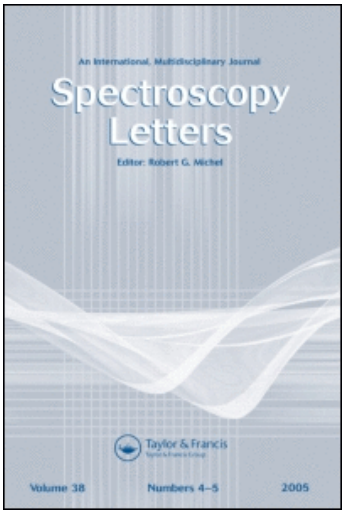

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Defect Structure and EPR Parameters of the Cu^{2+} Center in MNB Ternary Glasses

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ABSTRACT The electron paramagnetic resonance (EPR) parameters (g factors $g_{//}$, $g_{\perp}$ and hyperfine structure constants $A_{//}$, $A_{\perp}$) for 15MgO-15Na_2O-69B_2O_3 (MNB):Cu^{2+} ternary glasses were calculated based on the high-order perturbation formulae of $3d^9$ ion in a tetragonal symmetry. From the calculations, the defect structures of MNB:Cu^{2+} ternary glasses were obtained and a negative sign for $A_{//}$ and $A_{\perp}$ for the Cu^{2+} center is suggested in the discussion.

KEYWORDS defect structure, electron paramagnetic resonance (EPR), optical spectrum, MNB:Cu^{2+} glasses

INTRODUCTION

When a paramagnetic ion substitutes for the host ion in glasses, the local structure surrounding the impurity may be different from the corresponding structure in the host glasses because of size and/or valence mismatch.[1–3] The determination of the local environment of the impurity centers is an interesting and significant problem because the defects can influence strongly host glasses properties. Many experimental studies on electron paramagnetic resonance and optical spectra were made for the paramagnetic ions in glasses.[2–4] However, the theoretical studies of the local structure distortion of impurity center are quite fewer. The EPR parameters (g factors $g_{//}$, $g_{\perp}$ and hyperfine structure constants $A_{//}$, $A_{\perp}$) and optical spectrum of Cu^{2+} doping in the layer structure MNB glasses have been reported in recent years.[3] Whereas, the theoretical explanation for these EPR parameters and optical absorption spectrum has not been made, and the defect structure of Cu^{2+} impurity center has not been estimated from these EPR parameters either. The site symmetry of the cation Cu^{2+} in MNB glasses is D_{4h}. In the present paper, we calculate these EPR parameters and optical absorption spectrum of Cu^{2+} in MNB glasses from the high-order perturbation formulae and superposition model[5] for $3d^9$ ions in tetragonal octahedral site. At the same time, some useful information of defect structure for tetragonal Cu^{2+} center can be obtained from the calculations. The results are discussed.

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CALCULATION

For MNB:Cu^{2+} ternary glasses, the Cu^{2+} ions lie in the interspace of the three dimensional network and are surrounded by six oxygen atoms.[3] It is known that Cu^{2+} belongs to the electron system $3d^9$. Its energy level will be split into ^2E_g and $^2T_{2g}$ in a cubic field. The ground state is ^2E_g in octahedral symmetry. In the tetragonal field D_{4h} the energy levels will be split further. The ^2E_g level splits into two nondegenerate orbital singlets $^2A_{1g}$ and $^2B_{1g}$. $^2T_{2g}$ is split into a doublet ^2E_g and a singlet $^2B_{2g}$. E_g, T_{2g}, B_{1g} and B_{2g} are the irreducible representation in D_{4h} symmetry. $^2B_{1g}$ is the ground state in the MNB:Cu^{2+} ternary glasses.[3]

In a tetragonal field, the spin-Hamiltonian of the $3d^9$ ion can be described by the expression

$$H_s = \mu_B(g_\perp(H_xS_x + H_yS_y) + \mu_B H_zS_z + A_{//}I_zS_z + A_\perp(I_xS_x + I_yS_y) \quad (1)$$

where g_i ($i = \perp, //$) indicates the components of the g factor, μ_B is the Bohr magneton, 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. Using the Macfarlane's perturbation theory,[6] the g factors and A values can be obtained by the formulae

$$\begin{aligned} g_{//} &= g_s - \frac{8K\lambda}{E_1} - \frac{(g_s+K)\lambda^2}{E_2^2} - \frac{4K\lambda^2}{E_1E_2} \\ g_\perp &= g_s - \frac{2K\lambda}{E_2} - \frac{(g_s/2-K)\lambda^2}{E_2^2} - \frac{2g_s\lambda^2}{E_1^2} \\ A_{//} &= P\left[-\kappa - \frac{4}{7} + (g_{//}-g_s) + \frac{3(g_\perp - g_s)}{7}\right] \\ A_\perp &= P\left[\frac{2}{7} - \kappa + \frac{11}{14}(g_\perp - g_s)\right] \end{aligned} \quad (2)$$

where g_s (= 2.0023) is the free electron g value and λ is the spin-orbit coupling coefficient of the $3d^9$ ion. The relation between λ and the one-electron spin-orbit coupling coefficient ζ_d is $\lambda = -\zeta_d$. P is the dipolar hyperfine structure constant in glasses. K and κ are the orbital reduction factor and the core polarization constant. Because of the covalence reduction effect for $3d^n$ ions in glasses, we have[7,8]

