B_2^0, B_4^0 and B_4^4 can be obtained by fitting the calculated optical and EPR spectra data to the observed values. Thus, from the calculation, we have

$$k \approx 0.725, \kappa \approx 0.86, \quad B_2^0 \approx 22700\,cm^{-1},$$
$$B_4^0 \approx 18600\,cm^{-1}, \quad B_4^4 \approx 20150\,cm^{-1} \quad (6)$$

The calculated three optical spectrum band positions and four EPR parameters are compared with the experimental values in Table 1.

2.2. Model for the Construction of the CDM of a d^1 Configuration Ion in a Tetragonal Crystal Field

The perturbation Hamiltonian for a d^1 configuration V^{4+} ion in a tetragonal crystal field can be written as[13]

$$\hat{H} = \hat{H}_f + \hat{H}_{so} + \hat{H}_{cf} + \hat{H}_{Zeeman} = \sum_{i<j}\frac{e^2}{r_{i,j}} + \lambda\sum_i l_i s_i + \sum_i V_i + \sum_i \mu_B(k\vec{l}_i + g_s\vec{s}_i)\cdot\vec{H} \quad (7)$$

where $\hat{H}_f$ is the free ions interaction; $\hat{H}_{so}$ is the spin-orbit coupling interaction and λ is the spin-orbit coupling coefficient; $\hat{H}_{cf}$ is the crystal field interaction; V_i is the crystal field potential and $\hat{H}_{Zeeman}$ is the Zeeman interaction. The crystal field potential V_i may be expressed as:

$$V_i = \gamma_0^0 Z_0^0 + \gamma_2^0 r_i^2 Z_2^0(\theta_i, \varphi_i) + \gamma_4^0 r_i^4 Z_4^0(\theta_i, \varphi_i) \times \gamma_4^4 r_i^4 Z_4^4(\theta_i, \varphi_i) + \gamma_4^{4s} r_i^4 Z_4^{4s}(\theta_i, \varphi_i) \quad (8)$$

The 10×10 complete energy matrices for a d^1 configuration ion corresponding to the perturbation Hamiltonian (7) have been established. The matrix elements can be expressed as the functions of the spin-orbit coupling coefficient λ and the crystal field parameters. Generally, the z axis is chosen along fourfold axis to describe the crystal field. As for d^1 configuration ion with tetragonal symmetry, the crystal field parameters only include B_2^0, B_4^0, B_4^4, and other terms are equal to zero. B_2^0, B_4^0 and B_4^4 can be treated as fitting parameters and the same as the values of B_k^q in PTM. By diagonalizing the 10×10 complete energy matrices, the eigenvalues (i.e., theoretical optical spectrum bands) and the linear combination wave functions $\left|\pi, \pm\frac{1}{2}\right\rangle$ of ground state can be obtained. Depending on the equivalence between the spin-Hamiltonian and the Zeeman interaction, we have the formulas of g factors $g_{//}$, $g_\perp$,

$$g_{//} = 2\left\langle \pi, \frac{1}{2}\middle| kL_z + g_s S_z \middle|\pi, \frac{1}{2}\right\rangle$$
$$g_\perp = 2\left\langle \pi, \frac{1}{2}\middle| kL_z + g_s S_z \middle|\pi, -\frac{1}{2}\right\rangle \quad (9)$$

The hyperfine constants $A_{//}$ and $A_\perp$ are calculated from the $g_{//}$, $g_\perp$values and using Eq. (3). They are also listed in Table 1. Here, the same fitting parameters of Eq. (6) are used in calculation of CDM. In order to analyze the quality of optical band matching, the root-mean-square deviation σ has been defined as[14–16]

$$\sigma = \sum \left[\frac{(E_{calc} - E_{expt})^2}{n}\right]^{1/2} \quad (10)$$

where $E_{calc}-E_{expt}$ is the difference between calculated and observed energies, $n(=2)$ is the number of experimental levels. The values of σ have been obtained from the two models and given in conclusions.

3. CONCLUSIONS

The optical spectrum and EPR parameters have been studied with the two models for V^{4+} in CoMTH system. From the comparative analysis, we have the following conclusions:

1. Theoretically, the symbols of hyperfine constants $A_{//}$ and $A_\perp$ are often suggested in minus, whereas they are difficult to detect in experiment. Therefore, the results of $A_{//}$ and $A_\perp$ can be regarded as reasonable.
2. The crystal field parameters B_k^q have been evaluated by assigning the optical levels transitions. The orbit reduction factor k and core polarization constant κ are determined in the calculation and satisfy the values of usual range (i.e., $0.6 \sim 1$). In addition, the values of the root-mean-square deviation σ obtained from two models are, respectively, $6.01\,cm^{-1}$ and $6.36\,cm^{-1}$. The small values of root-mean-square deviation σ show that the calculated results are reasonable and reliable.
3. For $3d^n$ ions series, the number of electronic configuration of $3d^1$ (i.e., V^{4+}) is lesser than that of the other $3d^n$ ions (i.e., Ni^{2+}, Cr^{3+}, Mn^{2+}, etc.). So, the third-order formulas of PTM have the best approximation that of CDM. It seems that both theoretical models are effective in explanation of optical and EPR spectral parameters for $3d^1$ ions in crystals.

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