Theoretical Studies of the Local Structures and EPR Spectra for VO^{2+} in MB_4O_7 (M = Zn, Cd) Glasses

C.-Y. Li*,† AND X.-M. Zheng

School of Physics and Electronic Information, Shangrao Normal University, Shangrao Jiangxi 334000, P.R. China

Electron spin resonance spectral parameters (g factors $g_\parallel$, $g_\perp$ and hyperfine structure constants $A_\parallel$, $A_\perp$) of a tetragonal V^{4+} centers in MB_4O_7 (M = Zn, Cd) are theoretically investigated by using the perturbation formulae for a $3d^1$ ion in tetragonally compressed octahedra. In these formulae, the contributions to the g factors from the tetragonal distortion, characterized by the tetragonal field parameters D_s and D_t are taken into account by considering the local structures of the ligand octahedron around the V^{4+} due to the Jahn–Teller effect. Based on the calculations, the ligand octahedra around V^{4+} are suggested to suffer about 5.7% and 4.3% relative compression along C_4 axis for MB_4O_7 glasses with M = Zn and Cd, respectively, and negative signs of the hyperfine structure constants $A_\parallel$ and $A_\perp$ for V^{4+} centers in MB_4O_7 glasses were suggested in the discussion.

1. Introduction

Borate glasses containing transition metal (or rare earth) ions exhibit interesting ionic conductivity [1, 2], structure [3], luminescence [4], optical and electrical properties [5–7] and have potential usage as solid state electrolytes in batteries [8, 9]. Usually, these properties are believed to be sensitive to the internal electric and defect structures produced by impurities. As an effective tool to analyze the local structure of the impurity centre, the electron paramagnetic resonance (EPR) technique has been widely applied to obtain the local lattice structure information about the glassy network and to identify the point symmetry around the transition metal ions. Among these transition metal ions, vanadyl (VO^{2+}) has advantages as probe in studying local structures and properties in doped crystals, because of the strong V^{4+}–O^{2-} bonding in VO^{2+} ion, most of the VO^{2+} complexes in the crystals possess C_{4v} symmetry with both g and A values found to be axially symmetric.

For example, Murthy et al. measured the EPR spectra for V^{4+} centers in MB_4O_7 glasses (i.e., g factors $g_\parallel$ = 1.9370, $g_\perp$ = 1.9802, 1.9700 and hyperfine structure constants $A_\parallel$ = 176×10^{-4} cm⁻¹, $A_\perp$ = $57, 61 \times 10^{-4}$ cm⁻¹ for M = Zn, Cd, respectively) [10]. They found that the $[VO_6]^{8-}$ cluster is a tetragonally distorted octahedron. As known, an octahedral complex with a tetragonal compression would give $g_\parallel < g_\perp < g_s$ and $|A_\parallel| > |A_\perp|$ [11], 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, the $[VO_6]^{8-}$ cluster for the impurity VO^{2+}

complexes in MB_4O_7 glasses are in tetragonally distorted compressed octahedral. However, till now, the above EPR spectra have not been satisfactorily and quantitatively explained. Particularly, the microscopic mechanisms of V^{4+} centers in MB_4O_7 glasses related to its tetragonal distortion (characterized by $\Delta R = R_\parallel - R_\perp$, where $R_\parallel$ 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) were not made. Since the analysis of the EPR parameters can provide useful information about electronic states and local structures for the impurity V^{4+} centers, which would be helpful to understand the properties of this crystal, thus, further studies on the above EPR results are of specific and practical significance. The goal of this paper is to calculate the experimental EPR parameters for the impurity VO^{2+} in MB_4O_7 glasses by using the perturbation formulae of these parameters for a $3d^1$ ion in tetragonally compressed octahedra. From the calculations, these spectra data are explained and some useful information on the hyperfine structure constants ($A_\parallel$ and $A_\perp$) and local structure distortions for V^{4+} in MB_4O_7 glasses can be obtained.

2. Calculation

For VO^{2+} doped MB_4O_7 glasses, the V^{4+} ions lie in the interspace of the three-dimensional lattice and are surrounded by six oxygen atoms [12]. As a Jahn–Teller ion, V^{4+} will suffer the Jahn–Teller effect via stretching the four V^{4+}–O^{2-} bonds in the perpendicular plane and contracting the other two bonds along C_4 axis, which reduces the local symmetry to the square pyramid (C_{4v}). This point has been illustrated in various studies on V^{4+} in oxygen octahedral [11–13].

