INVESTIGATION OF THE OPTICAL SPECTRA AND SPIN-HAMILTONIAN PARAMETERS FOR VANADYL IN ZINC PHOSPHATE GLASS

C.-D. Feng, H.-X. Huang, W.-B. Xiao, H.-M. Zhang*

Key Laboratory of Nondestructive Testing, Ministry of Education,
Nanchang Hangkong University, Nanchang 330063, China; e-mail: huamingzhang66@gmail.com

The optical absorption spectra and spin-Hamiltonian parameters (g factors $g_{||}$, $g_{\perp}$, and hyperfine structure constants $A_{||}$, $A_{\perp}$) of vanadyl in zinc phosphate glass are investigated, using the high-order perturbation formulas for a $3d^1$ ion in tetragonally compressed octahedra. In the calculations, the required crystal-field parameters are estimated from the superposition model, and the optical absorption bands and spin-Hamiltonian parameters are linked with the tetragonal distortion (characterized by $\Delta R = R_{\perp} - R_{||}$, where $R_{\perp}$ and $R_{||}$ denote the bond lengths perpendicular and parallel to the C_4 axis). Based on the calculations, the tetragonal distortion ΔR (≈1.795 Å) was obtained, and negative signs of the hyperfine structure constants $A_{||}$ and $A_{\perp}$ are suggested.

Keywords: *optical spectra, spin-Hamiltonian parameters, local structure, zinc phosphate glass, vanadyl.*

ИССЛЕДОВАНИЕ ОПТИЧЕСКИХ СПЕКТРОВ И ПАРАМЕТРОВ СПИНОВОГО ГАМИЛЬТОНИАНА ВАНАДИЛА В ФОСФАТНО-ЦИНКОВОМ СТЕКЛЕ

C.-D. Feng, H.-X. Huang, W.-B. Xiao, H.-M. Zhang*

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Наньчанский университет Хангконг, Наньчан, 330063, Китай;
e-mail: huamingzhang66@gmail.com

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Исследованы спектры оптического поглощения и параметры спинового гамильтониана (g-факторы $g_{||}$, $g_{\perp}$ и константы сверхтонкой структуры $A_{||}$, $A_{\perp}$) ванадила в фосфатно-цинковом стекле с использованием формул возмущения высокого порядка для $3d^1$-иона в тетрагонально сжатых октаэдрах. В расчетах требуемые параметры кристаллического поля оцениваются по модели суперпозиции, оптические полосы поглощения и параметры спинового гамильтониана связаны с тетрагональным искажением, характеризуемым $\Delta R = R_{\perp} - R_{||}$, где $R_{\perp}$ и $R_{||}$ — длины связей, перпендикулярных и параллельных оси C_4. На основании расчетов получено тетрагональное искажение ΔR (≈1.795 Å), обсуждаются отрицательные знаки констант сверхтонкой структуры $A_{||}$, $A_{\perp}$.

Ключевые слова: *оптические спектры, параметры спинового гамильтониана, локальная структура, фосфатно-цинковое стекло, ванадил.*

Introduction. Phosphate glass shows interesting photoconducting [1], spectra and laser [2, 3], structure [4], and optical and thermal properties [5, 6] when doped with transition or rare metal (TM or RM) ions. Generally, the doping ions occupy either octahedral or tetrahedral sites in glasses, and the above-mentioned properties are sensitive to the internal electric, local structure, and the surrounding ligand field of the doping ions. Electron paramagnetic resonance (EPR) spectra of TM ions in glasses can give valuable information on the structure and dynamics of the host lattice [7, 8]. The optical absorption method reveals the crystal-field parameters and the energy level structure of the TM ions [9, 10]. Therefore, EPR and optical absorption studies are two powerful tools for investigating the point symmetry and dynamic properties of the paramagnetic ions in the host crystals. Vanadyl (VO^{2+}) is one of the most stable cations among some molecular paramagnetic TM ions and is used extensively as an impurity probe for EPR studies, which are sensitive to the crystal environment [11–13]. Many spectroscopic studies for phosphate glass containing TM ions have been carried out [14–17]. For example, Ravikumar et al. measured the optical absorption bands and the spin-Hamiltonian (SH) parameters (i.e., g factors $g_{\parallel} = 1.9329$, $g_{\perp} = 1.9824$ and hyperfine structure constants $A_{\parallel} = 157\times10^{-4}$ cm^{-1}, $A_{\perp} = 52\times10^{-4}$ cm^{-1}) of VO^{2+} in zinc phosphate glass by the EPR technique [18]. However, a theoretical study of the obtained results has not been made, and the local structure of VO^{2+} ion in zinc phosphate glass has not been obtained either. In this work, the four SH parameters and three optical absorption bands of VO^{2+} in zinc phosphate glass are theoretically investigated using the high-order perturbation formulas. In the calculations, tetragonal field parameters D_s and D_t are determined from the superposition model and correlated with the local structure of the V^{4+} center; the contributions from the ligand orbital and spin-orbit coupling interactions are taken into account. The local structure around V^{4+} ions in zinc phosphate glass has been determined in the calculations.