$$\zeta_d \approx K\zeta_d^0, P \approx KP_0 \quad (3)$$

in which ζ_d^0 and P_O are the corresponding values of free $3d^n$ ion. For a free Cu^{2+} ion, we take $\zeta_d^O \approx 829\,cm^{-1}$ and $P_O \approx 336 \times 10^{-4} cm^{-1}$ in our calculation.[9,10] In Equation (2), the energy denominators are $E_1 = E(^2B_{2g}) - E(^2B_{1g})$ and $E_2 = E(^2E_g) - E(^2B_{1g})$. The energy levels $E(^2B_{1g})$, $E(^2B_{2g})$ and $E(^2E_g)$ are given by

$$\begin{aligned} E(^2B_{1g}) &= E(|x^2-y^2\rangle) = 6Dq + 2Ds - Dt \\ E(^2B_{2g}) &= E(|xy\rangle) = -4Dq + 2Ds - Dt \\ E(^2E_g) &= E(|xz\rangle, |yz\rangle) = -4Dq - Ds + 4Dt \end{aligned} \quad (4)$$

where the crystal field parameters Dq, Ds and Dt by using the superposition model[5] can be expressed as

$$\begin{aligned} Dq &= \frac{4}{3}\overline{A}_4(R_0)\left(\frac{R_0}{R_\perp}\right)^{t_4} \\ Ds &= \frac{4}{7}\overline{A}_2(R_0)\left[\left(\frac{R_0}{R_{//}}\right)^{t_2} - \left(\frac{R_0}{R_\perp}\right)^{t_2}\right] \\ Dt &= \frac{16}{21}\overline{A}_4(R_0)\left[\left(\frac{R_0}{R_{//}}\right)^{t_4} - \left(\frac{R_0}{R_\perp}\right)^{t_4}\right] \end{aligned} \quad (5)$$

where the power-law exponents $t_2 \approx 3$ and $t_4 \approx 5$[11–13]. $\overline{A}_2(R_0)$ and $\overline{A}_4(R_0)$ are the intrinsic parameters with the reference distance R_0. The ratio $\overline{A}_2(R_0)/\overline{A}_4(R_0) \approx 9 \sim 12$ is obtained in many $3d^n$ systems[11–14]. So, we take $\overline{A}_2(R_0)/\overline{A}_4(R_0) \approx 12$ here. From the optical spectrum of MNB:Cu^{2+} ternary glasses,[3] we estimate $\overline{A}_4(R_0) \approx 755\,cm^{-1}$ with R_0 ≈0.21nm. In general, the local structural data of impurity centers are unlike the corresponding data in the host crystal because of the size and/or electronegativity mismatch. For MNB:Cu^{2+}, the impurity-ligand (Cu^{2+}-O^{2-}) distances $R_\perp$(≈0.198 nm) are estimated from the Ref. [15]. Thus, in the above formulas, only the parameters $R_{//}$, K and κ are not

TABLE 1 The EPR Parameters and the Optical Spectral Band for Cu^{2+} Center in 15MgO-15Na_2O-69B_2O_3: Cu^{2+} Glasses

	$g_{//}$	$g_\perp$	$A_{//}$ ($10^{-4}cm^{-1}$)	$A_\perp$ ($10^{-4}cm^{-1}$)	$^2B_{1g} \rightarrow {}^2B_{2g}$ (cm^{-1})
Calc.	2.3380	2.0451	−168	−17.1	13510
Expt. [3]	2.338 ± 0.002	2.095 ± 0.002	162 ± 2	19.6 ± 2	13513

known. By fitting the calculated EPR parameters (and also the optical spectrum) to the experimental values, we obtain

$$R_{//} \approx 2.7\text{Å}, \quad K \approx 0.837, \quad \kappa \approx 0.38 \qquad (6)$$

The calculated EPR parameters and optical absorption spectrum are compared with the experimental values in Table 1.

CONCLUSION AND DISCUSSION

In Table 1, one can see the absolute values of $A_{//}$ and $A_{\perp}$ are in good agreement with the experimental findings, but the signs of both are negative. Actually, the signs of the hyperfine structure constants are very difficult to ascertain. Thus, many experiments give them as a absolute ones.[16,18,19] However, the negative signs of constants A_i for $3d^n$ ions in many crystals were proposed.[16,18–21] So, the negative signs of $A_{//}$ and $A_{\perp}$ for Cu^{2+} center are suggested here.

From the Table 1, one can also find that the calculated EPR parameters $g_{//}$, $g_{\perp}$ and absorption spectrum are in reasonable agreement with the observed values. Base on the calculation, the local defect structure is established. Obviously, $R_{//} > R_{\perp}$, which indicates that Cu^{2+} ions exists in a tetragonal distortion (D_{4h}) octahedral site elongated along the C_4-axis, which may be caused by the strong Jahn-Teller effect. At the same time, $R_{\perp} < R_0$, which shows that the ionic radius of impurity ($r_i(Cu^{2+}) \approx 0.80$ Å)[17] should be smaller than that of the replaced host ion. For MNB:Cu^{2+} ternary glasses, the ionic radii of host ions are $r_b(Mg^{2+}) \approx 0.74$ Å, $r_b(Na^{+}) \approx 0.98$ Å, and $r_b(B^{3+}) \approx 0.20$ Å, respectively.[17] So, the Cu^{2+} ion replacing Na^{+} seems more likely. In addition, the introducing Cu^{2+} ion into the lattice instead of Na^{+} causes a charge imbalance, which can be compensated by introducing equal number of negative charge defects or the positive ion vacancy in the neighborhood of the lattice and can be deemed suitable in physics.

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