

Theoretical Studies of ESR Parameters and Local Lattice Structure of the Vanadate–Lithium–Borate Glasses

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Electron spin resonance spectral parameters of V^{4+} ions in vanadate–lithium–borate glasses have been calculated by the crystal-field theory. The theoretical results are $g_{\parallel} = 1.940$, $g_{\perp} = 1.983$ and $A_{\parallel} = -175 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = -65 \times 10^{-4} \text{ cm}^{-1}$ which are in good agreement with the experimental values ($g_{\parallel} = 1.939(3)$, $g_{\perp} = 1.998(3)$ and $A_{\parallel} = (170.6\text{--}176.4) \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = (61.3\text{--}71.4) \times 10^{-4} \text{ cm}^{-1}$). In addition, the bond lengths of the local lattice structure are, respectively, $R_{\parallel} = 1.5 \text{ \AA}$ and $R_{\perp} = 1.95 \text{ \AA}$ which have been shown to have a compressed tetrahedral geometry along the C_4 axis.

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1. Introduction

Glasses containing transition metal and rare earth ions have attracted a great deal of attention because of their memory and photoconducting characteristics. They also find potential applications in the development of new lasers, optical amplifiers, or luminescent materials. ESR/EPR technology can be used widely to investigate the local lattice structure information about the glassy network and to identify the point symmetry around the transition metal or rare earth ions [1–3].

V^{4+} , as an important probe ion, can provide useful information regarding the structure of their network environment in a glass, because their ESR spectra are simple [4, 5]. The ESR spectra of V^{4+} doped glasses have been studied extensively by many researchers in the systems of borate [6–9]. Among them, the ESR spectral parameters (characterized by g factors g_{\parallel} , g_{\perp} and hyperfine structure parameters A_{\parallel} , A_{\perp}) have been determined by Cozar et al. [9]. But there is no any theoretical analysis for these spectral data and local lattice structural parameters. In the present work, the authors bring out the theoretical results of the ESR spectral parameters and local lattice

structural data of V^{4+} ions in ternary vanadate–lithium–borate glasses. These results of calculations are in good agreement with experimental findings.

2. Theoretical model

2.1. Two spin–orbit coupling parameters

The linear combination of atomic orbitals–molecular orbital (LCAO–MO) method developed by Kivelson and Lee [10] for vanadium (vanadyl VO^{2+}) complexes has been considered in present work. In addition, related studies have also shown that the contribution to ESR data from the spin–orbit (SO) coupling coefficient (ζ_p^0) of the ligand cannot be ignored when its magnitude close to or more than that (ζ_d^0) of the centre transition metal ion [11–13]. It is the case of this present work because the value of ζ_p^0 ($= 150 \text{ cm}^{-1}$ [12]) is close to that of the ζ_d^0 ($= 248 \text{ cm}^{-1}$ [14]).

2.2. The superposition model

According to the superposition model which was proposed by Newman et al. [15, 16], the tetragonal crystal-field parameters D_s and D_t can be expressed as

$$D_s = (4/7)\overline{A_2}(R_0)[(R_0/R_{\perp})^{t_2} - (R_0/R_{\parallel})^{t_2}],$$

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$$Dt = (16/21)\bar{A}_4(R_0)[(R_0/R_\perp)^{t_4} - (R_0/R_\parallel)^{t_4}], \quad (1)$$

where R_0 is the reference distance which is characterized by the bond lengths (R_\parallel , R_\perp) of the local lattice structure. t_2 (=3) and t_4 (=5) are the power-law exponents. The intrinsic parameters $\bar{A}_k(R_0)$ (subscript $k = 2$ or 4 for d^n electronic configuration) can be determined from the cubic crystal-field parameter Dq via the relation [17–19]:

$$\bar{A}_4(R_0) = 3/4Dq, \quad \bar{A}_2(R_0) = (8 - 12)\bar{A}_4(R_0). \quad (2)$$

