Theoretical Studies of the Electron Paramagnetic Resonance Parameters and Local Structure for VO$^{2+}$ in Oxyfluoroborate Glasses

Huaming Zhang$^{1,2,*}$, Xiaopeng Yu$^{1,2}$ and Wenbo Xiao$^{1,2}$

$^1$Jiangxi Engineering Laboratory for Optoelectronics Testing Technology, Nanchang Hangkong University, Nanchang 330063, China
$^2$Key Laboratory of Nondestructive Testing, Ministry of Education, Nanchang Hangkong University, Nanchang 330063, China
*Corresponding author: zhm2071@163.com

Abstract: The electron paramagnetic resonance parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) of a tetragonal V$^{4+}$ center in oxyfluoroborate glasses (20Li$_2$O-10Li$_2$F$_2$-70B$_2$O$_3$) are theoretically investigated by using the perturbation formulas for a 3d$^1$ ion in tetragonally compressed octahedra. The calculated results are in good agreement with the experimental data. Local structure parameters of [VO$_6$]$^{8-}$ clusters are obtained from the calculation (i.e., $R_\parallel \approx 1.74$ Å and $R_\perp \approx 1.985$ Å for the metal-ligand distances parallel and perpendicular to the $C_4$ axis, respectively). It is shown that the local structure around the V$^{4+}$ ion possesses a compressed tetragonal distortion along $C_4$ axis. The signs of the hyperfine structure constants $A_\parallel$ and $A_\perp$ for V$^{4+}$ centers in oxyfluoroborate glasses were also suggested in the discussion.

1. Introduction
In recent years glasses doped with transition-metal (TM) ions have attracted a great deal of attraction because of their potential applications in the development of new tunable solid-state lasers, electro-optic switches, solar energy convectors, and fiber optic communication devices [1-6]. Usually, these properties are believed to be sensitive to the internal electric and defect structures produced by impurities. Since electron paramagnetic resonance (EPR) spectroscopy is a sensitive technique for the study local structures of transition-metal (TM) ions in solids. Many studies on EPR spectra of single TM ions in borate glasses have been made of recent years [7-10]. Amongst these TM ions, vanadyl ion (VO$^{2+}$) is the most stable and widely used EPR probe for probing the site symmetry of the central metal ion and the nature of the bonding with the ligands and this has also been used as an impurity for understanding the defect, structural, phase transition and orientation properties of the host lattice [1, 11, 12]. Because of the strong V$^{4+}$-O$^{2-}$ bonding in VO$^{2+}$ ion, most of the VO$^{2+}$ complexes in the crystals posses tetragonally compressed (along the V$^{4+}$-O$^{2-}$ bonding) octahedral or square pyramid symmetry ($C_{4v}$). This point has been confirmed by the optical and EPR spectral experiments for VO$^{2+}$ complexes in many crystals [7, 8, 11]. For example, the EPR experiments were carried out for VO$^{2+}$ doped oxyfluoroborate glasses (20Li$_2$O-10Li$_2$F$_2$-70B$_2$O$_3$), and the EPR parameters (i.e., g factors $g_\parallel = 1.9370$, $g_\perp = 1.9802$ and hyperfine structure constants $A_\parallel = 176$, $A_\perp = 57 \times 10^{-4}$ cm$^{-1}$) were also measured [13]. As is known, an octahedral complex with a tetragonal compression would give $g_\parallel < g_\perp < g_s$ and $|A_\parallel| > |A_\perp|$, where $g_s$ is the free-spin $g$ value of 2.0023. The observed values of the EPR parameters agree
with the relation. That is to say, VO$^{2+}$ complexes in oxyfluoroborate glasses present in tetragonally-compressed octahedral.

However, until now, no satisfactory interpretation to the above experimental results has been made, and information about defect structure for the impurity V$^{4+}$ center has not been obtained. Considering that microscopic mechanisms of the EPR parameters and information of impurity local structures can be helpful to understand the properties of this material with TM dopants, further studies on the above EPR parameters are of scientific and technical significance. In this work, the third-order perturbation formulas of these EPR parameters for a 3$d^$ ion in tetragonally compressed octahedra are applied. From the calculations, the experimental EPR parameters are explained and some useful information of defect structures for the impurity V$^{4+}$ center in oxyfluoroborate glasses can be acquired.