Calculation. For a $3d^1$ ion in tetragonally compressed octahedra, its higher orbital doublet ^2E_g in the original cubic case would split into two orbital singlets $^2B_{1g}$ and $^2A_{1g}$, while the original lower orbital triplet $^2T_{2g}$ would be separated into an orbital doublet ^2E_g and a singlet $^2B_{2g}$, where the latter is the lowest lying [19, 20] (Fig. 1). Based on the crystal-field theory, the d–d transitions of the three optical absorption bands can be expressed as

$$E_1 = E(^2B_1) - E(^2B_2) = 10D_q\,,$$
$$E_2 = E(^2E) - E(^2B_2) = -3D_s + 5D_t\,,$$
$$E_3 = E(^2A_1) - E(^2B_2) = 10D_q - 4D_s - 5D_t\,. \tag{1}$$

From the superposition model [21] and the geometrical relationship of the V^{4+} center in zinc phosphate glass, the crystal-field parameters D_q, D_s, and D_t can be determined as follows:

$$D_q = \frac{3}{4}\bar{A}_4(R)(R/R_{\perp})^{t_4}\,,$$
$$D_s = \frac{4}{7}\bar{A}_2(R)[(R/R_{\parallel}))^{t_2} - (R/R_{\perp})^{t_2}]\,,$$
$$D_t = \frac{8}{21}\bar{A}_2(R)[(R/R_{\parallel})^{t_4} - (R/R_{\perp})^{t_4}]\,. \tag{2}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [22–25]. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters, with the average reference bond length R. For the studied $(VO_6)^{8-}$ cluster, $R \approx R_{\perp} \approx 1.97$ Å [26] and $R_{\parallel} \approx R_{\perp} - \Delta R$, where ΔR is the tetragonal compression caused by the static Jahn-Teller effect.

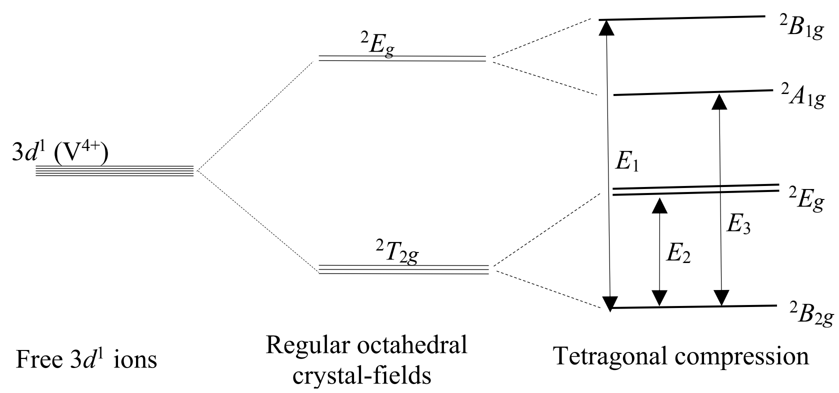

Fig. 1. Energy level splitting schemes of octahedral $3d^1$ clusters with tetragonal compression distortion. E_i ($i = 1, 2, 3$) are the corresponding energy differences.

From the perturbation theory, the perturbation formulas of the SH parameters for $3d^1$ ions in the tetragonal compressed symmetry can be described as follows [20, 23]:

$$g_{\parallel} = g_s - \frac{8k'\varsigma'}{E_1} - \frac{k\varsigma^2}{E_2^2} + \frac{2k'\varsigma'^2}{E_2^2}\,,$$

$$g_{\perp} = g_s - \frac{2k\varsigma}{E_1} + \frac{2k'\varsigma\varsigma'}{E_1^2}\left(1/E_1E_2 - 1/E_2^2\right) + \frac{g_s\varsigma^2}{2E_2^2},$$

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

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

where g_s (≈2.0023) is the spin-only g value of the free electron. ζ (or ζ'), k (or k'), and P (or P') are the spin-orbit coupling coefficients, the orbital reduction factors, and the dipolar hyperfine constants, respectively, which denote the diagonal (and off-diagonal) matrix elements of the spin-orbit coupling and the orbital angular momentum operators for the states T_{2g} and E_g under an octahedral $3d^9$ cluster. That is, ζ, k, and P are due to the interaction only within T_{2g} orbitals, ζ', k', and P' are due to the interaction between T_{2g} and E_g orbitals, and κ denotes the core polarization constant. Comparing the core polarization constant (≈0.6–1 [20, 24–26]) for VO^{2+} (or V^{4+}) in various glasses, we estimate $\kappa \approx 0.64$ for the studied system here.