The V^{4+} ion has the $3d^1$ electron configuration, its energy level ^2D will be split into ^2E_g and $^2T_{2g}$ in a cubic field [14]. However, in the tetragonal symmetry

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(C_{4v}) the energy levels will be split further, i.e., the 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 orbital triplet $^2T_{2g}$ would be separated into an orbital doublet $^2E_g(|d_{xz}\rangle$ and $|d_{yz}\rangle)$ and a singlet $^2B_{2g}(|d_{xy}\rangle)$ [13]. According to the crystal-field theory and the experimental EPR data, one can conclude that the ground state for V^{4+} in MB_4O_7 glasses is $^2B_2(|d_{xy}\rangle)$. Based on the crystal-field theory, the three optical absorption bands (i.e., d–d transitions) can be calculated from the energy matrices for a $3d^1$ ion under tetragonal symmetry in terms of the cubic field parameter D_q and the tetragonal field parameters D_s and D_t and can be expressed as

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

The spin Hamiltonian for $3d^1$ ions in tetragonal external magnetic field can be expressed as

$$H_s = \mu_B[g_\parallel H_z S_z + g_\perp(H_x S_x + H_y S_y)] + \mu_B H_z S_z$$
$$+ A_\parallel I_z S_z + A_\perp(I_x S_x + I_y S_y). \quad (2)$$

Here g_i $(i = \parallel, \perp)$ indicates the components of the g factor, S_i and I_i $(i = x, y, z)$ are electron and nuclear spin operators, and H_i $(i = x, y, z)$ indicates the components of the magnetic field along the x-, y- and z-axes. $A_\parallel$ and $A_\perp$ are the parallel and perpendicular components of the hyperfine tensor. Utilizing the perturbation method [15], the third-order perturbation formulae of EPR parameters for $3d^1$ ions in tetragonal symmetry with the ground state $^2B_2$ can be derived from the perturbation theory as [16]:

$$g_\parallel = g_s - \frac{8k\varsigma}{E_2} - \frac{(k+g_s)\varsigma_d^2}{E_2^2} + \frac{4k\varsigma^2}{E_1 E_2},$$

$$g_\perp = g_s - \frac{2k\varsigma}{E_1} + \frac{(k-g_s)\varsigma^2}{E_1^2} - \frac{2g_s\varsigma^2}{E_2^2},$$

$$A_\parallel = P\left[-\kappa - \frac{4N}{7} + (g_\parallel - g_s) + \frac{3(g_\perp - g_s)}{7}\right],$$

$$A_\perp = P\left[-\kappa + \frac{2N}{7} + \frac{11(g_\perp - g_s)}{14}\right]. \quad (3)$$

In the above formulae, 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. According to the optical spectra parameter for VO^{2+} doped in crystal with similar $[VO_6]^{8-}$ cluster [17, 18], the covalency factor N (≈ 0.87) for $MB_4O_7{:}VO^{2+}$ can be adopted. κ is the isotropic core polarization constant which indicates the contribution to the A_i $(i = \parallel$ or $\perp)$ by the unpaired s-electron. Generally, the value κ lies between 0.6 and 1.0 for VO^{2+} (or V^{4+}) in various oxide glasses and is sensitive to the even small deformations of the metal electron orbitals [10, 14, 16, 17, 19]. Here, we take $\kappa \approx 0.71$, which is the same as κ (≈ 0.71) obtained by the previous works [10] and is very close to that κ ($\approx 0.69 \sim 0.75$) with the similar tetragonal compressions $[VO_6]^{8-}$ octahedra for the impurity

VO^{2+} in some complexes [18, 20] and can be regarded as reasonably. ς_d and P are, respectively, the spin–orbit coupling coefficient and the dipolar hyperfine structure parameter for the $3d^9$ ion in crystals.

Taking into account the covalency effect (characterized by the covalence reduction factor N), the spin–orbit coupling parameter ζ and dipolar hyperfine constant P can be given as [16]:

$$\varsigma = N^2\varsigma_0, \quad P = N^2 P_0. \quad (4)$$

Hence, 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 $\zeta_0 \approx 248\,\text{cm}^{-1}$ [15] and $P_0 \approx 172 \times 10^{-4}\,\text{cm}^{-1}$ [21] for V^{4+} ion.
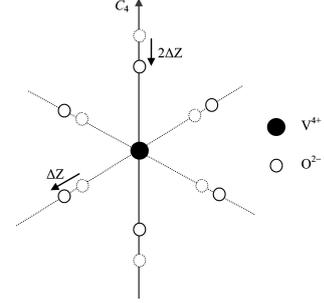
Fig. 1. Projective view of the local lattice structure for V^{4+} centers in the borate glasses MB_4O_7 with $M = $ Zn, Cd.

