Theoretical studies on the g-factors and the local structure of W^{5+} ions in tungsten phosphate glasses

B. F. Zhang[a], J. Z. Lin[b,*], Y. X. Wang[b], Y. Zhao[b] and Y. F. Zhang[b]

Department of electronic information engineering, Suzhou Institute of Technology,
Jiangsu university of science and technology, Zhangjiagang, China 215600.
Department of physics, Suzhou Institute of Technology,
Jiangsu university of science and technology, Zhangjiagang, China 215600.
**e-mail: linjizi@just.edu.cn*

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In this work, we adopt the three-order perturbation formulae for g-factors ($g_{\|}$, $g_{\perp}$) of d^1 ions in the octahedral environment to calculate the g-factors of W^{5+} ions in tungsten phosphate glasses containing lithium (P_2O_5-Li_2WO_4-Li_2O). In the light of the high valence state of the studied W^{5+} centers and hence the strong covalency of the studied octahedral $[WO_6]^{7-}$ cluster, we consider the contributions to g-factors from the ligand orbital and spin-orbit (SO) coupling interactions based on the cluster approach. The required tetragonal crystal-field parameters are calculated from the local structure of W^{5+} ions based on the superposition model. According to the theoretical calculations, we find that the octahedral $[WO_6]^{7-}$ clusters possess the tetragonally compressed distortion with a shorter W-O bond length (≈ 1.54 Å) and a longer one (≈ 2.26 Å) along C_4 axis and four normal W-O bond length (≈ 1.94 Å) in the perpendicular plane, which infers that the W^{5+} ions are in the form of tungstyl ions (*i.e.*, WO^{3+}). Based on the local structural data, the theoretical values of $g_{\|}$ and $g_{\perp}$ agree well with the experimental values.

Keywords: g-factors; W^{5+}; tungsten phosphate glasses; superposition model; cluster approach.

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1. Introduction

Glass doped with transition metal ions has many excellent properties (*e.g.* high refractive index [1–3], low phonon energy [4, 5], unique non-linear optical properties [6, 7]), which has attracted great interest of many researchers [8]. Many theoretical and experimental studies show that the different structures of oxygen coordination polyhedron in glass network strongly correlated with the excellent properties of the glasses system [8–10]. As it is known, one can adopt the electron paramagnetic resonance (EPR) technique to conveniently study the structures of the glasses by using probing agents such as the transition metal ions (*e.g.* W^{5+} [8, 11–13], Mo^{5+} [14–16], VO^{2+} [17–20], Cu^{2+} [17, 21–23], Cr^{5+} [24–26]). EPR experiments for the glasses system P_2O_5-Li_2WO_4-Li_2O were carried out decades ago [15] and the EPR parameters g-factors ($g_{\|}$ and $g_{\perp}$) of the W^{5+} ions reduced from W^{6+} in the formation of the glasses system P_2O_5-Li_2WO_4-Li_2O were obtained in the experiment [15]. From the property of the experimental g-factors (*i.e.*, $g_{\|} < g_{\perp} < g_e$, $g_e \approx 2.0023$ is the spin-only value), the W^{5+} ion was found to locate at the axially distorted octahedral environment, in which the metallic ion W^{5+} was in the form of tungstyl ion WO^{3+} with a short W-O bond length [15]. However, up to date, the g-factors of W^{5+} ions in the glasses system P_2O_5-Li_2WO_4-Li_2O have not been satisfactorily interpreted and the local structure of the metallic ions W^{5+} in the system has not been confirmed in the quantitative calculation. Considering that the microscopic mechanisms of the EPR parameters and the local structure of the metallic ion W^{5+} must be essential to understand the properties of the P_2O_5-Li_2WO_4-Li_2O glasses system, further theoretical investigations on the experimental results of the system are of great significance.

Here, we apply the three-order perturbation formulae of g-factors for the d^1 ions in the octahedral environment to theoretically investigate these factors of the studied W^{5+} ($5d^1$) ions. Because of the high valence state of the studied ion, one can expect significant orbital admixtures between the central ions and the ligand ions. Thus, the contributions to g-factors from the ligand orbital and spin-orbit (SO) coupling interactions are included in the perturbation formulae based on the cluster approach. According to the superposition model (SPM), the required crystal-field energy separations in these formulae are calculated from the parameter of the local environment around the studied W^{5+} ions. Thus, information on the local structure of the metallic ion is confirmed. The theoretical results ($g_{\|}$ and $g_{\perp}$) present here show good agreement with the experimental results.

