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Theoretical studies of the optical and EPR spectra for VO^{2+} in $Na_3C_6H_5O_7 \cdot 2H_2O$ single crystal

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On the basis of the perturbation formulas for a d^1 configuration ion in a tetragonal crystal field, the three optical absorption bands and electron paramagnetic resonance (EPR) parameters (g factors g_i and hyperfine structure constants A_i for $i = \parallel$ and $\perp$, respectively) of VO^{2+} in $Na_3C_6H_5O_7 \cdot 2H_2O$ single crystals were studied using the perturbation theory method. By simulating the calculated optical and EPR spectra to the observed values, local structure parameters and negative signs of the hyperfine structure constants A_i of the octahedral $(VO_6)^{8-}$ cluster in trisodium citrate dehydrate single crystal can be obtained.

Key words: *EPR, optical spectra, vanadyl, trisodium citrate dehydrate*

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1. Introduction

Electron paramagnetic resonance (EPR) has long been considered as one of the most useful tools for the experimental study of chemical bonding, structural information of the electronic and spatial configuration of paramagnetic centers [1–3]. The optical absorption method provides the crystal field parameters and the energy level structure of the metal ion [4, 5]. Thus, EPR and optical spectrum technique are two powerful tools for studying point symmetry and dynamic properties of the transition-metal ions in the host crystals. The vanadyl ion (i.e., VO^{2+}), having $3d^1$ configuration, is the most stable cation among a few molecular paramagnetic transition metal ions that is used extensively as an impurity probe for probing the site symmetry of the central ion and the bonding nature with the ligands EPR studies [1, 2, 6–8]. Moreover, due to the strong V=O bonding in VO^{2+} ion, most of the VO^{2+} complexes in the crystals posses C_{4v} symmetry with both g and A values found to be axially symmetric [6, 7]. For example, Karabulut et al. measured the optical spectra and EPR parameters for V^{4+} center in trisodium citrate dehydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$; TSCD hereafter) single crystal [8]. As is known, for $3d^1$ (VO^{2+} or V^{4+}) ion in crystals, an octahedral complex with a tetragonal compression would give $g_\parallel < g_\perp < g_s$ and $|A_\parallel| > |A_\perp|$ [9, 10], where g_s is the free-spin g value of 2.0023. The observed EPR parameters (see table 1) of TSCD:VO^{2+} agree with the relation. That is to say, the studied $(VO_6)^{8-}$ cluster in TSCD crystal is in tetragonally distorted compressed octahedral. Based on the crystal-field theory, theoretical calculations of the optical absorption and EPR spectra of TSCD:VO^{2+} were performed using the complete diagonalization energy matrix method (CDM) by Kalfaoglu and Karabulut, and the calculated results agree with the experimental data (see table 1, Cal[a].) [11]. However, the previous treatments fail to connect the optical and EPR spectra with the local structures of the system studied and local lattice distortion around the Jahn-Teller ion V^{4+} center was not taken into account. Consequently, the local structures information of the $(VO_6)^{8-}$ cluster in TSCD crystal was not obtained. Since the analysis of the optical and EPR spectra can provide useful information about electronic states and local structures of the octahedral $(VO_6)^{8-}$ cluster in TSCD single crystal, which would be helpful in understanding the properties of this crystal, further studies on

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the above experimental results are of specific scientific and practical significance. In this work, the optical and EPR spectra of VO^{2+} doped TSCD crystal are a reasonable explanation for using the perturbation theory method (PTM) for a $3d^1$ ion in tetragonally compressed octahedra. In the calculated formulas, the tetragonal field parameters D_s and D_t are estimated from the superposition model which makes it possible to correlate the crystal-field parameters and hence the EPR parameters with the tetragonal distortion ΔR ($= R_\perp - R_\parallel$) of $(VO_6)^{8-}$ cluster in TSCD crystal. Based on the above studies, some useful information of defect structures for the tetragonal V^{4+} centers in TSCD crystal can be obtained from the EPR and optical spectra analysis. The negative signs of hyperfine structure constants $A_\parallel$ and $A_\perp$ are also suggested from the calculations.

2. Calculation

For a $3d^1$ ion in tetragonally compressed octahedra, its higher orbital doublet ^2E_g of the original cubic case would split into two orbital singlets $^2B_{1g}(|d_{x^2-y^2}\rangle)$ and $^2A_{1g}(|d_{z^2}\rangle)$, while the original lower orbital triplet $^2T_{2g}$ would be separated into an orbital doublet $^2E_{1g}$ ($|d_{xz}\rangle$ and $|d_{yz}\rangle$) and a singlet $^2B_{2g}$ ($|d_{xy}\rangle$), with the latter lying lowest [12, 13]. Therefore, the three optical absorption bands can be given as:

$$\begin{aligned} E_1 &= E(^2B_{2g}) \rightarrow E(^2B_{1g}) = 10D_q, \\ E_2 &= E(^2B_{2g}) \rightarrow E(^2E_{1g}) = -3D_s + 5D_t, \\ E_3 &= E(^2B_{2g}) \rightarrow E(^2A_{1g}) = 10D_q - 4D_s - 5D_t. \end{aligned} \tag{1}$$

