

Theoretical studies of the electron paramagnetic resonance parameters and local structures for Cu^{2+} in $(100-2x)\text{TeO}_2-x\text{Ag}_2\text{O}-x\text{WO}_3$ glasses

H.-N. Dong and R. Zhang*

College of Physics and Engineering,
Chengdu Normal University, Chengdu 611130, P.R. China.

*e-mail: zhangrongcdnu@163.com

Received 26 July 2020; accepted 17 September 2020

The electron paramagnetic resonance (EPR) parameters and local structures for Cu^{2+} in $(100-2x)\text{TeO}_2-x\text{Ag}_2\text{O}-x\text{WO}_3$ (TAW) ($7.5 \leq x \leq 30$ mol%) glasses are quantitatively studied for distinct modifier concentrations x . The octahedral Cu^{2+} centers are subject to the medium tetragonal elongations of about 2% along the C_4 axis due to the Jahn-Teller effect. By utilizing only three adjusted coefficients a , b , and ω , the quantities (D_g , k , τ , and κ) can be suitably characterized by the Fourier type functions, which reasonably account for the experimental concentration dependences of the d-d transition bands and EPR parameters. The calculation results are discussed, and the mechanisms of the above concentration dependences of these quantities are illustrated by the modifications of the local structures and the electron cloud distribution around the Cu^{2+} dopant with the variations of the concentration x .

Keywords: Cu^{2+} ; $\text{TeO}_2-x\text{Ag}_2\text{O}-x\text{WO}_3$ glasses; defect structures; electron paramagnetic resonance.

PACS: 76.30.Fc; 75.10.Dg

DOI: <https://doi.org/10.31349/RevMexFis.67.1>

1. Introduction

Tellurite silver ($\text{TeO}_2\text{-Ag}_2\text{O}$) glasses exhibit useful dielectric [1], electrical [2], structural [3], thermal and Raman [4] and non-linear optical properties [5,6]. Similarly, tellurite tungsten ($\text{TeO}_2\text{-WO}_3$) glasses can provide unique electrical [7], linear optical [8], and luminescent properties for green laser [9] as well as efficient radiation shielding applications [10-12]. Thus, it is expected that a combination of the above glasses as tellurite silver tungsten ($\text{TeO}_2\text{-Ag}_2\text{O}\text{-WO}_3$ or TAW) systems may enhance the above properties and applications with two modifiers Ag_2O and WO_3 . In general, the above aspects of TAW glasses can be strongly relied on the local structures of the network of the glass systems, and they can be efficiently analyzed by means of the electron paramagnetic resonance (EPR) technique. As a popular dopant in oxide glasses, Cu^{2+} is widely used to probe the local structural properties due to the prominent EPR signals recordable at room temperature. Recently, d-d transition optical absorption and EPR experiments were performed for $(100-2x)\text{TeO}_2-x\text{Ag}_2\text{O}-x\text{WO}_3$ ($7.5 \leq x \leq 30$ mol %) glasses with 1 mol % CuO dopants [13]. The measured EPR parameters (g factors g_{\parallel} and g_{\perp} and hyperfine structure constants A_{\parallel}) were analyzed for the various WO_3 or Ag_2O concentrations by using the simple g formulas and some adjustable bonding parameters α^2 , β_1^2 , and β^2 (which are largely higher than unity) [13]. However, the defect structure around impurity Cu^{2+} in TAW glasses and its concentration dependence has not been theoretically obtained up to now. So, the concentration variations of the EPR parameters and local structures in the vicinity of the copper dopants in TAW glasses, as well as

their mechanisms, need to be further studied uniformly.

This article aims to perform theoretical calculations of the EPR parameters and local structures for Cu^{2+} in TAW glasses at distinct WO_3 or Ag_2O concentrations x based on the perturbation formulas of g factors and hyperfine structure constants for a $3d^9$ ion in tetragonally elongated octahedra. And the features of EPR parameters and local environments around the copper dopants are also analyzed because of the modifications of the local crystal-field strength and electron cloud distributions with the increase of the modifier concentration.

