Theoretical Calculation of the Optical and EPR Spectra for VO$^{2+}$ in Zinc Lactate Trihydrate Single Crystal

Ram Kripal and Awadhesh Kumar Yadav

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Abstract

The optical and electron paramagnetic resonance (EPR) spectra for VO$^{2+}$ ion in zinc lactate trihydrate (ZLT) single crystals are calculated using perturbation theory method (PTM). The calculated optical absorption bands and spin-Hamiltonian parameters are in reasonable agreement with the experimental values. It appears that theoretical method used is effective in explaining optical and EPR spectra of 3d$^1$ ion in crystals.

Keywords: A. Single crystal; D. Crystal fields; D. Optical properties; D. Electron paramagnetic resonance

1. Introduction

Electron paramagnetic resonance (EPR) is one of the most important tools for the experimental study of chemical bonding of paramagnetic centers (Kripal et al, 2010; Poonguzhali et al., 2000; Song et al., 013). The optical absorption provides the energy level structure of the metal ion (Feng, 2007; 2009). Thus, EPR and optical absorption techniques are two powerful tools for studying dynamic behaviour of the transition ions in crystals. The vanadyl, VO$^{2+}$ ion having 3d$^1$ configuration is the most stable cation used extensively as a probe for finding the site symmetry of central ion and its bonding with various ligands employing EPR studies (Kripal et al, 2010; Poonguzhali et al., 2000; Kripal and Shukla, 2011; Sivprasad et al., 1990; Kripal and Singh, 2006). Moreover, due to strong V=O bonding in VO$^{2+}$ ion, most of the VO$^{2+}$ complexes posses $C_4v$ symmetry with both g and A values being axially symmetric (Kripal and Shukla, 2011; Sivprasad et al., 1990). Kripal et al. (2006) measured the optical spectra and EPR parameters for VO$^{2+}$ in ZLT single crystal. As is known, for 3d$^1$ (VO$^{2+}$ or V$^{4+}$) ion in crystals, an octahedral complex with a tetragonal compression would give $g_\| < g_\perp < g_s$ and $|A_\| > |A_\perp|$ (Wei, 2010; Karabulut and Tufan, 2008), where $g_s$ is the free-spin g value ($= 2.0023$). The observed EPR parameters of ZLT: VO$^{2+}$ agree with the above relation.

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In this investigation, the optical and EPR spectra of VO\textsuperscript{2+} doped ZLT single crystal are calculated using perturbation theory method (PTM) for a 3d\textsuperscript{i} ion in tetragonally compressed octahedron. In the calculation, 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 $\Delta R (= R_\perp - R_\parallel)$ of (VO\textsubscript{6})\textsuperscript{8−} cluster in ZLT single crystal. On the basis of above, useful information of defect structure for the tetragonal VO\textsuperscript{2+} ions in ZLT single crystal can be obtained.

2. Crystal Structure

The crystal structure of zinc lactate trihydrate, Zn (CH\textsubscript{3}CHOHCOOH)\textsubscript{2}.3H\textsubscript{2}O is monoclinic having space group P2\textsubscript{1}/c, and the unit cell dimensions are $a = 9.38$ Å, $b = 5.83$ Å and $c = 22.00$ Å, $Z = 4$ and angle $\beta = 90.9^\circ$ (Song et al., 2013; Singh et al., 1975). The six oxygen atoms, two from water molecules and four from two lactate groups are nearest neighbors of Zn and they form a distorted octahedron around the zinc atom as shown in Fig.1. All three water molecules inter in hydrogen bonding, and hydroxyl groups in molecules are also involved. A network of hydrogen bonds plays an important role in stabilization of the structure.

![Fig. 1. Surroundings of VO\textsuperscript{2+} ion in ZLT](image)

3. Theoretical Calculation

For a 3d\textsuperscript{i} ion in tetragonally compressed octahedron, its higher orbital doublet $^2E_g$ splits into two orbital singlets $^2B_{1g}$ ($|dx^2−y^2>$) and $^2A_{1g}$ ($|dz^2>$), while the lower orbital triplet $^2T_{2g}$ splits into an orbital doublet $^2E_{1g}$ ($|dxz>$ and $|dyz>$) and a singlet $^2B_{2g}$ ($|dxy>$), latter being the lowest (Wu et al., 2008; Fang et al., 2008). Thus, the three optical absorption bands can be given as:
Ram Kripal and Awadhesh Kumar Yadav / Advances in Alloys and Compounds (2016) Vol. 3 No. 1 pp. 8-14

\[ E_1 = E(2B_{2g}) \rightarrow E(2B_{1g}) = 10Dq \]
\[ E_2 = E(2B_{2g}) \rightarrow E(2E_{1g}) = -3Ds + 5Dt \quad (1) \]
\[ E_3 = E(2B_{2g}) \rightarrow E(2A_{1g}) = 10Dq - 4Ds - 5Dt. \]