2. Calculations

2.1. The local structure and energy level splitting for W^{5+} in the P_2O_5-Li_2WO_4-Li_2O glasses system

In Ref. [15], the obtained EPR spectra characterized by the major signal can be ascribed to the W^{5+} ion reduced from the W^{6+} ion in the formation of the glasses system. Based

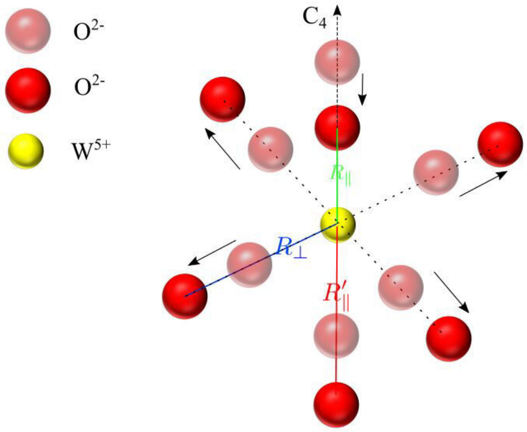

FIGURE 1. (Color online) Local structure of the octahedral $[WO_6]^{7-}$ cluster with tetragonally compressed distortion in P_2O_5-Li_2WO_4-Li_2O glasses. The W^{5+} ions are in the form of tungstyl ions WO^{3+} with a short W-O bond length $R_{\|}$ (described by the green solid line) and a long one $R'_{\|}$ (shown by red solid line) along the C_4 axis and four normal perpendicular W-O bond length $R_{\perp}$ (shown by the blue solid line).

FIGURE 2. (Color online) Crystal-field energy splitting of d^1 ion in an octahedral environment with the tetragonally compressed distortion.

on the feature $g_{\|} < g_{\perp} < g_e$ of the experimental g-factors, one can assume that these W^{5+} ions are coordinated by six oxygen ligands forming the octahedral environment. As observed in other glasses [8, 12, 13], the metallic ion W^{5+} should be very close to one of the two oxygen ligands along the C_4 axis leading to the axially compressed distortion octahedron (see Fig. 1). Therefore, the shorter axial bond length $R_{\|}$ and the longer axial bond length $R'_{\|}$ as well as the four normal W-O bond length $R_{\perp}$ in the perpendicular plane can be expressed by the reference length *R* and the relative tetragonal compression ratio ρ:

$$R_{\|} \approx R(1-\rho), \quad R'_{\|} \approx R(1+\rho),$$
$$R_{\perp} \approx R(1+\rho^2/2). \tag{1}$$

For the free d^1 ions, the d-orbital is five-fold degenerate. In cubic crystal field, the quintuple degeneracy is partially relieved and the octahedral d^1 cluster exhibits two energy levels ^2E_g $(|d_{z^2}\rangle, |d_{x^2-y^2}\rangle)$ and $^2T_{2g}(|d_{xy}\rangle, |d_{yz}\rangle, |d_{xz}\rangle)$, as shown in Fig. 2. The original lower orbital triplet $^2T_{2g}$ in cubic crystal-field would split into an orbital doublet ^2E_g $(|d_{yz}\rangle, |d_{xz}\rangle)$ and an orbital single $^2B_{2g}$ $(|d_{xy}\rangle)$ due to the tetragonally compressed distortion with the latter being lowest [27]. Meanwhile, the original upper orbital doublet ^2E_g would split into two orbital singlets $^2B_{1g}$ $(|d_{x^2-y^2}\rangle)$ and $^2A_{1g}$ $(|d_{z^2}\rangle)$. According to crystal field theory [27], the Hamiltonian matrices for d^1 ion in the tetragonally compressed octahedron can be expressed by the cubic crystal-field parameter (CF) D_q, the tetragonal CF parameters D_s and D_t,

$$\langle d_{z^2}|V|d_{z^2}\rangle = 6D_q - 2D_s - 6D_t,$$
$$\langle d_{x^2-y^2}|V|d_{x^2-y^2}\rangle = 6D_q + 2D_s - D_t,$$
$$\langle d_{xz}|V|d_{xz}\rangle = \langle d_{yz}|V|d_{yz}\rangle = -4D_q - D_s + 4D_t,$$
$$\langle d_{xy}|V|d_{xy}\rangle = -4D_q + 2D_s - D_t. \tag{2}$$