For the studied VO^{2+} doped MB_4O_7 glasses forming tetragonal $[VO_6]^{8-}$ clusters, due to the Jahn–Teller elongation, the parallel and perpendicular V^{4+}–O^{2-} bond lengths can be expressed in terms of the reference distance R_0 and the relative compression ΔZ as: $R_\parallel \approx R_0(1 - 2\Delta Z)$ and $R_\perp \approx R_0(1 + \Delta Z)$ (see Fig. 1). Thus, the cubic and tetragonal field parameters can be determined from the superposition model [22] and the geometrical relationship of the impurity V^{4+} centers

$$D_q = \frac{3}{4}\overline{A}_4(R_0)\left(\frac{R_0}{R_\perp}\right)^{t_4},$$

$$D_s = \frac{4}{7}\overline{A}_2(R_0)\left[\left(\frac{R_0}{R_\parallel}\right)^{t_2} - \left(\frac{R_0}{R_\perp}\right)^{t_2}\right],$$

$$D_t = \frac{8}{21}\overline{A}_2(R_0)\left[\left(\frac{R_0}{R_\parallel}\right)^{t_4} - \left(\frac{R_0}{R_\perp}\right)^{t_4}\right]. \quad (5)$$

Here, $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [12–14, 16, 17]. $\overline{A}_2(R_0)$ and $\overline{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0. For the studied $[VO_6]^{8-}$ clusters, the reference distance $R_0 \approx 1.95$ Å [11]. 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 [12–14, 23], and we take the mean value, i.e. $\overline{A}_2(R)/\overline{A}_4(R) \approx 10.5$.

Therefore, in the above formulae, only the intrinsic parameters $\overline{A}_4(R_0)$ and the relative elongation ΔZ are unknown in the above formulae. By fitting the calculated EPR parameters to the experimental values, one

TABLE

The calculated and experimental EPR parameters g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) for the doped VO^{2+} in MB$_4$O$_7$ (M = Zn, Cd) glasses.

Glasses		$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$
ZnB$_4$O$_7$	cal.	1.9374	1.9802	−176.5	−57.5
	expt. [10]	1.9370	1.9802	176	57
CdB$_4$O$_7$	cal.	1.9370	1.9698	−177.1	−58.6
	expt. [10]	1.9370	1.9700	176	61

can obtain

$\overline{A}_4(R_0) \approx 2290$ and 2030 cm^{-1},

$\Delta Z \approx 5.7\%$ and 4.3% $\qquad\qquad$ (6)

for the impurity V^{4+} centers in ZnB$_4$O$_7$ and CdB$_4$O$_7$ glasses, respectively. The corresponding calculated EPR parameters are compared with the experimental values in Table.

3. Discussion

From Table, one can see that the calculated EPR spectra data (g factors $g_\parallel$, $g_\perp$ and the hyperfine structure constants $A_\parallel$, $A_\perp$) for VO^{2+} in MB$_4$O$_7$ glasses based on the spectra parameters $\overline{A}_4(R_0)$ and relative tetragonal compressions ΔZ in Eq. (6) are in reasonable agreement with the experimental values. This indicates that the study method and the parameters used in this paper can be regarded as reasonable.

1) The positive sign of the tetragonal compression ΔZ in Eq. (6) illustrated that the impurity V^{4+} ion is located in the distorted octahedral sites (C_{4v}) compressed along C_4 axis, which is consistent with the experimental EPR results (i.e. $g_\parallel < g_\perp < g_e$ and $|A_\parallel| > |A_\perp|$) under the ground state B_{2g}. The compressed distortion could be explained by the 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 distortion caused by the Jahn–Teller effect was found for the $3d^1$ V^{4+} ion in SrTiO$_3$ [24] and VO^{2+} in Zn(antipyrine)$_2$(NO$_3$)$_2$ crystal [25].

2) The adopted covalency factor N can be usually determined from the relationship $N^2 \approx \varepsilon = 1 - h(L)k(M)$, where ε is square of the covalency factor, $h(L)$ and $k(M)$ are the characteristics of the ligand and central metal ions, respectively [26]. From the values $h(O^{2-}) \approx 1$ [26] and $k(V^{2+}) \approx 0.1$ [14] and $k(V^{3+}) \approx 0.15$ [14], one can reasonably obtain $k(V^{4+}) \approx 0.20$ here by extrapolation. Thus, we have N of about 0.89, this value is consistent with the adopted ones ($N \approx 0.87$) and can be regarded as suitable.

