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Investigations of the optical spectra and EPR parameters for VO^{2+} ion in Na$_3$C$_6$H$_5$O$_7$ · 2H$_2$O powders

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ABSTRACT

The optical spectrum band positions and EPR parameters (g factors $g_{//}$, $g_\perp$ and hyperfine structure constants $A_{//}$ and $A_\perp$) for VO^{2+} in Na$_3$C$_6$H$_5$O$_7$·2H$_2$O powders are calculated from compl- ete diagonalization method and perturbation theory method. The theoretical results from both me- thods are in good agreement with the experimental values. The negative signs of hyperfine struc- ture constants $A_{//}$ and $A_\perp$ for VO^{2+} in Na$_3$C$_6$H$_5$O$_7$·2H$_2$O powder are suggested from the calcul- ations.

Key words: Electron paramagnetic resonance (EPR), Crystal-fields and Spin Hamiltonians, VO^{2+}, Na$_3$C$_6$H$_5$O$_7$· 2H$_2$O

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INTRODUCTION

In the last few decades, the electron paramagnetic resonance (EPR) of VO^{2+} (or V^{4+}) ions doped in materials has attracted much attention, due to its advantages as a probe in studying local structures and properties in doped crystals [1-10]. For example, VO^{2+} in Na$_3$C$_6$H$_5$O$_7$ · 2H$_2$O powders [Trisodium Citrate Dihydrate, TSCD hereafter] have been examined by electron paramagnetic resonance (EPR) and optical absorption spectroscopy[6]. The EPR parameters g-factors ($g_{//}$=1.938, $g_\perp$=1.998) and hyperfine structure constants ($A_{//}$=183.7× 10^{-4} cm^{-1}, $A_\perp$=64.4× 10^{-4} cm^{-1}) were measured [6]. As known, an octahedral complex with a tetragonal compression would give g_e>$g_\perp$ > $g_{//}$and $|A_{//}|$>$|A_\perp|$ [10, 11], where g_e is the free-ion g value of 2.0023. The observed values of the EPR parameters agree with the relation. That is to say, the impurity VO^{2+} complexes in TSCD powders are of tetragonally distorted compressed octahedral symmetry. However, till now, the above EPR and optical spectra have not been satisfactorily. In this paper, the EPR parameters of VO^{2+} in TSCD powders are calculated by using perturbation theory (PTM) and complete diagonalization (of energy matrix) method (CDM). The crystal field parameters were obtained and the optical spectra are well explained. The results are discussed.

MATERIALS AND METHODS

1. PTM Calculations
Vanadyl ion (VO^{2+}) has the electronic configuration [Ar] 3d^1 and the free ion term is ^{2}D$_2$. In an octahedral field the ^{2}D$_2$ term split into ^{2}Eg and ^{2}T$_{2g}$ terms. However, in the tetragonal symmetry (C$_{4v}$), the energy levels will be split further, the orbital doublet ^{2}E$_g$ of the original cubic case would split into two orbital singlets ^{2}A$_1$ (θ) and ^{2}B$_1$(ε), while the original orbital triplet ^{2}T$_{2g}$ term would be separated into an orbital singlet ^{2}B$_2$ (ζ) and a doublet ^{2}E (η, ξ) [12]. According to the crystal-field theory and the experimental data, one can conclude that the ground state for VO^{2+} in TSCD powders is ^{2}B$_2$ (ζ). Thus, the energy intervals can be written in terms of the crystal field parameters

(D_s, D_t, D_q) as follows:

$E_1 = -3D_s + 5D_t$
$E_2 = 10D_q$
$E_3 = 10D_q - 4D_s - 5D_t$ (1)

Here, D_q is the cubic crystal parameter. D_s and D_t are the tetragonal field parameters. According to the perturbation method, the third order perturbation formulas of EPR parameters for $3d^1$ ions in tetragonal symmetry with the ground state $^2B_2$ (ζ) can be derived and given as follows[11]:

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

$g_\perp = g_e - 2k\zeta/E_1 + (k-g_e)\zeta^2/E_1 - 2g_e\zeta^2/E_2^2$

$A_{//} = P[-\kappa - 4/7 + (g_{//}-g_e) + 3(g_\perp-g_e)/7]$

$A_\perp = P[-\kappa + 2/7 + 11(g_\perp-g_e)/14]$ (2)

In the above formulas, g_e (≈ 2.0023) is the g factor of the free electron. ζ is the spin-orbit coupling coefficient of impurity ion in crystal, k is the orbital reduction factors. P is the dipolar hyperfine structure constants. κ is the isotropic core polarization constant. The energy denominators E_1 and E_2 stand for the energy separations between the excited ^2E, $^2B_1$ and the ground $^2B_2$ states which are given in equation (1). In consideration of the covalence reduction effect for d^n ions in crystals, the parameter N^2 are introduced to characterize the effect [11]. Thus, the ζ and k as well as P can be expressed in terms of the parameter N^2 and the spin-orbit coupling coefficient of center ion in free state:

$\zeta \approx N^2\zeta_0, \quad k \approx N^2, \quad P \approx N^2P_0$ (3)

Here $\zeta_0 \approx 248$ cm^{-1} [12] and $P_0 \approx 172 \times 10^{-4}$ cm^{-1} [13] for V^{4+} ion in free state. Thus by fitting the calculated results to the observed values, the crystal field parameters can be obtained and the theoretical optical band positions are confirmed. The calculated results are shown in Table 1.