2. Theory and calculation

In the light of the observed g factors ($2 < g_{\perp} < g_{\parallel}$) [13] for Cu^{2+} in TAW glasses at all concentrations x , the impurities Cu^{2+} are expected to locate at suitable octahedral sites, with the octahedral $[\text{CuO}_6]^{10-}$ clusters showing the tetragonal elongation distortions due to the Jahn-Teller effect [14-18]. For a tetragonally elongated $3d^9$ cluster, the original lower two-fold orbitally degenerated irreducible representation $2E_g$ of cubic symmetry may be separated into two orbital singlets ${}^2B_{1g}$ and ${}^2A_{1g}$, the former being the new ground state. The original upper three-fold orbitally degenerated representation ${}^2T_{2g}$ can split into an orbital doublet 2E_g and an orbital singlet ${}^2B_{2g}$ [16-18].

To study the EPR parameters and local structures for TAW: Cu^{2+} glasses, the perturbation formulas of these parameters for tetragonally elongated octahedral $3d^9$ clusters can be adopted here. Thus, we have [19,20]:

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

Here, g_s (≈ 2.0023) is the pure spin g ; value k , ζ , and P are, respectively, the orbital reduction factor, the spin-orbit coupling coefficient, and the dipolar hyperfine coupling parameter of the $3d^9$ ion in glasses, in terms of the relationships, $\zeta = k\zeta_0$ and $P = kP_0$ with the corresponding free-ion values ζ_0 and P_0 represents the core polarization constant, characteristic of the Fermi contact interactions related to the isotropic central ion $3d$ - $3s$ ($4s$) orbital admixtures. H denotes the reduction factor related to the anisotropic central ion $3d$ - $3s$ ($4s$) orbital admixtures due to the tetragonal elongation distortion [21].

In the above expressions, the energy separations E_1 and E_2 stand for the separations between the excited ${}^2B_{2g}$ and 2E_g states and the ground ${}^2B_{1g}$ state, which can be written in terms of the cubic crystal-field parameter Dq and the tetragonal crystal-field parameters D_s and D_t [17,18]:

$$\begin{aligned}
E_1 &= 10Dq, \\
E_2 &= 10Dq - 3D_s + 5D_t. \quad (2)
\end{aligned}$$

From the local structural properties of the studied $[\text{CuO}_6]^{10-}$ clusters, the tetragonal crystal-field parameters can be determined from the superposition model [21-22]:

$$\begin{aligned}
D_s &= -\frac{4}{7}\bar{A}_2(R_0) \left[\left(\frac{R_0}{R_{\perp}} \right)^{t_2} - \left(\frac{R_0}{R_{\parallel}} \right)^{t_2} \right], \\
D_t &= -\frac{16}{21}\bar{A}_4(R_0) \left[\left(\frac{R_0}{R_{\perp}} \right)^{t_4} - \left(\frac{R_0}{R_{\parallel}} \right)^{t_4} \right]. \quad (3)
\end{aligned}$$

Here the superscripts t_2 (≈ 3) and t_4 (≈ 5) are the power-law exponents [21]. With the reference distance R_0 ,

and are the intrinsic parameters, satisfying the relationships $\bar{A}_4(R_0) \approx (3/4)Dq$ and the ratio $\bar{A}_2(R_0)/\bar{A}_4(R_0) \approx 9 - 12$ for octahedral $3d^n$ groups [23-25]. And we take $\bar{A}_2(R_0) \approx 9\bar{A}_4(R_0)$ here. For convenience, the defect structure near the impurity Cu^{2+} can be characterized as two longer axial copper-oxygen bonds and four shorter planar ones, corresponding to a relative tetragonal elongation ratio τ and the positive g anisotropy $\Delta g (= g_{\parallel} - g_{\perp})$. Thus, the copper-oxygen distances parallel and perpendicular to the C_4 axis can be written in terms of the reference distance R_0 and the relative tetragonal elongation ratio τ as:

$$R_{\parallel}R(1 + 2\tau), \quad R_{\perp}R(1 - \tau). \quad (4)$$

Now the measured d-d transition absorption bands $E - 1 (= E_{xy})$ in Ref. [13] at various concentrations x are fitted in this section. Since 1) E_1 (or $10Dq$) shows the overall increase from 12376 cm^{-1} for 7.5 mol % to 12484 cm^{-1} for 30 mol % and medium fluctuations with x and 2) the measured g_{\parallel} and A_{\parallel} also exhibit sine / cosine like variations of x (see Fig. 3 of Ref. [13]). For convenience, the Fourier type function can be adopted to describe the above concentration variation of the cubic field parameter:

