Investigation on the Spin Hamiltonian Parameters and the Local Structures for Cu^{2+} Centers in Sodium Phosphate and Heavy Metal Fluoride Glasses

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The spin Hamiltonian parameters (the anisotropic g factors $g_{||}$, $g_{\perp}$ and hyperfine structure constants $A_{||}$, $A_{\perp}$) for the Cu^{2+} sites in sodium phosphate glasses $Na_2O-9P_2O_5$ and heavy metal fluoride glasses $60ZrF_4-5LaF_3-20BaF_2-15NaF$ are theoretically investigated by using the high (fourth-) order perturbation formulas of these parameters for a $3d^9$ ion in tetragonally elongated octahedra. In these formulas, the contributions to the g factors from the tetragonal distortion, characterized by the tetragonal field parameters Ds and Dt, are taken into account by considering the relative axial elongation of the ligand octahedron around the Cu^{2+} due to the Jahn–Teller effect. According to the calculations, the ligand octahedra around Cu^{2+} are suggested to suffer about 12% and 18% relative elongation along the C_4-axis for the studied $Na_2O-9P_2O_5$ and $60ZrF_4-5LaF_3-20BaF_2-15NaF$ glasses, respectively. The local structures characterized by the above axial elongations are discussed.

Key words: Electron Paramagnetic Resonance (EPR); Crystal-Field and Spin Hamiltonians; Glasses; Cu^{2+}; Local Structure.

1. Introduction

Sodium phosphate and heavy metal fluoride glasses usually exhibit unique properties such as high thermal expansion coefficient [1, 2], low glass transition temperature [3], and fluorescence characteristics [4] and may act as solid state electrolytes in batteries [5] as well as solid state lasers [1]. Especially, these glasses doped with transition-metal ions show unique optical and electrical [6 – 8], photoacoustic [9], and ion conductivity [10]. In general, the above properties or behaviours are sensitive to the local structures and electronic states of the doped transition-metal impurities, which can be analyzed by means of the electron paramagnetic resonance (EPR) technique. Among the transition-metal ions, copper (Cu^{2+}) is a model system with one $3d$ hole, corresponding to only one ground state and one excited state under ideal octahedral crystal-fields [11]. In fact, Cu^{2+} ions in the glasses are usually applied as probes to provide useful information about electronic states and local structures by means of the EPR technique. For example, EPR studies on Cu^{2+} doped $Na_2O-9P_2O_5$ (NP) and $60ZrF_4-5LaF_3-20BaF_2-15NaF$ (ZLBN) glasses were performed, and the spin Hamiltonian parameters (the anisotropic g factors $g_{||}$, $g_{\perp}$ and hyperfine structure constants $A_{||}$, $A_{\perp}$) were also measured [12, 13]. Although the above EPR spectra were assigned to the $^2B_{1g}$ $(|x^2-y^2>)$ ground state for a $3d^9$ ion in tetragonally elongated octahedra, these results have not been quantitatively interpreted. Moreover, the local structure around Cu^{2+} in these glasses has not been determined, either.

Considering that microscopic mechanisms of the spin Hamiltonian parameters and information of impurity local structures can be helpful to understand the properties of these materials with transition-metal dopants, further theoretical investigations on these spin Hamiltonian parameters and the local structures for the Cu^{2+} centers are of scientific and technical significance. In the present paper, the high (fourth-) order perturbation formulas of these spin Hamiltonian parameters for a $3d^9$ ion in tetragonally elongated octahedra are applied, the tetragonal distortions due to the

Jahn–Teller effect of the Cu^{2+} clusters are taken into account. Based on the studies, some useful information of defect structures for the impurity tetragonal Cu^{2+} centers in NP and ZLBN glasses can be acquired from the EPR analysis.

2. Calculations

In previous works [14–16], the EPR of Cu^{2+} ions doped in glasses has been widely investigated, the spectra of all these glasses shown that the impurity Cu^{2+} locates on octahedral sites with six nearest neighbour ligands. For the Jahn–Teller ion Cu^{2+} in octahedra, it may suffer the Jahn–Teller effect via relaxation and compression of the copper–ligand bonds parallel and perpendicular to the C_4-axis, which reduces the local symmetry of the impurity Cu^{2+} center to tetragonal (an elongated octahedron). Consequently, the local structures of the Cu^{2+} centers are characterized by the relative tetragonal elongation ratio ρ.

