Theoretical Explanations of the Optical Band Positions and Local Structure for Cu^{2+} Centers in ZnO-Bi_2O_3-B_2O_3-CuO Glasses

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The local structure, two optical band positions and three electronic spin resonance parameters for Cu^{2+} centers at the tetragonally-distorted octahedral sites in ZnO-Bi_2O_3-B_2O_3-CuO glasses are calculated from the high-order perturbation method based on the two-spin-orbit-parameter model, where the contributions from both the spin–orbit coupling parameters of central d^n ion and ligand ion are included. The theoretical results are in good agreement with the experimental values. The calculations show that the high-order perturbation method based on the two-spin-orbit-parameter model is effective in the explanations of optical spectra, electronic spin resonance parameters and local distortion structure for d^9 ions in glasses.

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1. Introduction

Glasses or crystals containing transition-metal ions have extensive applications in lasers, electronics and luminescent devices, etc. Thus, there is more and more interest in the investigations of these materials [1–5]. Especially, the electronic configuration of transition-metal ion Cu^{2+} is the simplest and most well suited as probe ion. Many related studies on defect structure, optical and electronic spin resonance (ESR) spectra have been investigated in recent years [6–12]. Among them, the Cu^{2+}-doped ZnO-Bi_2O_3-B_2O_3-CuO glasses have attracted attention because of the high refractive index, excellent infrared transmission, high nonlinear optical susceptibility, and high polarizability [12]. Singh et al. [12] studied the spectroscopic properties of Cu^{2+}-doped ZnO-Bi_2O_3-B_2O_3-CuO glasses synthesized by using bismuth trioxide, boric acid, zinc oxide and cupric oxide, and the result shows that Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses occupies the tetrahedral elongated tetragonal octahedral site. However, up to the present, there is no any theoretical analysis for this glasses system. In order to explain these optical and ESR data, to estimate the defect structures (i.e., the tetragonal elongations) for the Cu^{2+} centers in ZnO-Bi_2O_3-B_2O_3-CuO glasses, in this paper, we calculate these optical and ESR data together from the high-order perturbation based on the cluster approach (where the covalent effect due to the orbital admixture between the central transition-metal ion and ligand is taken into account). The results are discussed.

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2. Calculation

The ground state of Cu^{2+} ion in ZnO-Bi_2O_3-B_2O_3-CuO glasses is ${}^2B_{1g}(|d_{x^2-y^2}\rangle)$ and the expressions of ESR parameters g factors and hyperfine structure constants A factors for the single orbital term can be derived by the perturbation method [13, 14]:

$$g_{\parallel} = g_s + \frac{8k'\zeta'}{E_1} - \frac{4k\zeta\zeta'}{E_1E_2} - \frac{(k'+g_s/2)\zeta'^2}{E_2^2}, \tag{1}$$

$$g_{\perp}=g_s+\frac{2k'\zeta'}{E_2}+\frac{2k\zeta'^2-2k'\zeta\zeta'}{E_1E_2}-\frac{g_s\zeta'^2/2-k'\zeta\zeta'}{E_2^2}-\frac{2g_s\zeta'^2}{E_1^2},$$

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

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

where κ is the core polarization constant, $g_s \approx 2.0023$ is the g value of free electron. The optical absorption transitions (or crystal-field energy levels) E_i (i = 1, 2, 3), which are corresponding to ${}^2B_{1g}$ ($|d_{x^2-y^2}\rangle$) $\rightarrow^2 A_{1g}$ ($|d_{3z^2-r^2}\rangle$), ${}^2B_{1g}$ ($|d_{x^2-y^2}\rangle$) $\rightarrow^2 B_{2g}$ ($|d_{xy}\rangle$) and ${}^2B_{1g}$ ($|d_{x^2-y^2}\rangle$) $\rightarrow^2 E_g$ ($|d_{xz}\rangle$, $|d_{yz}\rangle$), can be expressed as

$$E_1=4Ds+5Dt,\ E_2=10Dq,\ E_3=10Dq+3Ds-5Dt, \tag{3}$$

where Dq is the cubic crystal-field parameter. Ds and Dt are the tetragonal crystal-field parameters. The parameters Ds and Dt can be calculated from the Newman superposition model [15–18] because there is a relation between the structure data and the crystal-field parameters of d^n clusters in glasses. Thus, we have