2. Calculation

When VO$^{2+}$ doped into oxyfluoroborate glasses, the V$^{4+}$ ions lie in the interspace of the three-dimensional lattice and are surrounded by six oxygen atoms. For a V$^{4+}$ (3$d^1$) ion in a tetragonally distorted octahedron, the energy level 3 of the free 3$d^1$ ion in a octahedral crystal field will split into $^2$E$^g$ and $^2$T$^g_2$ levels [14]. In the C$_{4v}$ crystal field, the $^2$T$^g_2$ level is further split into $^2$B$_{2g}$ and $^2$E$^g$ levels, and the $^2$E$^g$ level into $^2$B$_{1g}$ and $^2$A$_{1g}$ levels [14]. According to the crystal-field theory and the experimental EPR parameters, one can conclude that the ground state for V$^{4+}$ in oxyfluoroborate glasses is $^2$B$_{2g}$. Utilizing the perturbation method, the third-order perturbation formulas of the EPR parameters for 3$d^1$ ions in tetragonal symmetry with the ground state $^2$B$_{2g}$ can be derived from the perturbation theory as [15]:

\[
\begin{align*}
g_\| &= g_s - \frac{8k\zeta}{E_2} \left( \frac{k + g_s}{E_2} \right)^2 + 4k\zeta^2 \frac{E_1}{E_2}, \\
g_\perp &= g_s - \frac{2k\zeta}{E_1} \left( \frac{k - g_s}{E_1} \right)^2 - 2g_s\zeta^2 \frac{E_2}{E_1}, \\
A_\| &= P[\kappa - \frac{4N}{7} + (g_\| - g_s) + \frac{3(g_\|- g_s)}{7}], \\
A_\perp &= P[\kappa + \frac{2N}{7} + \frac{11(g_\|- g_s)}{14}] \tag{1}
\end{align*}
\]

In the above formulas, $k$ is the orbital reduction factor, which is equivalent to the covalency factor $N$, a characteristic of the covalency between the central ion and the ligands. $\zeta$ and $P$ are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter for the 3$d^1$ ion in crystals. $\kappa$ is the isotropic core polarization constant. $E_1$ and $E_2$ are the energy separations between the excited $^2$B$_{2g}$ and $^2$E$^g$ and the ground $^2$B$_{1g}$ states under tetragonal crystal fields. Based on the crystal-field theory, they can be calculated from the energy matrices for a 3$d^1$ ion under tetragonal symmetry in terms of the cubic field parameter $D_4$ and the tetragonal field parameters $D_s$ and $D_t$ and can be expressed as:

\[
\begin{align*}
E_1 &= E(\Delta E) - E(\Delta B_2) = -3D_s + 5D_t, \\
E_2 &= E(\Delta B_1) - E(\Delta B_2) = 10D_q \tag{2}
\end{align*}
\]

From the superposition model [16], the cubic and tetragonal field parameters can be determined as:

\[
\begin{align*}
D_q &= \frac{4}{3} A_4(R_0), \\
D_s &= \frac{4}{7} A_2(R_0)[\left(\frac{R_0}{R_1}\right)^2 - \left(\frac{R_0}{R_\perp}\right)^4],
\end{align*}
\]
Here, \( t_2 \approx 3 \) and \( t_4 \approx 5 \) are the power-law exponents [14, 15, 17]. \( R_\parallel \) is the impurity-ligand distance along the \( C_4 \) axis, \( R_\perp \) is the bonding length between \( V^{4+} \) and the original planar oxygen ions. \( R_0 (= R_\perp \approx 0.1985 \text{ nm} \{18\}) \) is the reference distance. \( A_2(R_0) \) and \( A_4(R_0) \) are the intrinsic parameters with the reference distance \( R_0 \). For \( 3d^n \) ions in octahedra, the ratio \( A_2(R_0)/A_4(R_0) \) is in the range of \( 9 \sim 12 \) in many crystals [14, 15, 17], and we take the average value \( A_2(R_0)/A_4(R_0) \approx 10.5 \) here. Thus, the EPR parameters is connected with the cubic and tetragonal field parameters and hence with the local structure of the studied systems.

Taking into account the covalency effect (characterized by the covalence reduction factor \( N \)), the spin–orbit coupling parameter \( \zeta \) and dipolar hyperfine constant \( P \) can be given as [15]

\[
\zeta = N^2 \zeta_0, \quad P = N^2 P_0
\]  

Hence, the spin-orbit coupling coefficient \( \zeta \) and the dipolar hyperfine structure parameter \( P \) can be acquired for the studied systems by using the free-ion data \( \zeta_0 (= 248 \text{ cm}^{-1} \{19\}) \) and \( P_0 (= 172 \times 10^4 \text{ cm}^{-1} \{20\}) \) for \( V^{4+} \) ion. From the optical absorption spectra for \( \text{VO}^{2+} \) doped in \( \text{Cs}_2\text{NO}_2 \) powder with the same \([\text{VO}_6]^{8-}\) octahedral clusters, the cubic field parameter \( D_0 \approx 1466 \text{ cm}^{-1} \{16\} \) can be obtained and adopted in this work. The core polarization constant \( \kappa \) lies between 0.6 and 1 for \( \text{VO}^{2+} \) (or \( V^{4+} \)) in various oxide glasses and is sensitive to the even small deformations of the metal electron orbitals [14, 15, 17]. Here, we take \( \kappa \approx 0.71 \).