For a Cu^{2+} ($3d^9$) ion in ideal octahedra, its energy level will be split into ^2E_g and $^2T_{2g}$. However, in the tetragonal symmetry the energy levels will be split further, i.e., the lower ^2E_g irreducible representation may be separated into two orbital singlets $^2B_{1g}$ and $^2A_{1g}$ with the former lying lowest, while the upper $^2T_{2g}$ representation would split into an orbital singlet $^2B_{2g}$ and a doublet ^2E_g [11, 17]. In order to study the spin Hamiltonian parameters for the Cu^{2+} centers in NP and ZLBN glasses, the high (fourth-) order perturbation formulas of the g factors and the hyperfine structure constants for a tetragonally elongated octahedral $3d^9$ cluster can be adopted here [18]:

$$\begin{aligned}
g_{\parallel} &= g_s + \frac{8k\varsigma_d}{E_1} + \frac{k\varsigma_d^2}{E_2^2} + \frac{4k\varsigma_d^2}{E_1E_2} - g_s\varsigma_d^2\left(\frac{1}{E_1^2} - \frac{1}{2E_2^2}\right) \\
&\quad + k\varsigma_d^3\left(\frac{4}{E_1E_2^2} - \frac{1}{E_2^3}\right) - 2k\varsigma_d^3\left(\frac{2}{E_1^2E_2} - \frac{1}{E_1E_2^2}\right) \\
&\quad + g_s\varsigma_d^3\left(\frac{1}{E_1E_2^2} - \frac{1}{2E_2^3}\right), \\
g_{\perp} &= g_s + \frac{2k\varsigma_d}{E_1} - \frac{4k\varsigma_d^2}{E_1E_2} + k\varsigma_d^2\left(\frac{2}{E_1E_2} - \frac{1}{E_2^2}\right) \qquad (1) \\
&\quad + \frac{2g_s\varsigma_d^2}{E_1^2} + k\varsigma_d^3\left(\frac{2}{E_1} - \frac{1}{E_2}\right)\left(\frac{1}{2E_2^2} + \frac{1}{E_1E_2}\right) \\
&\quad - g_s\varsigma_d^3\left(\frac{1}{2E_1^2E_2} - \frac{1}{2E_1E_2^2} + \frac{1}{2E_2^3}\right), \\
A_{\parallel} &= P\left[-\kappa - \frac{4N}{7} + (g_{\parallel} - g_s) + \frac{3(g_{\perp} - g_s)}{7}\right], \\
A_{\perp} &= P\left[-\kappa + \frac{2N}{7} + \frac{11(g_{\perp} - g_s)}{14}\right].
\end{aligned}$$

In the above formulas, g_s (≈ 2.0023) is the spin-only value. k is the orbital reduction factor, which is equivalent to the covalency factor N, a characteristic of the covalency between the central ion and the ligands. κ is the core polarization constant. ζ_d and P are, respectively, the spin–orbit coupling coefficient and the dipolar hyperfine structure parameter of the $3d^9$ ion in glasses. They can be written in terms of the corresponding free-ion values, i.e., $\zeta_d \approx N\zeta_d^0$ and $P \approx NP_0$. E_1 and E_2 are the energy separations between the excited $^2B_{2g}$ and ^2E_g and the ground $^2B_{1g}$ states under tetragonal crystal fields [18, 19]. They can be determined from the energy matrices for a $3d^9$ ion under tetragonal symmetry in terms of the cubic field parameter Dq and the tetragonal field parameters Ds and Dt:

$$\begin{aligned}
E_1 &= 10\mathrm{Dq}, \\
E_2 &= 10\mathrm{Dq} - 3\mathrm{Ds} + 5\mathrm{Dt}.
\end{aligned} \qquad (2)$$

For the Jahn–Teller elongated $[CuO_6]^{10-}$ (or $[CuF_6]^{4-}$) clusters for the studied NP (or ZLBN) glasses, the parallel and perpendicular impurity–ligand bond lengths can be expressed in terms of the relative tetragonal elongation ρ as: $R_{\parallel} \approx R(1+2\rho)$ and $R_{\perp} \approx R(1-\rho)$, with the reference impurity–ligand bond lengths R. Thus, the tetragonal field parameters are obtained from the superposition model [20, 21] and the relative elongation ratio ρ of the Cu^{2+} centers:

$$\begin{aligned}
\mathrm{Ds} &= \frac{4}{7}\bar{A}_2(R)\left[(1-\rho)^{-t_2} - (1+2\rho)^{-t_2}\right], \\
\mathrm{Dt} &= \frac{16}{21}\bar{A}_4(R)\left[(1-\rho)^{-t_4} - (1+2\rho)^{-t_4}\right].
\end{aligned} \qquad (3)$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents [20, 21]. $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters with the reference distance R. For $3d^n$ ions in octahedra, $\bar{A}_4(R) \approx 3/4\mathrm{Dq}$ and the ratio $\bar{A}_2(R)/\bar{A}_4(R)$ is in the range of $9 \sim 12$ in many crystals [19, 21–23], and we take $\bar{A}_2(R)/\bar{A}_4(R) \approx 12$ here. Thus, the g factors, especially the anisotropy Δg $(= g_{\parallel} - g_{\perp})$ is connected with the tetragonal field parameters and hence with the local structure (i.e., the relative tetragonal elongation ρ) of the impurity centers.