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

$$Dt = \frac{16}{21}\bar{A}_4(R_0)\left[\left(\frac{R_0}{R_{\perp}}\right)^{t_4}-\left(\frac{R_0}{R_{\parallel}}\right)^{t_4}\right] \tag{4}$$

where t_2 ($\approx$ 3) and t_4 ($\approx$ 5) are the power-law exponents [19, 20]. $\bar{A}_k(R_0)(k = 2, 4)$ are the intrinsic parameters with the reference distance R_0. $\bar{A}_4(R_0) \approx 3/4Dq$ for $3d^n$ ions in octahedral clusters [18–20], where Dq ($\approx$ 1745 cm^{-1}) can be obtained from the optical spectra [12]. The ratio of intrinsic parameter $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ is in the range 8–12 for $3d^n$ ions in many materials [18–23]. Thus, $\bar{A}_2(R_0) = 12\bar{A}_4(R_0)$ can be reasonably taken in the calculation. For Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses, the structural data $R_\perp = R_0$ (= 2.04 Å [24]) and $R_\parallel = R_0 + \Delta R$, where ΔR is the tetragonal elongation caused by the static Jahn–Teller effect (see Fig. 1).

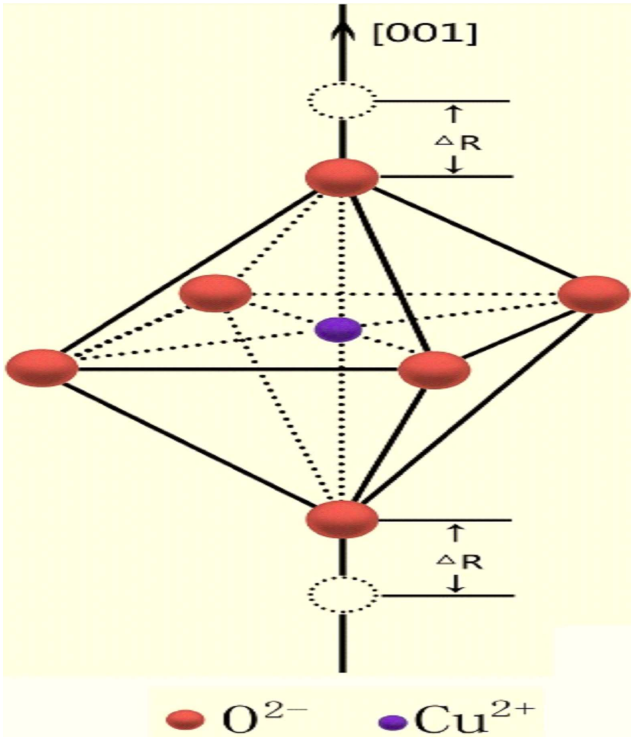

Fig. 1. The local structure of Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses.

In an octahedral d^n cluster, the single-electron basis functions based on the cluster approach can be written as the molecular orbitals including d orbitals $|d_\gamma\rangle$ of d^n ion and p orbitals $|p_\gamma\rangle$ of ligand [10, 25, 26],

$$|\varphi\rangle = N_\gamma(|d_\gamma\rangle - \lambda_\gamma|p_\gamma\rangle), \tag{5}$$

where γ (= t_2 or e_g) is the irreducible representation of O_h group. The normalization coefficient N_γ and the orbital mixing coefficient λ_γ have the following form [10, 25]:

$$N_\gamma^2(1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2) = 1, \tag{6}$$

where $S_{dp}(\gamma)$ are the group overlap integrals. They can be obtained from the Slater-type self-consistent field (SCF) functions [27, 28] and the metal-ligand distance R_0. The values of $S_{dp}(\gamma)$ for Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses can be obtained and the results are collected in Table I.

TABLE I

The group overlap integrals $S_{dp}(\gamma)$, the molecular orbital coefficients λ_γ and N_γ, the tetragonal elongation ΔR and core polarization constant κ for Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses.