We take $\bar{A}_2(R_0) = 12\bar{A}_4(R_0)$ in the calculation. The length of V–O bond $R_0 \approx R_\perp \approx 1.95$ Å which is corresponding to the cubic symmetry [20]. R_\parallel can be treated as fitting parameter. As much as we know, up to the present, the cubic crystal-field parameter Dq has not been reported. $Dq(\text{F}^-)$ (≈ 2012 cm $^{-1}$) value of $(\text{VF}_6)^{2-}$ cluster has been given in literature [21]. According to the chemical sequences of the optical spectra, there is $Dq(\text{F}^-) < Dq(\text{O}^{2-})$, thus, we take $Dq(\text{O}^{2-}) \approx 2150$ cm $^{-1}$ in the calculation and it can be regarded as reasonable.

2.3. The high order perturbation formulae

The electronic configuration of V^{4+} ion is $3d^1$. The g factors g_\parallel , g_\perp and hyperfine structure parameters A_\parallel , A_\perp of the ground state b_{2g} ($|d_{xy}\rangle$) can be obtained from high order perturbation methods [22],

$$g_\parallel = g_s - \frac{8k'\zeta'}{\Delta E(b_{1g})} - \frac{k\zeta^2}{[\Delta E(e_g)]^2} - \frac{4k'\zeta\zeta'}{\Delta E(e_g)\Delta E(b_{1g})} - \frac{g_s\zeta^2}{[\Delta E(e_g)]^2},$$

$$g_\perp = g_s - \frac{2k\zeta}{\Delta E(e_g)} + \frac{k\zeta^2}{[\Delta E(e_g)]^2} - \frac{2k\zeta'^2}{\Delta E(e_g)\Delta E(b_{1g})} + \frac{2k'\zeta\zeta'}{\Delta E(e_g)\Delta E(b_{1g})} - \frac{2g_s\zeta'^2}{[\Delta E(b_{1g})]^2} - \frac{g_s\zeta^2}{2[\Delta E(e_g)]^2}, \quad (3)$$

$$A_\parallel = P\left(-\kappa - \frac{4}{7}\right) - P'\left\{\frac{-8k'\zeta'}{\Delta E(b_{1g})} - \frac{6k\zeta}{7\Delta E(e_g)} - \frac{4k\zeta^2}{7[\Delta E(e_g)]^2} - \frac{6k\zeta'^2}{7\Delta E(e_g)\Delta E(b_{1g})} - \frac{22k'\zeta\zeta'}{7\Delta E(e_g)\Delta E(b_{1g})} - \frac{6g_s\zeta'^2}{7[\Delta E(b_{1g})]^2} - \frac{17g_s\zeta^2}{14[\Delta E(e_g)]^2}\right\},$$

$$A_\perp = P\left\{\frac{2}{7} - \kappa - \frac{11k\zeta}{7\Delta E(e_g)} + \frac{11k\zeta^2}{14[\Delta E(e_g)]^2} - \frac{11g_s\zeta^2}{7[\Delta E(b_{1g})]^2} - \frac{11g_s\zeta^2}{28[\Delta E(e_g)]^2}\right\}. \quad (4)$$

In Eqs. (3) and (4), g_s (=2.0023) is the g value of the free electron, κ is the Fermi contact parameter; k' and k are

the orbital reduction factors; and the energy differences between excited states b_{1g} , e_g and ground state b_{2g} are, respectively, $\Delta E(b_{1g})$ and $\Delta E(e_g)$,

$$\Delta E(b_{1g}) = 10Dq,$$

$$\Delta E(e_g) = -3Ds + 5Dt. \quad (5)$$

The two SO coupling parameters ζ and ζ' , two orbital reduction factors k and k' , and two dipole hyperfine structure parameters P , P' can be given as

$$\zeta = N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0/2),$$

$$\zeta' = (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0/2),$$

$$k = N_t(1 - 2\lambda_t S_{dp}(t_{2g}) + \lambda_t^2/2),$$

$$k' = (N_tN_e)^{1/2}(1 - \lambda_t S_{dp}(t_{2g}) - \lambda_e S_{dp}(e_g) - \lambda_t\lambda_e/2)$$