$$Dq = Dq_0 \{1 + a \cos(\omega x) + b \sin(\omega x)\}. \quad (5)$$

Here the adjustable coefficients a , b , and ω can be determined by fitting the experimental d-d transition bands. The reference value $Dq_0 \approx 1240 \text{ cm}^{-1}$ may be obtained from the optical spectral measurements for Cu^{2+} in various oxide glasses [15]. By fitting the theoretical E_1 to the experimental data at various concentrations x [13], the optimal quantities in Eq. (5) are obtained as:

$$a \approx -0.0112, \quad b \approx 0.0082, \quad \omega \approx 1898. \quad (6)$$

The corresponding d-d transition bands E_1 are calculated as 12393 , 12546 , 12394 , and 12429 cm^{-1} , which are comparable with the experimental values [13].

In the light of the perturbation formulas of EPR parameters in Eq. (1) and the expressions of the energy denominators in Eq. (2), similar but less significant fluctuations of orbital reduction factor k than Dq can be expected because of the whole increasing g factors (especially g_{\parallel}) and moderate fluctuations with x . For convenience, a factor $(-1/3)$ is added to the terms except 1 in the square bracket of Eq. (5). Then, the concentration dependence of the orbital reduction factor can be similarly expressed as the Fourier type function:

$$k = k_0 \left\{ \frac{1 - [a \cos(\omega x) - b \sin(\omega x)]}{3} \right\} \quad (7)$$

Here the reference value $k_0 \approx 0.812$ is obtained from the optical spectral analysis for Cu^{2+} in some oxide glasses [15]. Utilizing Eq. (7), $k \approx 0.805$, 0.811 , 0.820 and 0.804 are calculated for $x = 7.5$, 15 , 22.5 and 30 mol %, respectively.

The above values are qualitatively consistent with the averages ($\sim 0.81 - 0.82$ [13]) of the fitted bonding parameters α^2 and β_1^2 in the previous studies and can be regarded as reasonable.

From Eq. (1), the anisotropy $\Delta g (= g_{\parallel} - g_{\perp})$ is relevant to the denominator E_2 of g_{\perp} , which correlates closely with the tetragonal crystal-field parameters D_s and D_t and hence with the relative tetragonal elongation ratio τ . From the overall decreasing (from 0.278 at 7.5 mol % to 0.255 at 30 mol %) tendency and the slight fluctuations of the measured Δg with x [13], the relative elongation ratio can be expressed by the following Fourier type function:

$$\tau \approx \tau_0 \left\{ \frac{1 - [a \cos(\omega x) - b \sin(\omega x)]}{5} \right\} \quad (8)$$

where τ_0 is the reference value of the relative elongation ratio. Inputting the above values and the spin-orbit coupling coefficient $\zeta_0 (\approx 829 \text{ cm}^{-1}$ [30]) for free Cu^{2+} into the g formulas and matching the theoretical Δg to the observed results, we have $\tau_0 \approx 1.45\%$. The corresponding tetragonal elongation ratios $\tau \approx 1.78\%$, 2.11% , 2.44% and 2.77% are obtained for $x = 7.5, 15, 22.5$ and 30 mol %, respectively. The theoretical g factors (Cal.^b) for various concentrations x are shown in Table I. For comparison, the calculated g factors (Cal.^a) based on the simple g formulas and the fitted bonding parameters α^2 , β_1^2 and β^2 as well as the orbital reduction factor $K^2 = 0.77$ in the previous analysis [13] are also collected in Table I.