$S_{dp}(e_g)$	$S_{dp}(t_2)$	λ_γ	N_t	N_e	ΔR [nm]	κ
0.0273763	0.0081352	0.2150	0.9793	0.9832	0.0250	0.1244

From Eqs. (5) and (6), two spin–orbit parameters ζ, ζ', two orbital reduction factors k, k' and two dipolar hyperfine structure constants P, P' are written as

$$\begin{aligned}
&\zeta = N_t^2\left(\zeta_d^0 + \frac{1}{2}\lambda_t^2\zeta_p^0\right), \quad \zeta' = N_tN_e\left(\zeta_d^0 - \frac{1}{2}\lambda_t\lambda_e\zeta_p^0\right),\\
&k = N_t^2\left(1 + 2\lambda_t S_{dp}(t) + \frac{1}{2}\lambda_t^2\right),\\
&k' = N_tN_e\left(1 + \lambda_e S_{dp}(e) + \lambda_t S_{dp}(t) - \frac{1}{2}\lambda_t\lambda_e\right),\\
&P = N_t^2 P_0, \quad P' = N_tN_eP_0,
\end{aligned} \tag{7}$$

where ζ_d^0 and P_0 are the corresponding parameters of free d^n ion, and ζ_p^0 is the spin–orbit coupling parameter of free ligand ion. For $(CuO_6)^{10-}$ cluster under study, we have $\zeta_d^0 \approx 829$ cm^{-1} [13], $P_0 \approx 360 \times 10^{-4}$ cm^{-1} [10], $\zeta_p^0 \approx 150$ cm^{-1}[10]. These theoretical values can be obtained and the results are listed in Table II.

TABLE II

The spin–orbit parameters (in cm^{-1}), the orbital reduction factors and dipolar hyperfine structure constants (in 10^{-4} cm^{-1}) for Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses.

ζ	ζ'	k	k'	P	P'
798.3556	794.8658	0.9845	0.9479	345.2486	346.6265

In Eq. (6), if the coefficient λ_γ is known, the coefficient N_γ can be calculated and then the parameters in Eq. (7) can be obtained. In order to decrease the number of adjustable parameters, we assume $\lambda_t \approx \lambda_e \approx \lambda_\gamma$. Thus, in the above formulae, three parameters $\Delta R, \lambda_\gamma$ and κ are left as the adjustable parameters to get good fit to the experimental optical and ESR data. By calculating the optical and ESR data of Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses by the high-order perturbation formulae, the three parameters are also obtained in Table I that produce the good match between the calculated and experimental optical spectral and ESR data (see Table III).

TABLE III

The optical band positions (in nm) and electron spin resonance (ESR) parameters of Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses.

	$^2B_{1g} \rightarrow {}^2B_{2g}$	$^2B_{1g} \rightarrow {}^2E_g$	$g_\parallel$	$g_\perp$	$A_\parallel$ [G]	$A_\perp$ [G]
calc.	786	432	2.339	2.059	−123	76
expt. [12]	785	438	2.339	2.077	123	–

3. Discussion and conclusion

It can be found from Table III that the calculated values from the high-order perturbation method agree well with the experimental ones. The tetragonal distortion can be given by ΔR ($= R_{\parallel} - R_{\perp} = 0.250$ Å). The value (0.250 Å) of ΔR has shown that CuO_6 octahedron has a strong tetragonal distortion. In addition, $\Delta R > 0$ indicates that Cu^{2+} in ZnO-Bi_2O_3-B_2O_3-CuO glasses is sited in a tetragonal elongated octahedron which is in good agreement with the glasses structure analysis of Singh et al. [12].

The orbital mixing coefficient λ_γ (=0.2150) for CuO_6 octahedron in ZnO-Bi_2O_3-B_2O_3-CuO glasses obtained from the above calculation is reasonable because λ_γ is found to be in the range of 0.2...0.6 in many materials [7–10]. The sign of hyperfine structure constants are often reported by using absolute value in experiment [12, 29]. The hyperfine structure constant component $A_{\parallel}$ is negative but that of $A_{\perp}$ is positive which are suited with the literatures' reports [30] and can be regarded as sound.