The cubic and tetragonal field parameters (i.e., D_q, D_s and D_t) can be determined from the superposition model [13] and the geometrical relationship of the impurity V^{4+} center:

$$\begin{aligned} D_q &= \frac{3}{4}\overline{A}_4(R), \\ D_s &= \frac{4}{7}\overline{A}_2(R)\left[\left(\frac{\overline{R}}{R_\parallel}\right)^{t_2} - \left(\frac{\overline{R}}{R_\perp}\right)^{t_2}\right], \\ D_t &= \frac{16}{21}\overline{A}_4(R)\left[\left(\frac{\overline{R}}{R_\parallel}\right)^{t_4} - \left(\frac{\overline{R}}{R_\perp}\right)^{t_4}\right]. \end{aligned} \tag{2}$$

Here, $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents in view of the ionic nature of the bonds [14–16]. $\overline{R} = (R_\parallel + 2R_\perp)/3$ is the average impurity-ligand (V-O) distance, where $R_\parallel$ is the (V-O) distance along the C_4 axis, and $R_\perp$ is the bonding length between V^{4+} and the original planar oxygen ions. $\overline{A}_2(R)$ and $\overline{A}_4(R)$ are the intrinsic parameters with the reference distance R, where R ($\approx R_\perp \approx 1.985$ Å [17]) is taken for the VO^{2+} in cubic field. For $3d^n$ ions in octahedra, the ratio $\overline{A}_2(R)/\overline{A}_4(R)$ is in the range of 9–12 in many crystals [4, 12, 13, 18–20]. Here, we take the mean value, i.e. $\overline{A}_2(R)/\overline{A}_4(R) \approx 10.5$.

Within the high order perturbation theory, the third-order perturbation formulas of EPR parameters (g factors $g_\parallel$, $g_\perp$ and the hyperfine structure constants $A_\parallel$, $A_\perp$) for $3d^1$ ions in tetragonal symmetry with the ground state $^2B_{2g}$ ($|d_{xy}\rangle$) can be derived as [9, 20]:

$$\begin{aligned} g_\parallel &= g_s - 8k\frac{\zeta}{E_2} - (k+g_s)\frac{\zeta^2}{E_2^2} + 4k\frac{\zeta^2}{E_1E_2}, \\ g_\perp &= g_s - 2k\frac{\zeta}{E_1} + (k-g_s)\frac{\zeta^2}{E_1^2} - 2g_s\frac{\zeta^2}{E_2^2}, \\ A_\parallel &= P\left[\left(-\kappa - \frac{4}{7}\right) + (g_\parallel - g_s) + \frac{3}{7}(g_\perp - g_s)\right], \\ A_\perp &= P\left[\left(-\kappa + \frac{2}{7}\right) + \frac{11}{14}(g_\perp - g_s)\right]. \end{aligned} \tag{3}$$

In the above formulas, k is the orbital reduction factor. ζ and P are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter for the center $3d^1$ ion (i.e., V^{4+}) in crystals. κ is the isotropic core polarization constant. Generally, the value of κ within the range 0.6–1.0 for

Table 1. The calculated and experimental optical spectra (in cm^{-1}) and EPR parameters g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) for TSCD:VO^{2+} cryatal.

	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$^2B_{2g} \rightarrow {}^2E_{1g}$	$^2B_{2g} \rightarrow {}^2B_{1g}$	$^2B_{2g} \rightarrow {}^2A_{1g}$
Cal[a].	1.932	1.992	−182.4	−65.3	12168	16873	23957
Cal[b].	1.939	1.988	−180.9	−66.1	12410	16893	24625
Expt.[8]	1.938	1.998	183.7	64.4	12195	16892	24631

[a] Calculated by Kalfaoglu and Karabulut using the complete diagonalization energy matrix method (CDM) in reference [11].
[b] Calculated in this work based on the perturbation theory method (PTM).

VO^{2+} in various crystal [4, 10, 19–22], here, we take $\kappa \approx 0.80$, which is comparable with that κ (≈ 0.72) obtained by the previous work and can be regarded as reasonable. Thus, the g factors, especially the anisotropy Δg ($= g_\parallel - g_\perp$) is connected with the tetragonal field parameters and hence with the local structure (i.e., the relative tetragonal elongation $R_\parallel - R_\perp$) of the studied systems. Due to the covalence reduction effect for $3d^n$ ions in crystals, we have [19–22]

$$\zeta = N^2\zeta_0 \qquad \text{and} \qquad P = N^2P_0\,. \tag{4}$$

Here, N ($\approx k$) is the covalency reduction factor characteristic of the covalency effect of the systems studied. Thus, the spin-orbit coupling coefficient ζ and the dipolar hyperfine structure parameter P can be acquired for the studied systems by using the free-ion data ζ_0 (≈ 248 cm^{-1} [23]) and P_0 ($\approx 172 \times 10^{-4}$ cm^{-1} [24]) for V^{4+} ion. So, in the above formulas, only the parameters N, $\overline{A}_4(R)$ and $R_\parallel$ are unknown. By fitting the calculated optical and EPR spectra to the experimental values, one can obtain

$$N \approx 0.855, \qquad \overline{A}_4(R) \approx 1277 \text{ cm}^{-1} \qquad \text{and} \qquad R_\parallel \approx 1.733 \text{ Å}. \tag{5}$$