Thus, only the impurity-ligand distance \( R_0 \) and the covalency factors \( N \) (i.e., the orbital reduction factor \( k \)) are unknown in the formulas of the EPR parameters. Substituting these parameters into Eq.(1) and fitting the calculated EPR parameters to the experimental values, one can obtain:

\[
R_\parallel \approx 0.174 \text{ nm} \quad \text{and} \quad N \approx 0.86
\]  

The corresponding theoretical results of the spin Hamiltonian parameters are compared with the observed values in Table 1.

| Glasses          | \( g_\parallel \) | \( g_\perp \) | \( A_\parallel \) | \( A_\perp \) |
|------------------|-------------------|--------------|----------------|----------|
| \( 20\text{Li}_2\text{O}-10\text{Li}_2\text{F}_2\cdot70\text{B}_2\text{O}_3 \) | 1.9370           | 1.9698       | -177.1        | -58.6    |

### 3. Discussion

From Table 1, one can be seen that the calculated EPR parameters (\( g \) factors \( g_\parallel, g_\perp \) and the hyperfine structure constants \( A_\parallel, A_\perp \)) for \( \text{VO}^{2+} \) in oxyfluoroborate glasses based on the adopted parameters in Eq. (6) are in reasonable agreement with the experimental values. This indicates that the study method and the local structure parameters in Eq. (6) obtained in this work can be regarded as reasonable.

1) By fitting the calculated values to the experimental results, one can obtained that the impurity-ligand distance \( R_0 (= 0.245 \text{ Å} \) along the \( C_4 \) axis for \( V^{4+} \) center in oxyfluoroborate glasses, this means that the \([\text{VO}_6]^{8-}\) octahedron around \( V^{4+} \) ion is significantily compressed (\( \Delta R = R_\perp - R_\parallel \approx 0.245 \text{ Å} \) along the \( C_4 \) axis, which is consistent with the experimental EPR results (i.e. \( g_\parallel < g_\perp \) and \( |A_\parallel| > |A_\perp| \)) under the ground state \( B_{2g} \). The compressed distortion could be explained by Jahn–Teller effect. Because in compression, the ground state is orbit singlet, while in elongation, the ground state is orbit doublet, it can be expected that the latter is unstable. Similar local distortions were also found for the
$3d^1$ (VO$_{3+}$) ion in various oxides glasses. For example, $\Delta R \approx (0.395 \ \text{Å})$ was found for VO$_{3+}$ in Zn (antipyrine)$_2$(NO$_3$)$_2$ [21]. Therefore, the local distortion obtained in this study can be regard as reasonable.

2) The sign of the hyperfine structure constants is very difficult to ascertain [14, 15]. Thus, the experimental results of constants $A$ reported in many crystals are actually the absolute values and they are often written as positive values [22-26]. Muncaster and Parke [27] have proved that the signs of $A$ should be negative for VO$_{3+}$ ions in hydrated salts and glasses. In this paper, we found, that the signs of for VO$_{2+}$ in oxyfluoroborate glasses also should be negative, thus, the signs of the $A_\parallel$ and $A_\perp$ obtained in this work can be regarded as suitable.

3) The validity of the covalency factors $N$ adopted can be roughly illustrated from the empirical formula: $N^2 = 1 - h(L)k(M)$ [28], where the parameters $h(O^{2-}) \approx 1.0$ [28] is the characteristic of the ligand, and $k(M)$ is the characteristic of the central metal ions. From the values $k(V^{2+}) \approx 0.1$ and $k(V^{3+}) \approx 0.15$ [28], one can reasonably obtain $k(V^{4+}) \approx 0.20$ here by extrapolation. Thus, we have $N (\approx 0.86)$. This value is the same as $N (\approx 0.86)$ adopted in this work.

4. Conclusion and

The experimental EPR parameters for V$^{4+}$ center in oxyfluoroborate glasses are theoretically investigated from the perturbation formulas for a 3d$^1$ ion in tetragonally compressed octahedra. From the calculations, the bond length are $R_\parallel \approx 0.174 \ \text{nm}$ for [VO$_6$]$^{8-}$ octahedral clusters. The negative signs of the calculated $A_\parallel$ and $A_\perp$ obtained in this work can be regarded as suitable.

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6. References

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