Based on the cluster approach, the electron wave functions containing the contributions from p- and s-orbitals of ligands can be described as [20]

$$\Psi_t = N_t^{1/2}(\phi_t - \lambda_t\chi_{pt}),$$

$$\Psi_e = N_e^{1/2}(\phi_e - \lambda_e\chi_{pe} - \lambda_s\chi_s). \tag{4}$$

Here the subscript γ (=t and e) denoting the irreducible representations T_{2g} and E_g of O_h group, respectively, $\chi_{p\gamma}$ and χ_s are the p-orbital and s-orbital of the ligands, N_γ represent the normalization factors, and λ_γ (and λ_s) are the orbital admixture coefficients.

Using the cluster approach [27], the spin-orbit coupling coefficients (ζ and ζ'), the orbital reduction factors (k and k'), and the dipolar hyperfine structure parameters (P and P') in Eq. (3) can be expressed as

$$\varsigma = N_t(\varsigma_d^0 + \lambda_t^2\varsigma_p^0/2), \quad \varsigma' = \sqrt{N_tN_e}(\varsigma_d^0 - \lambda_t\lambda_e\varsigma_p^0/2),$$

$$k = N_t(1 + \lambda_t^2/2), \; k' = \sqrt{N_tN_e}[1 - \lambda_t(\lambda_e + \lambda_s A)/2],$$

$$P = N_tP_0, \; P' = \sqrt{N_tN_e}P_0. \tag{5}$$

Here, ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of free $3d^n$ ions and ligand ions, respectively. P_0 (≈172×10^{-4} cm^{-1} [28]) is the dipolar hyperfine structure constant of the free central ion, N_γ is the normalization factor, and λ_γ (or λ_s) is the orbital admixture coefficients; A denotes the integral $R\left\langle ns\left|\frac{\partial}{\partial y}\right|np_y\right\rangle$, with R the reference impurity-ligand distance; N_γ and λ_γ (or λ_s) can be determined from the normalization conditions:

$$N_t(1 - 2\lambda_tS_{dpt} + \lambda_t^2) = 1,$$

$$N_e(1 - 2\lambda_eS_{dpe} - 2\lambda_sS_{ds} + \lambda_e^2 + \lambda_s^2) = 1, \tag{6}$$

and the approximate relationships

$$N^2 = N_t^2(1 + \lambda_t^2S_{dpt}^2 - 2\lambda_tS_{dpt}),$$

$$N^2 = N_e^2(1 + \lambda_e^2S_{dpe}^2 + \lambda_s^2S_{ds}^2 - 2\lambda_eS_{dpe} - 2\lambda_sS_{ds}). \tag{7}$$

Here $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. Generally, λ_γ (or λ_s) increase with increasing $S_{dp\gamma}$ (or S_{ds}), and the approximately relationship $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$ can be made within the same irreducible representation e_g. The group overlap integrals $S_{dpt} \approx 0.0477$, $S_{dpe} \approx 0.1239$, $S_{ds} \approx 0.0986$, and $A \approx 1.0206$ can be calculated from the Slater-type self-consistent field (SCF) functions [29, 30] with the metal-ligand reference distance R of the studied system. Then, N_γ and λ_γ can be calculated by Eqs. (6) and (7). For the studied $(VO_6)^{8-}$ cluster, we have $\zeta_d^0 \approx 248$ cm^{-1} [31] and $\zeta_d^0 \approx 151$ cm^{-1} [32]; then, the parameters ζ (ζ') and k (k') in formula (3) can be determined from Eq. (5): $N_t = 0.812$, $N_e = 0.869$, $\lambda_t = 0.486$, $\lambda_e = 0.535$, $\lambda_s = 0.011$, $\zeta = 215.8$, $\zeta' = 191.8$, $k = 0.908$, $k' = 0.728$.