The calculated results are compared with the experimental values in table 1. Interestingly, the obtained V-O distance along the C_4 axis V–O bond lengths ($R_\parallel \approx 1.733$ Å) of the studied $(VO_6)^{8-}$ cluster in TSCD crystal, which is very close to that $R_\parallel$ (≈ 1.739 Å [4] and 1.60 Å [20]) for VO^{2+} doped in calcium aluminoborate glasses (CaAB) and $CdNaPO_4 \cdot 6H_2O$ crystal with similar tetragonally compressed $(VO_6)^{8-}$ cluster can be regarded as reasonable.

3. Discussion

1) From table 1, one can find that the calculated (Cal[b].) optical and EPR spectra are in reasonable agreement with the observed values. Thus, the optical and EPR spectra of the system studied are quantitatively interpreted and the local defect structure of the octahedral $(VO_6)^{8-}$ cluster in TSCD crystal is established. The results $R_\perp > R_\parallel$ indicate that the studied $(VO_6)^{8-}$ cluster exists in a tetragonal distortion octahedral site compressed along the C_4-axis, which is consistent with the experimental EPR results (i.e., $g_\parallel < g_\perp < g_s$ and $|A_\parallel| > |A_\perp|$) under the ground state B_{2g}.

2) The validity of the adopted covalency factor N can be further illustrated by the relationship $N^2 \approx 1 - h(L)k(M)$ [25], where the parameters $h(L)$ (≈ 1) is the characteristic of the ligands L ($= O^{2-}$), and $k(M)$ is the characteristic of the central metal ion [26]. From the values $k(V^{2+}) \approx 0.1$ [26] and $k(V^{3+}) \approx 0.2$ [26], one can here reasonably obtain $k(V^{4+}) \approx 0.3$ by extrapolation. Thus, we have N of about 0.84, which is close to the adopted ones ($N \approx 0.855$) and can be regarded as reasonable.

3) The above calculations suggested that the hyperfine structure constants $A_\parallel$ and $A_\perp$ of VO^{2+} in TSCD crystal are negative (see table 1), but the observed values given in reference [8] are positive. It should be pointed out that the signs of constants $A_\parallel$ and $A_\perp$ cannot be determined solely from EPR measurement [27]. Thus, the experimental values of constants $A_\parallel$ and $A_\perp$ are actually absolute values [6–8]. In this paper, we found, that the signs of $A_\parallel$ and $A_\perp$ for VO^{2+} in TSCD crystal should be negative, and

this is consistent with a number of theoretical investigations [4, 9, 19–22] and the previous calculation [11]. Therefore, the above calculated $A_{\parallel}$ and $A_{\perp}$ of the hyperfine structure constants for TSCD:VO^{2+} are reasonable in signs and in magnitude.

4. Summary

The optical and EPR spectra of the tetragonal V^{4+} center in TSCD single crystal are theoretically investigated based on PTM and related equations, the calculated results are in good agreement with the observed values. Large tetragonal compressed distortion ΔR (= 0.252 Å) of $(VO_6)^{8-}$ cluster in TSCD single crystal are reasonably established. Obviously, the calculated method is also effective for other similar systems.

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Теоретичні дослідження оптичних спектрів та спектрів ЕПР для VO^{2+} у монокристалі $Na_3C_6H_5O_7 \cdot 2H_2O$

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Базуючись на пертурбаційних формулах для іону конфігурації d^1 у тетрагональному кристалічному полі, було досліджено три смуги оптичного поглинання та параметри електронного парамагнітного резонансу (ЕПР) (g-фактори g_i та константи надтонкої структури A_i для $i = \parallel$ і $\perp$, відповідно) для VO^{2+} у монокристалах $Na_3C_6H_5O_7 \cdot 2H_2O$, використовуючи метод теорії збурень. Допасовуючи обчислені оптичні спектри та спектри ЕПР до спостережуваних значень, можна отримати локальні структурні параметри та від'ємні знаки констант надтонкої структури A_i октаедричного кластера $(VO_6)^{8-}$ в монокристалі тринатрійцитрат дигідрату.

Ключові слова: *ЕПР, оптичні спектри, ванадил, тринатрійцитрат дигідрат*