

# Investigations of the Optical Band Positions and Spin-Hamiltonian Parameters for the Rhombic $\text{VO}^{2+}$ Complex in CsCl Crystal

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The optical band positions and spin-Hamiltonian parameters ( $g$  factors  $g_i$  and hyperfine structure constants  $A_i$ , where  $i = x, y, z$ ) of the rhombic  $\text{VO}^{2+}$  complex in CsCl crystal are calculated together from two theoretical methods. One is the complete diagonalization (of energy matrix) method and another is the perturbation theory method. The calculated results from the two methods coincide and are in reasonable agreement with the experimental values. So, both methods are effective in the explanations of optical and electron paramagnetic resonance (EPR) data for  $d^1$  ions in crystals. The calculations also suggest that in  $d^1$  rhombic octahedra the ground state is almost a pure  $|d_{xy}\rangle$  state. This point is different from that of conjugate  $d^9$  (e.g.,  $\text{Cu}^{2+}$ ) ions in rhombic octahedra where the ground state should be an admixture of ground and first excited states.

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## 1. Introduction

Vanadium (V) belongs to the first series transition metal ( $3d^n$ ) group. It readily reacts to form some oxy-cations and the simplest is vanadyl ion,  $\text{VO}^{2+}$ . This molecular ion can be thought of as consisting of a  $\text{V}^{4+}(3d^1)$  ion and a closed shell  $\text{O}^{2-}$  ion. Because of strong  $\text{V}^{4+}-\text{O}^{2-}$  covalence bonding in  $\text{VO}^{2+}$  ion, most of the  $\text{VO}^{2+}$  complexes in crystals possess tetragonally-compressed (along the  $\text{V}^{4+}-\text{O}^{2-}$  bonding) octahedral or square pyramid symmetry ( $C_{4v}$ ). This point has been supported by optical and electron paramagnetic (EPR) studies for  $\text{VO}^{2+}$  ions in a number of crystals [1–7].

It is noted that in some cases, the crystal field symmetry of  $\text{VO}^{2+}$  complex is found to be reduced to rhombic or lower symmetry. For example, in vanadium-doped CsCl crystal grown from aqueous solutions, the anisotropic EPR spectra due to  $\text{VO}^{2+}$  complex were observed [8]. Elbers and Lehmann [8] thought that it is most likely a  $[\text{VO}(\text{H}_2\text{O})\text{Cl}_4]^{2-}$  unit in which a small rhombic distortion is addition to large tetragonal ( $C_{4v}$ ) unit. The origin of the small rhombic distortion is an open question [8]. The optical and EPR data (i.e., the optical band positions and spin-Hamiltonian parameters,  $g$  factors  $g_i$  and hyperfine structure constant  $A_i$ ,  $i = x, y, z$ ) of the rhombic  $\text{VO}^{2+}$  complex in CsCl crystal were measured [8]. However, to date no satisfactory theoretical explanations for these spectroscopic data have been performed.

It is agreed that in crystal field theory, the optical and EPR data of  $d^n$  ions in crystals can be calculated from two theoretical methods. One is the complete diagonalization (of energy matrix) method (CDM) and another is the perturbation theory method (PTM) [9–13].

The aim of this study is to calculate the optical band positions and spin-Hamiltonian parameters for the rhombic  $\text{VO}^{2+}$  complex in CsCl crystal from CDM and PTM methods. The results are discussed.

## 2. CDM calculation

The measurement of spin-Hamiltonian parameters in EPR experiment needs an external magnetic field and the hyperfine structure constants  $A_i$  are due to the hyperfine interaction. So the Hamiltonian concerning the optical and EPR data for  $d^1$  ions in rhombic crystal field and under an external magnetic field  $H_M$  should be represented as

$$\hat{H} = H_f + H_{\text{so}}(\zeta) + H_{\text{CF}}(B_k^l) + H_{\text{ze}}(k) + H_{\text{hf}}(P), \quad (1)$$

where the five terms are, respectively, the free-ion, the spin-orbit, the crystal-field, the Zeeman (or magnetic) and hyperfine interaction terms. The latter four terms can be written as [9, 14]:

$$\hat{H}_{\text{so}} = \zeta \mathbf{L} \cdot \mathbf{S}, \quad (2)$$

$$\hat{H}_{\text{CF}} = B_{20}C_{20} + B_{22}(C_{22} + C_{2,-2}) + B_{40}C_{40}$$

$$+ B_{42}(C_{42} + C_{4,-2}) + B_{44}(C_{44} + C_{4,-4}), \quad (3)$$

$$\hat{H}_{\text{Ze}} = \mu_B(\mathbf{L} + g_e\mathbf{S}) \cdot \mathbf{H}_M, \quad (4)$$