Here, *V* denotes the crystal field potential energy of the d^1 electron. Thus, the energy differences E_i (i=1,2,3, see Fig. 2) between the excited ^2E_g, $^2B_{1g}$, $^2A_{1g}$ and the ground state $^2B_{2g}$ can be calculated [28–30]:

$$E_1 = 5D_t - 3D_s, \quad E_2 = 10Dq,$$
$$E_3 = 10D_q - 4D_s - 5D_t. \tag{3}$$

According to the superposition model [31] and the local geometrical relationship (see Fig. 1), the tetragonal CF parameters D_s and D_t can be written as follows:

$$D_s = (2/7)\bar{A}_2(R)[2(R/R_{\perp})^{t_2} - (R/R_{\|})^{t_2} - (R/R'_{\|})^{t_2}],$$
$$D_t = -(8/21)\bar{A}_4(R)[2(R/R_{\perp})^{t_4}$$
$$-(R/R_{\|})^{t_4} - (R/R'_{\|})^{t_4}], \tag{4}$$

where $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters with the reference length R [31]. The radios $\bar{A}_4(R)/D_q \approx 3/4$, $\bar{A}_2(R)/\bar{A}_4(R) \approx 10.8$ have been proved to be valid for d^n ions in octahedral crystal-field environments for many glasses systems [9,32,33]. They can be reasonably applied in the present work. t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents [31]. According to the optical absorption spectra of the similar $[WO_6]^{7-}$ cluster in some tungstate glasses [13], one can obtain $D_q \approx 2500$ cm^{-1}. Thus, only the parameter ρ is unknown in Eq. (4).

2.2. Perturbation formulae of g-factors

In the light of the high valence state of the metallic W^{5+} ion in $[WO_6]^{7-}$ cluster, one can expect the strong covalency effect and hence the obvious mixings between the orbitals of the ligand O^{2-} and the central W^{5+} ions. Thus, the contributions to EPR parameters ($g_{\|}$, $g_{\perp}$) from the ligand orbital and SO coupling interactions become significant, which has been proved in many theoretical works [13]. For the W^{5+} ion in the tetragonally compressed octahedral environment, the high-order perturbation formulae of g-factors including

TABLE I. (ζ, ζ') (in cm^{-1}), N_γ, $(\lambda_\gamma, \lambda_s)$ and (k, k') for W^{5+} ion in P$_2$O$_5$-Li$_2$WO$_4$-Li$_2$O glasses.

N_t	N_e	λ_t	λ_e	λ_s	ζ	ζ'	k	k'
0.6708	0.7180	0.7334	0.5878	0.4720	2457	2339	0.8512	0.3898

the above contributions can be derived on the basis of the cluster approach [34–36]:

$$g_\parallel = g_e - 8k'\zeta'/E_2 - 2k\zeta^2/E_1^2 - 4k'\zeta\zeta'/E_1E_2 - 2\zeta^2/E_1^2,$$

$$g_\perp = g_e - 2k\zeta/E_1 + k\zeta^2/E_1^2 - 2k\zeta'^2/E_1E_2 + 2\kappa'\zeta'\zeta/E_1E_2 - 4\zeta'/E_2^2 - \zeta^2/E_1^2. \qquad (5)$$