According to the optical spectra for Cu^{2+} in the similarly oxide glasses (i.e. $Al_2O_3-P_2O_5$) [13], the cubic field parameter Dq ($\approx 1050\,\text{cm}^{-1}$) and the orbital reduction factor N (≈ 0.85) can be obtained and used for the studied NP glasses by fitting the observed d–d transitions. Nevertheless, for the studied Cu^{2+} centers in ZLBN glasses, the cubic field parameter Dq ($\approx 1052\,\text{cm}^{-1}$) was found by the experimental optical spectra [12]. Due to the stronger ionicity of the ligand F^- ion than O^{2-}, the covalency for the $[CuF_6]^{4-}$ clusters in the ZLBN glasses may be weaker. Thus the orbital reduction factor N (≈ 0.89) is adopted. The spin–orbit coupling coefficient ζ_d and the dipolar hyperfine structure parameter are acquired for the studied systems by using the free-ion data ζ_d^0 ($\approx 829\,\text{cm}^{-1}$) [18] and P_0 ($\approx 416 \cdot 10^{-4}\,\text{cm}^{-1}$) [19, 24]. As a result, only the relative tetragonal elongation ρ and the core polarization constant κ are unknown in the formulas of the EPR parameters. Substituting these values into (1) and fitting the calculated spin Hamiltonian parameters to the experimental data, one can obtain

$$\rho \approx 12\% \text{ and } 18\%, \quad \kappa \approx 0.32 \text{ and } 0.24 \qquad (4)$$

for the Cu^{2+} centers in NP and ZLBN glasses, respectively. The corresponding theoretical results are shown in Table 1.

3. Discussion

Table 1 reveals that the calculated spin Hamiltonian parameters for both systems based on the relative tetragonal elongation ratios ρ and the core polarization constants κ in (4) are in good agreement with the experimental values. Thus, the experimental spin Hamiltonian parameters for both NP and ZLBN glasses are satisfactorily interpreted in a uniform way, and the local structures information for the impurity Cu^{2+} centers of the studied NP and ZLBN glasses are obtained, respectively.

i) The relative tetragonal elongation ratios $\rho \approx 12\%$ and 18% are obtained by theoretically connecting the spin Hamiltonian parameters with the local structures of the studied systems. The large anisotropies Δg ($= g_{||} - g_{\perp}$) for Cu^{2+} centers in NP and ZLBN glasses may be ascribed to the large tetragonal elongation ratios ρ due to the Jahn–Teller effect via stretching and compressing of the parallel and perpendicular impurity–ligand bonds. This point is also supported by the EPR measurements for Cu^{2+} (or Ni^{3+} and Ir^{2+} with the same ground state ^2E_g) in various complexes [14, 15, 25 – 29]. Consequently, Cu^{2+} (or Ni^{3+} and Ir^{2+}) with ^2E_g ground state tends to exhibit tetragonal elongation distortion due to the Jahn–Teller effect under octahedral environments, although the original octahedral site may not show tetragonal symmetry. Interestingly, a similar relative elongation ratio of about 14% is also reported for the tetragonally elongated $[CuO_6]^{10-}$ cluster in $15\,MgO$–$15\,Na_2O$–$69\,B_2O_3$ (MNB) glasses doped with Cu^{2+} based on perturbation formulas calculation [25]. However, for the studied Cu^{2+} doped in ZLBN glasses, the cubic field parameter Dq ($\approx 1052\,\text{cm}^{-1}$) [12] was significantly lower than that of the typical Cu–F bonds [12] Dq ($\approx 4500 - 5500\,\text{cm}^{-1}$). Further, from the empirical relationship Dq $\sim R^{-5}$ [30, 31], the larger impurity–ligand distance R in the studied ZLBN glasses would be possibly account for the smaller Dq. Therefore, the relatively larger ρ for ZLBN : Cu^{2+} than that for SP : Cu^{2+} is in agreement with the weaker chemical bonding and lower elastic constant of the impurity–ligand bond due to the longer distance R and lower valence state of the ligand ion in the former. Thus, the order NP > ZLBN of the relative tetragonal elongation ratio ρ in (4) may be regarded as valid in physics. Finally, it is noted that a crude estimation of the contributions of the still higher (fifth) order perturbation terms in the formulas for the g factors in (1) yields $\zeta^4/(E_1^3 E_2)$, which is in the order of 10^{-6} and safely negligible.