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$$\hat{H}_{\text{hf}} = P \left\{ \mathbf{L} + \left( \frac{4}{7} - \kappa \right) \mathbf{S} - \frac{1}{7} [(\mathbf{L} \cdot \mathbf{S}) \mathbf{L} + \mathbf{L} (\mathbf{L} \cdot \mathbf{S})] \right\} \cdot \mathbf{I}, \quad (5)$$

where  $\zeta$  is the spin-orbit parameter.  $B_{kl}$  are the crystal-field parameters,  $k$  is the orbit reduction factor.  $g_e$  ( $\approx 2.0023$ ) is the  $g$  factor of free electron.  $P$  is the dipolar hyperfine structure constant.  $\kappa$  is the core polarization constant. The rest notations are conventional. In consideration of the covalence reduction effect for  $d^n$  ions in crystals, we introduce a parameter  $N^2$  to characterize the effect [15, 16]. Thus, we have [15–18]:

$$\zeta \approx N^2 \zeta_0, \quad k \approx N^2, \quad P \approx N^2 P_0, \quad (6)$$

in which  $\zeta_0$  and  $P_0$  are the corresponding parameters in free state. For free  $V^{4+}$  ion,  $\zeta_0 \approx 248 \text{ cm}^{-1}$  [9] and  $P_0 \approx 172 \times 10^{-4} \text{ cm}^{-1}$  [19].

By means of the strong field basis functions [20], the  $10 \times 10$  complete energy matrix of the Hamiltonian in Eq. (1) is constructed. The optical band positions (or crystal field energy levels) can be obtained from the eigenvalues of the energy matrix and the spin-Hamiltonian parameters are calculated by the following formulae:

$$g_i = \frac{\Delta E_{Z_e}(i)}{\mu_B H_i}, \quad A_i = \Delta E_{\text{hf}}(i), \quad i = x, y, z, \quad (7)$$

in which  $\Delta E_{Z_e}(i)$  is the Zeeman splitting with an external magnetic field along  $i$  direction and  $\Delta E_{\text{hf}}(i)$  is the hyperfine splitting with the operators in Eq. (5) along  $i$  direction. They can be acquired by diagonalizing the energy matrix.

TABLE

The optical band position (in  $\text{cm}^{-1}$ ) and spin-Hamiltonian parameters for  $\text{VO}^{2+}$  complex in CsCl crystal.

	Calculation		Experiment [8]
	CDM	PTM	
$ d_{xy}\rangle \rightarrow  d_{yz}\rangle$	13060	13070	12930
$\rightarrow  d_{xz}\rangle$	14180	14210	13740
$\rightarrow  d_{x^2-y^2}\rangle$	14484	14460	14570
$\rightarrow  d_{z^2}\rangle$	22032	22000	21800
$g_x$	1.98435	1.9843	1.980(1)
$g_y$	1.98285	1.9828	1.979(1)
$g_z$	1.93315	1.9331	1.9342(5)
$A_x$ ( $10^{-4} \text{ cm}^{-1}$ )	-65.9	-65.3	67(2) <sup>a</sup>
$A_y$ ( $10^{-4} \text{ cm}^{-1}$ )	-66.2	-65.6	71(2) <sup>a</sup>
$A_z$ ( $10^{-4} \text{ cm}^{-1}$ )	-180.1	-177.0	180(1) <sup>a</sup>

<sup>a</sup> The values are actually the absolute values (see Sect. 4).

In the energy matrix, the parameters  $\zeta$ ,  $B_{kl}$  and  $\kappa$  are taken as adjustable parameters. By matching the calculated optical band positions and spin-Hamiltonian parameters using CDM to the experimental values, we obtain

$$N^2 \approx 0.84, \quad \kappa \approx 0.82, \quad B_{20} \approx 21180 \text{ cm}^{-1}, \\ B_{22} \approx -1286 \text{ cm}^{-1}, \quad B_{40} \approx 11200 \text{ cm}^{-1},$$

$$B_{42} \approx -398 \text{ cm}^{-1}, \quad B_{44} \approx 18147 \text{ cm}^{-1}. \quad (8)$$