Here, energy separations E_1 and E_2 corresponding to d-d transitions are given in Eq. (3). ζ and ζ' are the SO coupling coefficients, k and k' are the orbital reduction factors characterizing the degree of covalency between the central W^{5+} and the ligands O^{2-} in present glasses system. These quantities (ζ, ζ', k, k') can be derived from the cluster approach [9, 35]:

$$\zeta = N_t\left(\zeta_d + \lambda_t^2\zeta_p/2\right),$$

$$\zeta' = (N_tN_e)^{1/2}\left(\zeta_d - \lambda_t\lambda_e\zeta_p/2\right),$$

$$k = N_t\left(1 + \lambda_t^2/2\right),$$

$$k' = (N_tN_e)^{1/2}\left[1 - \lambda_t\left(\lambda_e + \lambda_s A\right)/2\right]. \qquad (6)$$

The subscript $\gamma = e$ and t denote the irreducible representations T$_{2g}$ and E$_g$ of the O$_h$ group, respectively. N_γ-is the normalization factor. λ_γ or (λ_s)is the orbital mixing coefficients. ζ_d and ζ_p are the SO coupling coefficients of the metal and ligand ions in free state, respectively. Based on the cluster approach, these molecular orbital parameters are calculated by using the covalency factor N, the group overlap integrals (S_{dpt}, S_{dpe}, S_{ds}) and the integral A. Here, the overlap integrals S_{dpt} and S_{dpe} involve the W(d) orbital and the O(2p) orbitals with the same T_{2g} and E_g symmetries, respectively. Also, S_{ds} involves the W(d) and the O(2s) orbitals with the same A_{1g} symmetry. A denotes the integral $R\langle ns\,|\partial/\partial y|\,np_y\rangle$ with the impurity-ligand distance R of the studied system. More information can be found in the literatures [28, 35, 37, 38].

2.3. Calculated results of the g-factors for W^{5+} ions in P$_2$O$_5$-Li$_2$WO$_4$-Li$_2$O glasses system

For the octahedral cluster [WO$_6$]$^{7-}$ in some tungsten phosphate glasses [12], the average bond length is about 1.9 Å, which can be reasonably taken as the reference length in this work. Utilizing the length R ($\approx$ 1.9Å [12]) and the Slater-type SCF functions, the group overlap integrals $S_{dpt} \approx 0.03211$, $S_{dpe} \approx 0.09075$, $S_{ds} \approx 0.07287$ and the integral $A \approx 1.2371$ are determined. From the free-ion values $\zeta_d \approx 3500$ cm^{-1} [36, 39] for W^{5+} and $\zeta_p \approx 151$ cm^{-1} [9, 28] for O^{2-}, the SO coupling coefficients (ζ, ζ') and the orbital reduction factors (k, k') are determined as the covalency factor N is known. By inserting the relevant quantities (E_1, E_2, ζ, ζ') into the formulae of g-factors (Eq. (5)) and fitting the theoretical g-factors to the experimental results, N and ρ are determined:

$$N \approx 0.655; \quad \rho \approx 0.1915. \qquad (7)$$

TABLE II. The g-factors for W^{5+} ion in P$_2$O$_5$-Li$_2$WO$_4$-Li$_2$O glasses.

	Cal^a	Cal^b	Cal^c	Exp^d
g$_\parallel$	1.4142	1.7106	1.5949	1.5932-1.6015
g$_\perp$	1.8114	1.7331	1.7321	1.7321-1.7398

^{a}Theoretical results based on Eqs. (5)-(7) but neglecting the ligand contributions. ^{b}Theoretical results based on Eqs. (6), (7) and the second-order perturbation formulae (*i.e.*, the formulae of g-factors include only the first two terms in Eq. (5)). ^{c}Theoretical results based on Eqs. (5)-(7) including the ligand contributions. ^{d}Ref. [15].

The corresponding calculated results (N_γ, λ_γ, λ_s, ζ, ζ', k, k') are collected in Table I and the corresponding g-factors ($g_\parallel$, $g_\perp$) are gathered in Table II. For the convenience of comparison and discussion, the calculated results (Cal^a) based on the relative compression ratio ρ without the ligand orbital and SO coupling contributions (*i.e.*, $\zeta = \zeta' = N\zeta_d$ and $k = k' = N$) are collected in Table II. The calculated results (Cal^b) based on the second-order perturbation formulae including the ligand contributions are also shown in Table II.