$$P = N_tP_0, \quad P' = (N_tN_e)^{1/2}P_0, \quad (6)$$

in which N_t , N_e are the normalized parameters. λ_e , λ_t are the orbital mixing coefficients, we assume that $\lambda_\gamma \approx \lambda_e \approx \lambda_t$ for the simplicity in the calculation. The group overlap integrals $S_{dp}(e_g)$ and $S_{dp}(t_{2g})$ can be obtained from the Slater-type SCF functions [23, 24] and the metal–ligand reference distance R_0 . P_0 ($= 136 \times 10^{-4}$ cm $^{-1}$ [14, 20]) is the hyperfine structure constant of the V^{4+} ion.

3. Application

From formulae (1)–(4), the relation between ESR spectra (g_\parallel , g_\perp and A_\parallel , A_\perp) and the local lattice structural parameters (R_\parallel , R_\perp) has been established by using two SO coupling parameter model, the superposition model, and high-order perturbation theory. As an application, we calculated the ESR data and structural parameters of V^{4+} ion in ternary vanadate–lithium–borate glasses. The values of the fitting parameters can be obtained from the calculation of ESR data of V^{4+} in vanadate–lithium–borate glasses,

$$\lambda_\gamma \approx \lambda_e \approx \lambda_t \approx 0.41, \quad R_\parallel = 0.150 \text{ nm}, \quad \kappa = 0.81. \quad (7)$$

The correlative values of the overlap integrals, normalized parameters, two SO coupling parameters, and two orbital reduction factors are collected in Table I. The calculated ESR parameters are compared with the experimental values in Table II.

TABLE I
The correlative calculated parameters for V^{4+} in vanadate–lithium–borate glasses.

$S_{dp}(t_{2g})$	$S_{dp}(e_g)$	N_t	N_e	ζ	ζ'	k	k'
0.0508	0.1297	0.8877	0.9418	231.3	215.2	0.9254	0.7699

4. Discussions and conclusions

Majority vanadyl complexes [10, 14] and also oxovanadium coordination polyhedra realized in oxide glasses

have practically the some pentacoordinated C_{4v} symmetry (square-pyramidal) where the V=O bond oriented along the C_4 axis is stronger [and $R(\text{V=O})$ smaller] than the four V–O bonds from xOy plane (pyramidal base) [10, 14]. In solutions and also in oxide glasses the coordination of the sixth oxygen atom below the V^{4+} site in opposition with “yl” oxygen forming O–VO₄–O units (hexacoordinated octahedral distorted) occur. In this case the V=O bond weakens (V–O) and the R_{\parallel} increases [25–30]. Thus, vanadyl complexes R_{\parallel} [≈ 1.5 Å, $R(\text{V=O})$ bond] and R_{\perp} [≈ 1.95 Å, $R(\text{V–O})$ bonds] are suggested in present studied system.

In summary, from Table II, it is good agreement between the theoretical data and the experimental values of ESR spectra. It should be pointed out that the signs of hyperfine structure parameters A_{\parallel} , A_{\perp} are actually given as absolute values in literature [9]. The negative signs of the calculated A_{\parallel} , A_{\perp} are suggested in this work.

TABLE II

g factors and hyperfine structure constants A_i for V^{4+} in vanadate–lithium–borate glasses.

ESR parameters	Calc.	Expt. [9]
g_{\parallel}	1.940	1.939(3)
g_{\perp}	1.983	1.998(3)
A_{\parallel} [10^{-4} cm ⁻¹]	-175	170.6–176.4 ^a
A_{\perp} [10^{-4} cm ⁻¹]	-65	61.3–71.4 ^a

^a The data are given by absolute values.

The octahedron around V^{4+} ion is compressed along C_4 axis because the calculated value of R_{\parallel} is less than that of R_{\perp} . The magnitude of the tetragonal distortion ΔR ($= R_{\perp} - R_{\parallel} = 0.045$ nm) has also been shown that V–O bonds are stronger along the C_4 -axis direction than other V–O bonds of the complex.

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