Therefore, only the parameters N, $R_{\|}$, $\bar{A}_2(R_0)$, and $\bar{A}_4(R_0)$ are unknown. By fitting the calculated optical absorption bands and EPR parameters to the experimental data, we have

$$N \approx 0.81,\ R_{\|} \approx 1.795\ \text{Å},\ \bar{A}_2(R) \approx 1503\ \text{cm}^{-1},\ \bar{A}_4(R) \approx 10013\ \text{cm}^{-1}, \tag{8}$$

for the impurity VO^{2+} in zinc phosphate glass. The corresponding calculated optical and EPR parameters are compared with the experimental values in Table 1.

TABLE 1. EPR Parameters (g factors $g_{\|}$, $g_{\perp}$ and hyperfine structure constants $A_{\|}$, $A_{\perp}$) and d-d Transitions (cm^{-1}) of Vanadyl in Zinc Phosphate Glass

Parameter	$g_{\|}$	$g_{\perp}$	$A_{\|}$	$A_{\perp}$	${}^2B_{2g}\to{}^2B_{1g}$	${}^2B_{2g}\to{}^2E_g$	${}^2B_{2g}\to{}^2A_{1g}$
Cal.	1.9331	1.9809	–156.6	–51.8	16125	12192	21733
Exp. [18]	1.9329	1.9824	157	51	16120	12160	21787

Result and discussion. From Table 1, it can be seen that the calculated optical absorption bands and SH parameters for the VO^{2+} center in zinc phosphate glass are in reasonable agreement with the experimental values. This indicates that the method and the parameters used in this paper can be regarded as reasonable.

Based on the above calculation, the tetragonal distortion $\Delta R = R_{\perp} - R_{\|} \approx 0.175$ Å can be obtained. This indicates that $(VO_6)^{8-}$ cluster is a tetragonal compressed distortion octahedral. The compressed distortion ΔR can be explained by the Jahn-Teller effect. In the compression, the ground state for the V^{4+} ($3d^1$) ion is an orbit singlet, whereas in the elongation, the ground state is an orbit doublet, while the latter is unstable. Similar tetragonal distortion $\Delta R \approx 0.2445$ and 0.186 Å was found for VO^{2+} in $MgKPO_4{\cdot}6H_2O$ [33] and alkaline-earth aluminoborate glasses [34], respectively, caused by the Jahn-Teller effect.

The calculated hyperfine structure constants $A_{\|}$ and $A_{\perp}$ listed in Table 1 are negative, whereas the values given by [18] are positive. Actually, the signs of the hyperfine structure constants $A_{\|}$ and $A_{\perp}$ are very difficult to detect in the experiment [19, 28, 35]. So, the experimental results of the constants $A_{\|}$ and $A_{\perp}$ are actually the absolute values. Muncaster and Parke [36] have confirmed that the signs of $A_{\|}$ and $A_{\perp}$ should be negative for VO^{2+} ions in glasses. Therefore, the signs of the hyperfine structure constants $A_{\|}$ and $A_{\perp}$ obtained in this work can be regarded as reasonable.

Conclusions. Based on the cluster approach and related equations used in this work, the three optical absorption bands and SH parameters as well as the local structural parameters of the VO^{2+} ion in zinc phosphate glass are theoretically investigated from the perturbation formulas for a $3d^1$ ion in tetragonally compressed octahedra. Based on the studied, the oxygen octahedra around V^{4+} are found to suffer the magnitude of tetragonal distortion is $\Delta R = R_{\perp} - R_{\|} \approx 0.175$ Å. The negative signs of the constants $A_{\|}$ and $A_{\perp}$ are also suggested in this work.

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REFERENCES

1. K. Srinivasulu, I. Omkaram, H. Obeid, A. S. Kumar, J. L. Rao, *Physica B*, **407**, 4741–4748 (2012).
2. R. V. S. S. N. Ravikumar, R. Komatsu, K. Ikeda, A. V. Chandrasekhar, B. J. Reddyc, Y. P. Reddy, P. S. Rao, *Solid State Commun*., **126**, 251–253 (2003).
3. N. G. Boetti, J. Lousteau, E. Ceci-Ginistrelli, E. Bertone, F. Geobaldo, D. Milanese, *J. Alloys Compd*., **657**, 678–683 (2016).
4. K. Srinivasulu, I. Omkaram, H. Obeid, A. S. Kumar, J. L. Rao, *J. Phys. Chem. A*, **116**, 3547–3555 (2012).
5. S. C. Colak, E. Aral, *J. Alloys Compd*., **509**, 4935–4939 (2011).
6. R. Lakshmikantha, N. H. Ayachit, R. V. Anavekar, *J. Phys. Chem. Solids*, **75**, 168–173 (2014).
7. B. Natarajan, S. Deepa, S. Mithira, R. V. S. S. N. Ravikumar, P. S. Rao, *Phys. Scr*., **76**, 253–258 (2007).
8. C. C Ding, S. Y. Wu, L. Peng, L. N. Wu, Z. H. Zhang, Q. S. Zhu, M. H. Wu, B. H. Teng, *J. Non-Cryst. Solids*, **481**, 103–109 (2018).