The calculated optical and EPR data are compared with the experimental values in Table. The ground state wavefunction corresponds to one (related to the ground state) of the eigenvalues of the energy matrix and can be given from CDM calculation. The result is

$$\varphi = 0.99988 |d_{xy}\rangle - 0.0062i |d_{xz}\rangle - 0.0067 |d_{yz}\rangle \\ + 0.0122i |d_{x^2-y^2}\rangle - 0.0002i |d_{z^2}\rangle. \quad (9)$$

### 3. PTM calculation

The perturbation formulae of spin-Hamiltonian parameters for  $d^1$  (or  $d^9$ ) ions in crystals depend upon the ground state. For the conjugate  $d^9$  ions in the rhombic octahedral crystal field, the ground states is not a pure state (e.g.,  $|d_{x^2-y^2}\rangle$  or  $|d_{z^2}\rangle$ ), but is the admixture of  $|d_{x^2-y^2}\rangle$  and  $|d_{z^2}\rangle$  states, i.e. [21–24],

$$\varphi = a |d_{x^2-y^2}\rangle + b |d_{z^2}\rangle, \quad (10)$$

where  $a$  and  $b$  ( $a^2 + b^2 = 1$ ) are the mixing coefficients due to the rhombic field components. Thus, the mixing coefficients  $a$  and  $b$  can be found in the perturbation formulae of spin-Hamiltonian parameters [21–24]. If the admixture is neglected (e.g., let  $b = 0$ ), the calculated spin-Hamiltonian parameters (e.g.,  $g$  factors) are in poor agreement with the experimental values [24]. However, for  $3d^1$  ions in rhombic octahedral crystal field, e.g.  $\text{VO}^{2+}$  complex in CsCl crystal under study, from Eq. (9), one can find that the admixture of the ground and excited states is too small to be considered. In order to further confirm this point, the calculations of the spin-Hamiltonian parameters (and also the optical band positions) for  $\text{VO}^{2+}$  complex in CsCl crystal through the perturbation formulae with the pure ground state  $|d_{xy}\rangle$  should be made. From the perturbation theory, the high-order perturbation formulae of spin-Hamiltonian parameters for  $3d^1$  ions in the rhombic octahedra with the pure  $|d_{xy}\rangle$  as ground state are derived as

$$g_x = g_e - \frac{2k\zeta}{E_1} + \frac{k\zeta^2}{E_1 E_2} + \frac{2k\zeta^2}{E_2 E_3} - \frac{2k\zeta^2}{E_1 E_3} - \frac{g_e \zeta^2}{2E_2^2} - \frac{2g_e \zeta^2}{E_3^2}, \\ g_y = g_e - \frac{2k\zeta}{E_2} + \frac{k\zeta^2}{E_1 E_2} + \frac{2k\zeta^2}{E_1 E_3} - \frac{2k\zeta^2}{E_2 E_3} - \frac{g_e \zeta^2}{2E_1^2} - \frac{2g_e \zeta^2}{E_3^2}, \\ g_z = g_e - \frac{8k\zeta}{E_3} - \frac{k\zeta^2}{E_1 E_2} - \frac{2k\zeta^2}{E_1 E_3} - \frac{2k\zeta^2}{E_2 E_3} - \frac{g_e \zeta^2}{2E_1^2} - \frac{g_e \zeta^2}{2E_2^2}, \quad (11)$$

$$A_x = P \left[ -\kappa + \frac{2}{7} + (g_x - g_e) + \frac{3}{14}(g_y - g_e) \right],$$

$$A_y = P \left[ -\kappa + \frac{2}{7} + (g_y - g_e) + \frac{3}{14}(g_x - g_e) \right],$$

$$A_z = P \left[ -\kappa - \frac{4}{7} + (g_z - g_e) + \frac{3}{14}(g_y - g_e) + \frac{3}{14}(g_x - g_e) \right], \quad (12)$$

where the crystal field energy levels  $E_i$  (which correspond to the optical band positions) are

$$\begin{aligned} E_1 &= E(|d_{xz}\rangle - E(|d_{xy}\rangle)) = \frac{3}{7}B_{20} + \frac{\sqrt{6}}{7}B_{22} - \frac{5}{21}B_{40} \\ &\quad + \frac{2\sqrt{10}}{21}B_{42} + \frac{\sqrt{70}}{21}B_{44}, \\ E_2 &= E(|d_{yz}\rangle - E(|d_{xy}\rangle)) = \frac{3}{7}B_{20} - \frac{\sqrt{6}}{7}B_{22} - \frac{5}{21}B_{40} \\ &\quad - \frac{2\sqrt{10}}{21}B_{42} + \frac{\sqrt{70}}{21}B_{44}, \\ E_3 &= E(|d_{x^2-y^2}\rangle - E(|d_{xy}\rangle)) = \frac{2\sqrt{70}}{21}B_{44}, \\ E_4 &= E(|d_{z^2}\rangle - E(|d_{xy}\rangle)) \\ &= \frac{4}{7}B_{20} + \frac{5}{21}B_{40} + \frac{\sqrt{70}}{21}B_{44}. \end{aligned} \quad (13)$$