3. Discussion

From Table II, one can find that the theoretical g-factors (Cal^c) based on the three-order perturbation formulae of these factors for d^1 ions in the tetragonally compressed octahedral environment including the contributions from the ligand orbital and SO coupling interactions as well as the relative tetragonal compression ratio ρ are in good agreement with the experimental results reported in Ref. [15]. Therefore, the experimental EPR spectra are satisfactorily explained and the local structure is quantitatively confirmed.

(1) Based on the relative compression ratio $\rho(\approx 0.1915)$ and the reference length $R(\approx 1.9$Å [15]), one can obtain the local structural data for the studied cluster [WO$_6$]$^{7-}$ including the very short W-O bond length $R_\parallel(\approx 1.54$Å) and the long one $R'_\parallel$ (≈ 2.26Å) along the C$_4$ axis and the four normal perpendicular W-O bond length $R_\perp$ (≈ 1.94Å), which infers a tetragonal compression distortion along the C$_4$ axis (see Fig. 1). This

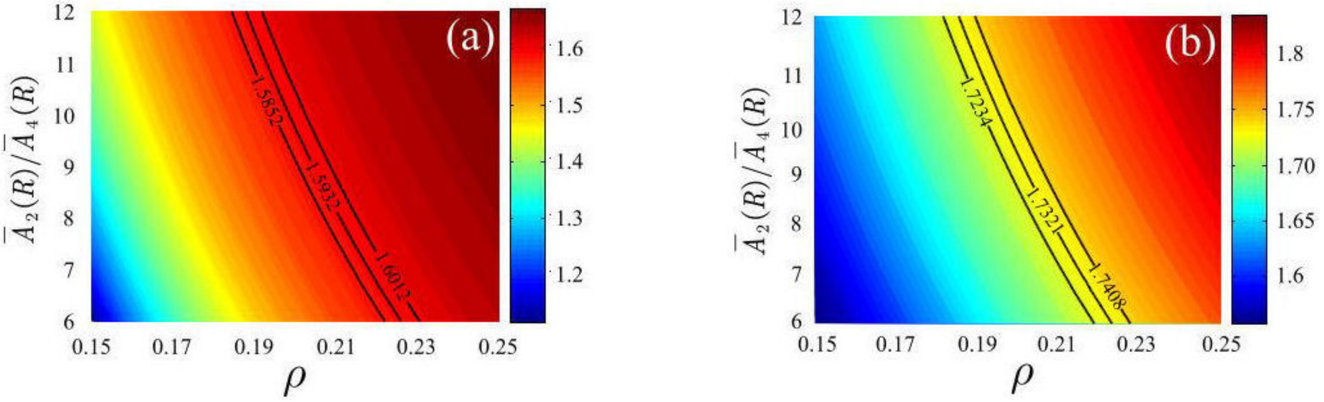

FIGURE 3. (Color online) $g_\parallel$ and $g_\perp$ as functions of the relative compression ratio ρ and the ratio $\bar{A}_2(R)/\bar{A}_4(R)$ are shown in Panels a) and b), respectively. In the two panels, the three black curves from left to right represent 99.5%, 100% and 100.5% of the corresponding experimental values, respectively.

may suitably explain the observed property ($g_\parallel < g_\perp < g_e$) of g-factors. Similar tetragonally compressed distortions of the octahedral W^{5+} centers are also found in other tungstate phosphate glasses (*e.g.* $R_\perp \approx 1.6$Å, $R'_\parallel \approx 2.2$Å, $R_\perp \approx 1.9$ Å) [12] by EPR analysis. Many theoretical works demonstrate that the similar distortions may be ascribed to the Jahn-Teller effect which may modify the immediate local environment by stretching or shrinking the metal-ligand bond lengths [8, 9, 28, 40, 41]. Thus, the local environment around the W^{5+} ion confirmed in this work is suitable.