The cubic and tetragonal field parameters \((Dq, Ds\) and \(Dt)\) can be determined from the superposition model (Fang et al., 2008; Li et al., 2015) and the following relations:

\[
Dq = 3 - \left( -\frac{2}{7} A_4(R) \left( \frac{R}{R_{||}} \right)^{t_2} - \left( \frac{R}{R_{\perp}} \right)^{t_2} \right)
\]

\[
Ds = 4 - \left( \frac{1}{7} A_2(R) \left( \frac{R}{R_{||}} \right)^{t_2} - \left( \frac{R}{R_{\perp}} \right)^{t_2} \right)
\]

\[
Dt = \frac{16}{21} A_4(R) \left( \frac{R}{R_{||}} \right)^{t_4} - \left( \frac{R}{R_{\perp}} \right)^{t_4}
\]

Here, \(t_2 \approx 3\) and \(t_4 \approx 5\) are the power-law exponents (Newman and Ng, 1989; Dong et al., 2004; Lin et al., 2006). \(\tilde{R} = (R_{||} + 2R_{\perp})/3\) is the average impurity-ligand (V-O) distance, where \(R_{||}\) is the (V-O) distance along the \(C_4\) axis, and \(R_{\perp}\) is the bond length between \(V^{4+}\) and the planar oxygen ions. \(\tilde{A}_2(R)\) and \(\tilde{A}_4(R)\) are the intrinsic parameters, where the reference distance \(R \approx R_{\perp} \approx 2.141\) Å (Gong et al., 2010) is taken for the VO\(^{2+}\) in cubic field. For \(3d^n\) ions in octahedral coordination, the ratio \(\tilde{A}_2(R) / \tilde{A}_4(R)\) is in the range of 9–12 (Feng, 2007, 2009; Wu et al., 2008; Fang et al., 2008; Kuang et al., 2012; Zhang et al., 2014; Huang et al., 2013). Here, we take \(\tilde{A}_2(R) / \tilde{A}_4(R) \approx 9.5\).

The third-order perturbation formulae of EPR parameters \((g\) factors \(g_{||}\) and \(g_{\perp}\) and the hyperfine structure constants \(A_{||}\) and \(A_{\perp}\)) for \(3d^n\) ions in tetragonal symmetry with the ground state \(^2B_{2g}\) \((|dxy>\)) are obtained as (Wei, 2010; Huang et al., 2013):

\[
g_{||} = g_S - 8k - \frac{\xi^2}{E_2} = -(k + g_S) \frac{\xi^2}{E_2} + 4k \frac{\xi^2}{E_1 E_2}
\]

\[
g_{\perp} = g_S - 2k \frac{\xi^2}{E_1} + (k - g_S) \frac{\xi^2}{E_1 E_2} - 2g_S \frac{\xi^2}{E_2}
\]

(3)
In the above formulae, $k$ is the orbital reduction factor. $\xi$ and $P$ are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter for $3d^n$ ion in crystals. $K$ is the isotropic core polarization constant. In general, the value of $K$ is in the range 0.6–1.0 for VO$^{2+}$ ion in various crystals (Feng, 2007, 2009; Karabulut and Tufan, 2008; Kuang et al., 2012; Zhang et al., 2014; Huang et al., 2013; Li and Zheng, 2014; Zheng et al, 2008). Here, we take $K \approx 0.86$, which is comparable with the value of $K (\approx 0.72)$ obtained earlier (Fang et al., 2008). Thus, the anisotropy $\Delta g (= g_\parallel - g_\perp)$ is connected with the tetragonal field parameters and hence with the local structure of the studied system. Considering covalency effect for $3d^n$ ions in crystals, we have (Zhang et al., 2014; Huang et al., 2013; Li and Zheng, 2014; Zheng et al, 2008)

$$
\xi = N^2 \xi_0 \quad \text{and} \quad P = N^2 P_0.
$$

(4)

where $N \approx K$ is the covalency reduction factor. Thus, the spin-orbit coupling coefficient $\xi$ and the dipolar hyperfine structure parameter $P$ can be obtained for the studied system by using the free-ion data $\xi_0$ (\approx 248 cm$^{-1}$ (Griffith, 1964)) and $P_0$ (\approx 172\times10^{-4}$ cm$^{-1}$ (Mc Garvey, 1967)) for VO$^{2+}$ ion. By fitting the calculated optical and EPR spectra to the experimental values, one gets

$$
N \approx 0.861, \quad A_\parallel (R) \approx 2550$ cm$^{-1} \quad \text{and} \quad R_\parallel \approx 1.965$ Å.
$$

(5)

The calculated results are compared with the experimental values in Table 1 and Table 2. The obtained V-O distance along C$_4$ axis ($R_\parallel \approx 1.965$ Å) is close to $R_\parallel \approx 1.984$ Å (Feng, 2007; 2009).