3) From Table, one can see the absolute values of $A_\parallel$ and $A_\perp$ are in good agreement with the experimental findings and the signs of both are negative, but the observed values given by Murthy et al. are positive [10]. Actually, the signs of the hyperfine structure constants

are very difficult to ascertain. Thus, many experiments give them as absolute ones [10, 19, 27, 28]. However, the negative signs of the hyperfine structure constants $A_\parallel$ and $A_\perp$ for V^{4+} ions in many crystals were suggested [11–14, 16, 17]. 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 ($g_{\parallel,\perp} - g_s$) and the covalency factor N. Therefore, the signs of the hyperfine structure constants for the V^{4+} centers in MB$_4$O$_7$ glasses were theoretically determined.

4) There are some errors in the above calculations.

First, approximation of the theoretical model and the perturbation formulae adopted in this work can lead to some errors.

Second, the covalency factor N estimated from those of the similar [VO$_6$]$^{8-}$ cluster [17, 18] may also introduce some errors into the calculation results. As N changes by 10%, the errors for the resultants of the g factors are estimated to be not more than 0.4%, because the covalency influences mainly the average of the g factors.
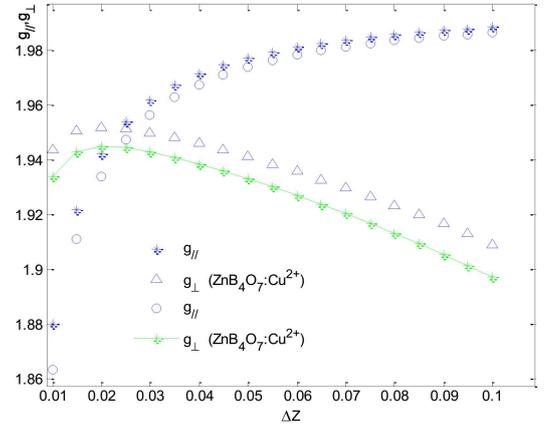
Fig. 2. The EPR g factors varied with the relative elongation ΔZ within the range of 0.01–0.1 with the fixed intrinsic parameters $\overline{A}_4(R_0) \approx 2290$ and 2230 cm^{-1} for VO^{2+} doped in borate glasses ZnB$_4$O$_7$ and CdB$_4$O$_7$, respectively.

Third, the errors may arise from the approximation of the relationship $\overline{A}_2(R) \approx 10.5\overline{A}_4(R)$ for the tetragonal field parameters. The deviation of the relative elongation ΔZ is estimated to be about 3% as the ratio $\overline{A}_2(R)/\overline{A}_4(R)$ varies within the widely accepted range of 9–12. In addition, the power law components t_2 and t_4 may deviate from 3 and 5 of the corresponding point charge model values, which can also bring forward some errors for the final spin Hamiltonian parameters. If the above values change to $t_2 \approx 4$ and $t_4 \approx 6$, the errors for the resultant g and A factors would be no more than 1%. Finally, if the adopted intrinsic parameters $\overline{A}_4(R_0)$ (or the relative elongation ΔZ) changed, the results for the EPR g factors varied as shown in Fig. 2 (or Fig. 3).
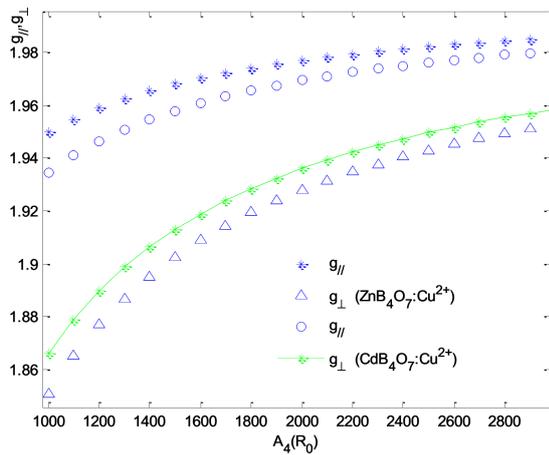
Fig. 3. The EPR g factors varies with the intrinsic parameters $\overline{A}_4(R_0)$ within the range of 1000–3000 cm^{-1} with the fixed relative elongation $\Delta Z \approx 5.7\%$ and 4.3% for VO^{2+} doped in borate glasses ZnB$_4$O$_7$ and CdB$_4$O$_7$, respectively.

4. Conclusion

The experimental EPR spectra, and the local structural distortions of the impurity VO^{2+} in MB$_4$O$_7$ (M = Zn, Cd) glasses are theoretically investigated from the perturbation formulae for a $3d^1$ ion in tetragonally compressed octahedra. Based on the studies, the oxygen octahedra around V^{4+} are found to suffer the relative tetragonal compressions of about 5.7% and 4.3% due to the Jahn–Teller effect for the impurity centers in ZnB$_4$O$_7$ and CdB$_4$O$_7$ glasses, respectively, and the negative signs of the calculated $A_\parallel$ and $A_\perp$ are also suggested in this work.

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