From Eq. (1), hyperfine structure constants depend mainly upon the isotropic contributions from the core polarization constant κ_0 and the anisotropic ones related to reduction factor H or g -shifts. Because of absence of the perpendicular components of A factors in Ref. [13], the concentration variations of A_{\parallel} may be attributed to the related concentration variations of the core polarization constant κ and orbital reduction factor k as well as the g -shifts ($g_i - g_s$, with $i = \parallel$ and \perp). Thus, the concentration dependence of the core polarization constant can be similarly expressed as the Fourier type function:

$$\kappa = \kappa_0 \left\{ \frac{1 - [a \cos(\omega x) - b \sin(\omega x)]}{3} \right\}. \quad (9)$$

Here κ_0 is the reference value, which is usually taken as the expectation value 0.3 for 3d transition-metal ions in crystals [26]. The above expression yields $\kappa \approx 0.301, 0.289, 0.311$ and 0.298 for $x = 7.5, 15, 22.5$ and 30 mol %, respectively. The reduction factor can be fixed as 0.81 (*i.e.*, about 20% reduction from the ideal value of unity in the absence of tetragonal elongation distortion) for the sake of reduction in the number of adjustable parameters. Substituting these values and the dipolar hyperfine coupling parameter $P_0 (\approx 402 \times 10^{-4} \text{ cm}^{-1}$ [27]) for a free Cu^{2+} ion into Eq. (1), the concentration dependences of hyperfine structure constants (Cal. ^b) are obtained and compared with the experimental data in Table I.

3. Results and discussion

Table I displays that the calculated EPR parameters based on the above Fourier type functions of cubic field parameter, orbital reduction factor, relative tetragonal elongation ratio, and core polarization constant with concentration x by using only three adjustable coefficients (a , b , and ω) for Cu^{2+} in TAW glasses show reasonable agreement with the observed results. Thus, the previous EPR results for the studied systems are suitably interpreted uniformly. Several points may be discussed here.

(1) The concentration variations of the d-d transition optical spectra reflect the modifications of the local crystal-field strength of the Cu^{2+} centers with the concentration variations of the modifier induced NBOs and the difference in field strength between $\text{Ag}^+/\text{W}^{6+}$ and Te^{4+} cations. First, the increases of the concentration of WO_3 bring forward increasing NBOs with much higher polarizability, which mainly acts as the ligands of the Cu^{2+} dopants and leads to the fluctuations of the local crystal-fields. Second, when Te^{4+} is gradually replaced by W^{6+} with higher field strength, the original Te-O-Te linkages in the glass network are partially substituted by the new Te-O-W or W-O-W ones through some TeO_4 units transforming into TeO_3 ones, as indicated by the 460 - 490 cm^{-1} bands in the IR measurements [13]. Third, the strength of the Cu-O bonds in the $[\text{CuO}_6]^{10-}$ groups may be enhanced, because of the increasing density of TAG glasses

TABLE I. The concentration variations of g factors and hyperfine structure constants (in 10^{-4} cm^{-1}) for Cu^{2+} in TAW glasses.

x (mol%)	g_{\parallel}			g_{\perp}			A_{\parallel}		A_{\perp}	
	Cal. ^a	Cal. ^b	Expt. [13]	Cal. ^a	Cal. ^b	Expt.[13]	Cal. ^b	Expt. [13]	Cal. ^b	Expt.
7.5	2.352	2.356	2.352(1)	2.105	2.099	2.103(1)	-121.7	-124(0.5)	-0.7	-
15	2.357	2.357	2.358(1)	2.083	2.089	2.083(1)	-116.2	-113(0.5)	2.9	-
22.5	2.362	2.369	2.362(1)	2.088	2.088	2.088(1)	-119.5	-118(0.5)	-3.2	-
30	2.358	2.355	2.357(1)	2.077	2.086	2.079(1)	-116.3	-114(0.5)	-0.1	-

^aCalculated g factors based on the simple g formulas using the adjustable bonding parameters α^2, β_1^2 , and β^2 as well as the orbital reduction factor $K^2 = 0.77$ in the previous work [13].

^bCalculations based on the uniform perturbation formulas of the EPR parameters and the concentration dependences of the relevant quantities in this work.

with x [13]. This point can also be illustrated by the blue shifts of the IR bands in 650- 680 and 730-780 cm^{-1} regions, which reflects enhancing stretching vibrations of TeO_3 units [13]. Thus, the overall increasing d-d transition bands with some fluctuations for Cu^{2+} in TAW glasses can be understood.