Substituting the same parameters  $N^2$ ,  $\kappa$  and  $B_{kl}$  used in CDM calculation into the formulae (11)–(13), the spin-Hamiltonian parameters and optical band positions of  $\text{VO}^{2+}$  complex in CsCl crystal are calculated together by using PTM. The results are also shown in Table.

#### 4. Discussion

For  $\text{V}^{4+}$  (or  $\text{VO}^{2+}$ ) ions in many crystals, the studies of the hyperfine structure constants  $A_i$  suggested that the core polarization constant  $\kappa \approx 0.6$ – $1.0$  [3–8, 23]. Our value  $\kappa \approx 0.82$  obtained for  $\text{VO}^{2+}$  complex in CsCl crystal is within the range, so it is suitable.

Our calculated hyperfine structure constants  $A_i$  are negative. However, the experimental values obtained from EPR spectra given in Ref. [8] are positive. The difference is because the signs of hyperfine structure constants  $A_i$  for  $d^n$  and  $f^n$  ions in crystals are difficult to be measured solely from EPR experiment [14, 19, 25–27]. So, the observed values of  $A_i$  acquired from EPR experiments are actually the absolute values [25–27] although they are often written as positive values in some papers (including the studied  $\text{VO}^{2+}$  complex in CsCl crystal in [8]). It is noted that the negative signs of hyperfine structure constants  $A_i$  for  $\text{V}^{4+}$  octahedral clusters in crystals were pointed out in Refs. [19, 28–32]. So, our calculated hyperfine structure constants  $A_i$  are rational.

The calculated optical and the EPR data from PTM based on the pure  $|d_{xy}\rangle$  ground state are very close to those from CDM (see Table). This confirms that the admixture of ground state with the excited states is indeed too small to be considered. Importantly, the optical and EPR data calculated from CDM and PTM for  $\text{VO}^{2+}$  complex in CsCl crystal are in reasonable agreement with the experimental values (see Table, note: the

small differences of optical and EPR data between calculation and experiment are because the contributions of electron–phonon interaction to these data are not considered in the calculations). So both methods are effective in the investigations of the optical and EPR data for  $\text{VO}^{2+}$  ( $\text{V}^{4+}$ ) ions in crystals. It should be pointed out that the almost pure  $|d_{xy}\rangle$  ground state for the rhombic  $\text{VO}^{2+}$  octahedra in crystals is not due to the small rhombic components. In fact, if the rhombic components  $B_{22}$ ,  $B_{42}$  are largely increased (which can lead the difference between  $g_x$  and  $g_y$  to become larger), we find that the above admixture is still very small and so the ground state can be approximately regarded as a pure  $|d_{xy}\rangle$ . This point is different from the conjugate  $d^9$  rhombic octahedral clusters in crystals where the ground state is the admixture of  $|d_{x^2-y^2}\rangle$  and  $|d_{z^2}\rangle$  states.

#### 5. Conclusion

The optical band positions and spin-Hamiltonian parameters ( $g$  factors  $g_i$  and hyperfine structure constants  $A_i$ , where  $i = x, y, z$ ) of the rhombic  $\text{VO}^{2+}$  complex in CsCl crystal are investigated by both the methods of CDM and PTM. The investigations indicate that both methods are effective in the explanations of optical and electron paramagnetic resonance (EPR) data for  $d^1$  ions in crystals. The crystal field parameters  $B_{kl}$ , the covalence reduction parameter  $N^2$  and core polarization constant  $\kappa$  are determined. The calculations also suggest that in  $d^1$  rhombic octahedra the ground state is almost a pure  $|d_{xy}\rangle$  state which is different from that of conjugate  $d^9$  (e.g.,  $\text{Cu}^{2+}$ ) ions in rhombic octahedra where the ground state should be an admixture of ground and first excited states.

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