Table 1. The optical spectrum band positions (in cm^{-1}) and EPR parameters
(A constants are in units of 10^{-4} cm^{-1}) for VO^{2+} ions in TSCD powders

	calculation		Expt[6]
	PTM	CDM	
$^2B_2 \rightarrow {}^2E_{2g}$	12191	12100	12195
		12283	
$^2B_{2g} \rightarrow {}^2B_{1g}$	16900	16901	16892
$^2B_2 \rightarrow {}^2A_{1g}$	24638	24637	24631
$g_{//}$	1.9395	1.9386	1.938
$g_\perp$	1.9810	1.9810	1.998
$A_{//}$	-178.7	-178.9	183.7
$A_\perp$	-64.2	-64.3	64.4

2. CDM calculations
The Hamiltonian for the d^1 ion in crystal-field can be written as [14]:

$H = H_f + H_{so}(\zeta) + H_{CF}(D_q, D_s, D_t)$ (4)

Where H_f is the free-ion term. $H_{so}(\zeta)$ is the spin-orbit coupling interactions related to the spin-orbit coupling constant ζ. H_{CF} is the crystal-field Hamiltonian for $3d^1$ ion in tetragonal symmetry. By means of the strong field basis functions in tetragonal symmetry [14], we obtain the 10×10 complete Hamiltonian matrix elements of the crystal field and spin-orbit coupling. And the optical band positions (the energy levels) can be obtained from the eigenvalues. The wave functions ($|\Psi^+>$ and $|\Psi^->$) of the ground state can be also obtained. Considering the equivalence between the SH and Zeeman interaction, the g factors can be expressed as [15]:

$g_{//} = 2<\Psi^+|kL_z + g_eS_z|\Psi^+>$
$g_\perp = 2<\Psi^+|kL_x + g_eS_x|\Psi^->$ (5)

where L_z (L_x) and S_z (S_x) are the operators of orbit and spin angular momentums. The expressions of $A_{//}$ and $A_\perp$ are the same as those in equation (2). Then using the wave functions of ground state ($|\Psi^+>$ and $|\Psi^->$), the g factors can

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be calculated and hence the hyperfine structure constants are obtained. The calculated results are also shown in Table 1.

RESULTS AND DISCUSSION

From table 1, one can find that the calculated optical band positions and EPR parameters from two methods (CDM and PTM) are not only very close to each other but also in keeping with the observed values. This suggests that the explanation of the EPR and optical spectra of VO^{2+} in TSCD can be regarded as reasonable.

(1)   The calculated results based on CDM are more close to the observed values than those by PTM. This may be attributed to the fact that CDM considers the contributions to EPR parameters from all the $3d^n$ excited states, while the PTM considers the contributions from a selected subset of the $3d^n$ excited state. So the former can yield more accurate theoretical results. However, for $3d^1$ or $3d^9$ ions in crystals, there are little numbers of excited states, and the disparity of the calculated results between CDM and PTM are small (see Table 1), and both methods can be used to calculate the EPR parameters.

(2)   The observed values of $A_{//}$ and $A_{\perp}$ given in Ref.[6] are positive, while the calculated results are negative. Actually the signs of hyperfine structure constants A for $3d^n$ ions in crystals should not be determined from EPR spectra directly. Thus many experimental values give them as absolute ones [2-10]. And the negative signs of A constants for V^{4+} ions in many crystal were suggested [11,16,17,18]. This can be illustrated by the larger magnitudes of the negative terms related to κ than those of the positive ones related to the anisotropic contributions from g shifts ($g_{//}-g_e$ and $g_{\perp}-g_e$, see Eq.(2)) and the covalency factor N. So the above calculated $A_{//}$ and $A_{\perp}$ are reasonable in sign and in magnitude. Moreover, many studies show that the core polarization constant κ is in the range 0.6-1.0[9,10,11], The value $\kappa \approx 0.78$ obtained in this work is within the range and can be regarded as suitable.

(3)   In this work, the covalency factor N (≈ 0.86) is close to VO^{2+} doped in other crystals (e.g. $N \approx 0.87$ for VO^{2+} in MB_4O_7, M=Zn and Cd [11]) and can be regarded as rational. Moreover, the crystal field parameters ($D_s \approx -2847$ cm^{-1}, $D_t \approx 730$ cm^{-1}, $D_q \approx 1690$ cm^{-1}) determined from the optical absorption spectrum and the equation (1) are similar as VO^{2+} in other crystals [8,10,19]. This means that the crystal field parameters obtained in this work are reliable and the theoretical calculations can be regarded as reasonable.

CONCLUSION

The optical band positions and spin Hamiltonian parameters ($g_{//}$, $g_{\perp}$, $A_{//}$, $A_{\perp}$) of the tetragonal VO^{2+} center in TSCD powders are theoretical investigated by both methods of CDM and PTM. The calculated results show that both methods are effective in the explanations of the optical spectra and EPR parameters for d^1 ions in crystals. The sign of the hyperfine structure constants $A_{//}$ and $A_{\perp}$ for VO^{2+} in $Na_3C_6H_5O_7 \cdot 2H_2O$ powders are suggested from the calculations.

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