9. R. Kripal, M. Maurya, *Physica B*, **404**, 1532–1537 (2009).
10. M. Farouk, A. Samir, M. El Okr, *Physica B*, **530**, 43–48 (2018).
11. S. Mukherjee, A. K. Pal, *J. Phys.: Condens. Matter*, **20**, 255202 (2008).
12. B. Karabulut, A. Tufan, *Spectrochim. Acta A*, **65**, 742–748 (2006).
13. B. Srinivas, A. Hameed, G. Ramadevudu, M. N. Chary, Md. Shareefuddin, *J. Phys. Chem*. Solids, **129**, 22–30 (2019).
14. O. Cozar, D. A. Magdas, I. Ardelean, *J. Optoelectron, Adv. Mater*., **9**, 1730–1735 (2007).
15. P. S. Rao, P. M. V. Teja, A. R. Babu, Ch. Rajyasree, D. K. Rao, *J. Non-Cryst. Solids*, **358**, 3372–3381 (2012).
16. B. Srinivas, A. Hameed, R. V. Kumar, M. C. Narasimha, Md. Shareefuddin, *Philos. Mag*., **98**, 1625–1640 (2018).
17. V. Sreenivasulu, G. Upender, V. C. Mouli, M. Prasad, *Spectrochim. Acta A*, **148**, 215–222 (2015).
18. R. V. S. S. N. Ravikumar, B. C. Jamalaiah, A. V. Chandrasekhar, B. J. Reddy, Y. P. Reddy, P. S. Rao, *J. Alloys Compd*., **287**, 84–86 (1999).
19. A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Oxford University Press, London (1970).
20. C. C. Ding, S. Y. Wu, L. N. Wu, L. J. Zhang, L. Peng, M. H. Wu, B. H. Teng, *J. Phys. Chem. Solids*, **113**, 102–107 (2018).
21. D. J. Newman, B. Ng. *Rep. Prog. Phys*., **52**, 699–763 (1989).
22. M. Q. Kuang, S. Y. Wu, G. L. Li, X. F. Hu, *Mol. Phys*., **113**, 698–702 (2015).
23. H. M. Zhang, S. Y. Wu, M. Q. Kuang, Z. H. Zhang, *J. Phys. Chem. Solids*, **73**, 846–850 (2012).
24. M. N. Li, Z. H. Zhang, S. Y. Wu, *Z. Naturforsch. A*, **72**, 1139–1143 (2017).
25. R. M. Krishna, J. J. Andre, V. P. Seth, S. Khasa, S. K. Gupta, *Mater. Res. Bull*., **34**, 1089–1097 (1999).
26. C. Y. Li, X. M. Zheng, *Acta Phys. Pol. A*, **125**, 73–76 (2014).
27. S. Y. Wu, X. Y. Gao, H. N. Dong, *J. Magn. Magn. Mater*., **301**, 67–73 (2006).
28. B. R. McGarvey, *J. Phys. Chem*., **71**, 51–66 (1967).
29. E. Clementi, D. L. Raimondi, W. P. Reinhardt, *J. Chem. Phys*., **47**, 1300–1307 (1967).
30. E. Clementi, D. L. Raimondi, *J. Chem. Phys*., **38**, 2686–2689 (1963).
31. J. S. Griffith, *The Theory of Transition-metal Ions*, Cambridge University Press, London (1964).
32. E. K. Hodgson, I. Fridovich, *Biophys. Biochem. Res. Commun*., **54**, 270–274 (1973).
33. H. M. Zhang, W. B. Xiao, X. Wan, *Physica B*, **449**, 225–228 (2014).
34. W. L. Feng, *Philos. Mag*., **89**, 1391–1394 (2009).
35. R. Muncaster, S. Parke, *J. Non-Cryst. Solids*, **24**, 399–412 (1977).
36. E. Kalfaoğlu, B. Karabulut, *J. Magn. Magn. Mater*., **324**, 1593–1595 (2012).