In conclusion, the ESR parameters for the tetragonal CuO_6 clusters in ZnO-Bi_2O_3-B_2O_3-CuO glasses arising from the static Jahn–Teller effects are explained satisfactorily by using the high-order perturbation formulae based on the two-spin-orbital-parameter model. The tetragonal distortion around Cu^{2+} center in ZnO-Bi_2O_3-B_2O_3-CuO glasses and the sign of hyperfine structure constants are also determined from the present calculations. The calculations show that the present theoretical model is effective in the explanations of optical spectra, ESR parameters and local distortion structure for d^9 ions in glasses.

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References

[1] M. Açıkgöz, *Radiat. Eff. Def. Solids* **169**, 300 (2014).

[2] W.L. Feng, W.Q. Yang, W.C. Zheng, *Radiat. Eff. Def. Solids* **166**, 160 (2011).

[3] M.G. Brik, I.V. Kityk, *J. Phys. Chem. Solids* **72**, 1256 (2011).

[4] M.G. Brik, A.M. Srivastava, N.M. Avram, A. Suchocki, *J. Lumin.* **148**, 338 (2014).

[5] W.L. Feng, W.Q. Yang, W.C. Zheng, B.X. Li, *Radiat. Eff. Def. Solids* **165**, 260 (2010).

[6] J.L. Rao, G. Sivaramaiah, N.O. Gopal, *Physica B* **349**, 206 (2004).

[7] W.L. Feng, X.M. Li, W.C. Zheng, Y.G. Yang, W.Q. Yang, *J. Magn. Magn. Mater.* **323**, 528 (2011).

[8] W.L. Feng, L.C. Pu, X.Z. Yang, N. Hu, *J. Magn. Magn. Mater.* **323**, 2828 (2011).

[9] R. Kripal, M. Bajpai, M. Maurya, H. Govind, *Physica B* **403**, 3693 (2008).

[10] W.L. Feng, *Physica B* **407**, 3865 (2012).

[11] H.M. Zhang, S.Y. Wu, Z.H. Zhang, *J. Non-Cryst. Solids* **357**, 2054 (2011).

[12] S.P. Singh, R.P.S. Chakradhar, J.L. Rao, B. Karmakar, *J. Magn. Magn. Mater.* **346**, 21 (2013).

[13] J.S. Griffith, *The Theory of Transition Metal Ions*, Cambridge University Press, London 1964.

[14] W.L. Feng, W.C. Zheng, *Philos. Mag.* **93**, 3690 (2013).

[15] D.J. Newman, B. Ng, *Rep. Prog. Phys.* **52**, 699 (1989).

[16] W.L. Feng, J.Y. Xue, *Physica B* **407**, 2344 (2012).

[17] W.L. Feng, X.Z. Yang, Y. Jin, T.X. Zeng, R.F. Li, *Phys. Scr.* **83**, 065705 (2011).

[18] W.C. Zheng, S.Y. Wu, *Spectrochim. Acta A* **57**, 1177 (2001).

[19] C. Rudowicz, Y.Y. Zhou, *J. Magn. Magn. Mater.* **111**, 153 (1992).

[20] W.L. Feng, X.X. Wu, W.C. Zheng, *Radiat. Eff. Def. Solids* **163**, 29 (2008).

[21] W.L. Feng, *J. Magn. Magn. Mater.* **324**, 4061 (2012).

[22] W.L. Feng, *Philos. Mag. Lett.* **92**, 368 (2012).

[23] W.L. Feng, W.C. Zheng, H.G. Liu, M.F. Zhao, *Spectrosc. Lett.* **45**, 404 (2012).

[24] R.C. Weast, *CRC Handbook of Chemistry and Physics*, CRC Press, Roca Raton 1989, p. F-187.

[25] W.L. Feng, W.C. Zheng, *Radiat. Eff. Def. Solids* **163**, 857 (2008).

[26] W.L. Feng, L. He, W.Q. Yang, W.C. Zheng, *Mol. Phys.* **107**, 2293 (2009).

[27] E. Clementi, D.L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).

[28] E. Clementi, D.L. Raimondi, W.P. Reinhardt, *J. Chem. Phys.* **47**, 1300 (1967).

[29] W.L. Feng, *Philos. Mag. Lett.* **90**, 533 (2010).

[30] B.R. McGarvey, *J. Phys. Chem.* **71**, 51 (1967).