ii) The studied systems have weak covalency (described as the covalency factor $N \approx 0.85$ and 0.89) due to the dominant ionicity of the Cu–O and Cu–F combination. In addition, the spin–orbit coupling coefficient ($\approx 151\,\text{cm}^{-1}$ [18] or $220\,\text{cm}^{-1}$ [23]) of the ligand oxygen (or fluoride) is much smaller than that ($\approx 829\,\text{cm}^{-1}$ [18, 19]) of the central ion Cu^{2+}. Thus, the perturbation formulas of the spin Hamiltonian parameters based on the conventional crystal-field model

Table 1. Spin Hamiltonian g factors and hyperfine structure constants (in $10^{-4}\,\text{cm}^{-1}$) for the Cu^{2+} centers in NP and ZLBN glasses.

Glasses		$g_{\|\|}$	$g_{\perp}$	$A_{\|\|}$	$A_{\perp}$
$Na_2O - 9P_2O_5$	Cal.	2.455	2.071	−113	−8.5
	Expt. [12, 13]	2.456	2.068	112	< 15
$60ZrF_4 - 5LaF_3 -$	Cal.	2.50	2.068	−83	24
$20BaF_2 - 15NaF$	Expt. [12]	2.50	2.065	80	25

are the suitable approximations, and the ligand orbital and spin–orbit coupling contributions may be ignored for simplicity. In addition, the large magnitudes of the A factors also indicate the insignificant covalency of the systems, since the absolute values of the hyperfine structure constants usually increase with the decline of covalency. Moreover, the covalency factor is usually determined from the relationship $N^2 \approx \varepsilon = 1 - h(L)k(M)$, where ε is square of the covalency factor, and $h(L)$ and $k(M)$ are the characteristics of the ligand and central metal ions, respectively [29]. From $k(M) \approx 0.3$ [32] for Cu^{2+}, $h(L) \approx 1.0$ and 0.9 [32] for ligands O^{2-} and F^-, yielding $N \approx 0.85$ and 0.88 for the studied oxide and fluoride glasses, respectively. These values are consistent with the adopted ones (i.e., $N \approx 0.85$ and 0.89 for NP and ZLBN glasses, respectively), and can be regarded as reasonable.

iii) The values of constants A_i obtained from EPR measurements in [12, 13] are practically the absolute values as [19, 23, 25]. Our calculations suggest that $A_{||}$ is negative and $A_\perp$ for oxide and fluoride glasses is negative and positive, respectively. The core polarization constant κ, accounting for the isotropic contributions of the hyperfine interactions [11, 33] (when the symmetry of the centre ion is lower than tetragonal, the anisotropic polarization constant κ' contributes to the anisotropic constants A_x and A_y), satisfies the relationship $\kappa \approx -2\chi/(3\langle r^{-3}\rangle)$ [11]. Here χ is the characteristic of the density of unpaired spins at the nucleus of the central ion, and $\langle r^{-3}\rangle$ is the expectation value of the inverse cube of the radial wave function of the $3d$ orbital in crystals in terms of the related free-ion value $\langle r^{-3}\rangle_0$ multiplying the covalency factor N. From the magnitudes $\langle r^{-3}\rangle_0 \approx 8.252$ a.u. [11] for Cu^{2+} and χ (≈ -3.4 a.u.) [24] for Cu^{2+} in oxide, one can obtain the value κ (≈ 0.32) in consideration of the covalency factor N (≈ 0.85), consistent with the adopted κ (≈ 0.32) in (4) for the studied NP glasses here and can be regarded as reasonable. However, for the studied ZLBN glasses, the relatively larger axial elongation ρ ($\approx 18\%$) of the $[CuF_6]^{4-}$ cluster may lead to smaller Cu^{2+} $3d$–$3s$ orbital admixtures, resulting in a reduction of the core polarization constant. Thus, the adopted κ (≈ 0.24) for the ZLBN glasses comparable with but smaller than the expectation for the studied NP glasses can be understand.

4. Conclusion

The spin Hamiltonian parameters (the anisotropic g factors $g_{||}$, $g_\perp$ and hyperfine structure constants $A_{||}, A_\perp$) and the local structures of the tetragonal Cu^{2+} centers in both studied systems are theoretically investigated from the perturbation formulas for a $3d^9$ ion in tetragonally elongated octahedra. The ligand octahedra around Cu^{2+} are found to suffer the relative tetragonal elongations of about 12% and 18% due to the Jahn–Teller effect for the centers in NP and ZLBN glasses, respectively.

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