(2) It can be seen from Table II that the calculated g-factors (Cal^c) based on Eqs. (5), (6) and (7) are more consistent with the experimental results than the calculated results (Cal^a) based on Eqs. (5) and (7) without the contributions from the ligand orbital and spin-orbit coupling interactions. Particularly, the calculated value of $g_\parallel$ from the results (Cal^a) is much smaller than the experimental value. According to our calculations, the relative discrepancy between the calculated results (Cal^a) and the experimental values are about 11.3% and 4.6% for $g_\parallel$ and $g_\perp$ respectively, which can hardly be eliminated by freely adjusting the relative tetragonal compression ratio ρ and the covalency factor N. In fact, one can expect the strong covalency and hence the obvious mixings between the metal and ligand orbitals because of the high valence state of W^{5+}. This point is supported by the small covalency factor N ($\approx 0.655 << 1$) and the significant mixing coefficients ($\lambda_t \approx 0.7334$, $\lambda_e \approx 0.5878$ and $\lambda_s \approx 0.4720$) (see Table I). By comparing the results between Cal^a and Cal^b in Table II, we also find that the contributions from the ligand orbital and SO coupling interactions are more important than those from the third-order terms. Therefore, the high-order perturbation formulae of the g-factors including the ligand contributions seem to be much applicable in the explanations of these parameters.

(3) The possible errors of the present work may be analyzed in the following aspects. Firstly, only the contributions from the nearest neighbor oxygen ligands of the metallic W^{5+} ion are considered from the cluster approach. Fortunately, the approach has been proved to be valid by many theoretical works on EPR parameters [8, 9, 28, 29, 32–34, 38–40].

Secondly, the empirical relationship $\bar{A}_2(R)/\bar{A}_4(R) \approx 10.8$ applied in the calculations of tetragonal CF parameters may bring some errors to the compression ratio ρ and hence the g-factors (note that the relationship $\bar{A}_2(R)/\bar{A}_4(R) \approx 9 \sim 12$ for d^n ions has been proved to be valid in many theoretical works [29, 31, 33, 40, 42–47]). According to our calculations, the errors of the final g-factors and the relative compression ratio ρ are estimated not to exceed 1% and 6% (see Fig. 3) respectively, as the ratio $\bar{A}_2(R)/\bar{A}_4(R)$ changes by 10% around 10.8. Thirdly, in the calculations of the group overlap integrals, the reference bonding length of the studied $[\mathrm{WO}_6]^{7-}$ cluster is obtained from the similar cluster with tetragonally compressed distortion in the other tungstate phosphate glasses. This would introduce small errors into the integrals and hence bring forward an influence in the calculated g-factors. However, because of the small integrals, one can expect the errors arising from the uncertainty of the integrals must be very small. According to the calculations, when the integrals change by 10%, the errors of the final g-factors are estimated not to exceed 1%. Finally, only the contributions from the crystal-field mechanism are considered in the calculations of the g-factors, while the contributions due to the charge-transfer mechanism are not included. This should lead to some errors in the final g-factors. However, considering that (i) some adjustable parameters (*e.g.* the bonding molecular orbit coefficients, charge-transfer energy levels [34, 36, 39, 47]) should be introduced in the calculations if the charge-transfer mechanism is adopted. (ii) Based on the theoretical studies of the octahedral clusters for the d^1 ions (*e.g.* V^{4+} [47, 48], Mo^{5+} [34, 49], W^{5+} [36, 39], Cr^{5+} [25,47,48]) doping in the crystals or glasses, the contribution to the g-factors from the charge-transfer mechanism is much smaller than that from the crystal-field mechanism, neglecting the contribution to g-factors from the charge-transfer mechanism is acceptable. The theoretical g-factors (Cal^c) show good agreement with the experimental values, which further supports this point.

4. Conclusion

The g-factors ($g_{\|}$, $g_{\perp}$) and the local structure for tetragonal W^{5+} centers in tungsten phosphate glasses containing lithium (P_2O_5-Li_2WO_4-Li_2O) are quantitatively investigated through the three-order perturbation formulae for the d^1 ions in the octahedral environment. In these formulae, the contributions to g-factors from the ligand orbital and SO coupling interactions are taken into account because of the strong covalency of the studied cluster $[WO_6]^{7-}$. According to our calculations, the relative tetragonal compression ratio ρ is found to be about 0.1915 due to the Jahn-Teller effect. Based on the local structural data and the three-order perturbation formulae, the theoretical results of g-factors are in good agreement with the experimental results.

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