4. Result and Discussion

Table 1 The calculated and experimental EPR parameters (g factors and the hyperfine structure constants (in 10$^{-4}$ cm$^{-1}$)) for ZLT: VO$^{2+}$ single crystal.

<table>
<thead>
<tr>
<th></th>
<th>$g$ factors</th>
<th>Hyperfine structure constants (in 10$^{-4}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_\parallel$</td>
<td>$g_\perp$</td>
</tr>
<tr>
<td>Cal.</td>
<td>1.9133</td>
<td>1.9841</td>
</tr>
<tr>
<td>Expt.</td>
<td>1.9236</td>
<td>1.9999</td>
</tr>
</tbody>
</table>

(Kripal and Singh, 2006)
Table 2 The calculated and experimental optical parameters for ZLT: VO\(^{2+}\) single crystal.

<table>
<thead>
<tr>
<th>Octahedral and Tetragonal parameters(\text{cm}^{-1})</th>
<th>Optical absorption bands (in cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dq, Ds, Dt</td>
<td>(^{2}B_{2g} \rightarrow ^{2}E_{1g})</td>
</tr>
<tr>
<td>Cal. 1912 -2987 1194</td>
<td>15,031 19,120 25,103</td>
</tr>
<tr>
<td>Expt. 1988 -2800 1265</td>
<td>14,727 19,880 24,752</td>
</tr>
</tbody>
</table>

From Table 1 & Table 2, one can find that the calculated EPR and optical spectra are in reasonable agreement with the observed values. Thus, the optical and EPR spectra of VO\(^{2+}\) doped ZLT are quantitatively interpreted and the local defect structure of the octahedral \((\text{VO}_6)^{8-}\) cluster in the crystal is established. The value \(R_\perp > R_\parallel\) indicates that the studied \((\text{VO}_6)^{8-}\) cluster exists in a tetragonally distorted octahedral site compressed along the \(C_4\)-axis, which is consistent with the experimental EPR results (\(g_\parallel < g_\perp < g_s\) and \(|A_\parallel| > |A_\perp|\)).

The validity of the covalency factor \(N\) can be further illustrated using \(N^2 \approx 1 - h(L)k(M)\) (Zhang and Wan, 2013), where the parameter \(h(L)\) \((\approx 1)\) is the characteristic of the ligands \(L\) \((= O^{2-})\), and \(k(M)\) is the characteristic of the central metal ion (Li et al., 2015). From the values \(k(V^{2+}) \approx 0.1\) (Li et al., 2015) and \(k(V^{3+}) \approx 0.2\) (Li et al., 2015), one can reasonably obtain \(k(V^{4+}) \approx 0.3\). Thus, we have \(N\) of about 0.84, which is close to \(N \approx 0.861\) taken here and can be considered as reasonable.

The above calculations suggested that the hyperfine structure constants \(A_\parallel\) and \(A_\perp\) of VO\(^{2+}\) in ZLT single crystal are negative (see Table 1), but the observed values given in reference (Kripal and Singh, 2006) are positive. It should be noted that the signs of constants \(A_\parallel\) and \(A_\perp\) cannot be determined only from EPR measurement (Havlicek et al., 1974). Thus, the experimental values of constants \(A_\parallel\) and \(A_\perp\) are actually absolute values (Kripal and Shukla, 2011; Sivprasad et al., 1990; Kripal and Singh, 2006). In the present paper, we found that the signs of \(A_\parallel\) and \(A_\perp\) for VO\(^{2+}\) in ZLT single crystal should be negative. This is consistent with other theoretical investigations (Feng, 2007, 2009; Wei, 2010; Zhang et al., 2014; Huang et al., 2013; Li and Zheng, 2014; Zheng et al., 2008). Therefore, the calculated values of \(A_\parallel\) and \(A_\perp\) for ZLT: VO\(^{2+}\) are reasonable in signs as well as in magnitude.

5. Conclusions

The optical and EPR spectra of VO\(^{2+}\) in ZLT single crystal are theoretically investigated using PTM. The calculated results are in good agreement with the observed ones. Large tetragonally compressed distortion \(\Delta R \approx 0.176 \text{ Å}\) of \((\text{VO}_6)^{8-}\) cluster in ZLT single crystal is reasonably established.

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