(2) The features of g factors can be briefly analyzed here. The overall slightly increasing g_{\parallel} is attributed to the combined effects of the moderately increasing k at two middle concentrations and the quiveringly increasing Dq , and the former effect is slightly stronger. The highest g_{\parallel} at 22.5 mol% is mainly attributable to the biggest k and the moderate increase of Dq at this concentration. On the other hand, the slightly decreasing g_{\perp} can be ascribed to the increasing relative elongation ratio τ and hence the increasing magnitude of the negative tetragonal crystal-field parameter Ds , leading to the increasing denominator E_2 . Further, the whole increasing anisotropy Δg (related to the nearly unchanging g_{\parallel} and the slightly decreasing g_{\perp}) is consistent with the increasing relative elongation ratio τ . Finally, although the theoretical g_{\parallel} and g_{\perp} (Cal. ^a) based on the simple g formulas and the fitted bonding parameters α^2 , β_1^2 and β^2 (which were even largely higher than unity) and the orbital reduction factor $K^2 = 0.77$ in Ref. [13] show good agreement with the experimental data. Present calculations can be regarded as an improvement to the previous studies given the inclusion of the detailed local structures around the Cu^{2+} dopants, adoption of fewer adjustable parameters, and uniform treatments of both g factors and hyperfine structure constants. Interestingly, the present orbital reduction factors k ($\approx 0.805, 0.811, 0.820$ and 0.804) from Eq. (7) show largely consistent tendency with the averages ($\approx 0.809, 0.823, 0.824$ and 0.821 [13]) of the fitted α^2 and β_1^2 at 7.5, 15, 22.5 and 30 mol%, respectively, and the same maximum at 22.5 mol%. So, present calculations can be regarded as suitable in physics, which conformably reveal the overall weakening covalency with the weakest covalency of the copper-oxygen bonds at 22.5 mol %. Physically, the concentration dependence of covalency can be ascribed to the modification of the electronic cloud distribution around the copper dopants. For example, the electronic cloud density around oxygen ions at the middle concentrations (especially 22.5%) can be enhanced and lead to the significant decline of the $\text{Cu}^{2+}-\text{O}^{2-}$ orbital admixtures, yielding the weakest covalency and highest k .

(3) The studied Cu^{2+} centers in TAG glasses exhibit the tetragonal elongations of about 2 – 3% due to the Jahn-Teller effect. Interestingly, analogous moderate tetragonal elongation ratios ($\approx 3\%$ and 4%) were also found for Cu^{2+} in $x\text{Li}_2\text{O}\cdot(30-x)\text{K}_2\text{O}\cdot 70\text{B}_2\text{O}_3$ ($0 \leq x \leq 25$ mol %) [28] or $40\text{MgO}\cdot(10-x)\text{PbF}_2\cdot 50\text{SiO}_2-x\text{CuO}$ ($0.1 \leq x \leq 1.0$ mol %) [29] and $(70-x)\text{Bi}-2\text{O}_3-x\text{Li}_2\text{O}-30(\text{ZnO}-\text{B}_2\text{O}_3)$ ($0 \leq x \leq 20$ mol %) glasses [30]. The nearly linearly increasing relative elongation ratios τ (from 1.78 to 2.77 mol%) can re-

fect the moderate tetragonal elongations around the copper dopants in TAW glasses. The increasing tendency of the relative elongation can be ascribed to the enhancing vibrational interactions due to the strengthened copper-oxygen bonding (*i.e.*, the increasing Dq) with increasing x . Thus, the relative tetragonal elongation ratio and its concentration dependence obtained in this work by analyzing the g anisotropy for Cu^{2+} in TAW glasses can be regarded as reasonable.

(4) The magnitude of hyperfine structure constant A_{\parallel} exhibits an overall decreasing rule with slight fluctuations, yielding a slight decrease at 15 mol%. This can be illustrated as the competitive influences from the overall decreasing κ , k , and $g_{\perp} - g_s$ under the fixed reduction factor H . The obvious decline of the magnitude for A_{\parallel} at 15 mol% with respect to the other concentrations is mainly attributed to the significant decrease (by 4%) of the core polarization constant. This point is ascribed to the decrease of the electronic cloud density around copper arising from the enhancing electronic cloud of oxygen, leading to the weakest isotropic copper 3d-3s (4s) admixtures and hence the lowest κ at this concentration. Normally, the hyperfine structure constants in the EPR measurements are given as the absolute values [13]. From present calculations, both A_{\parallel} and A_{\perp} are negative, because of the dominant-negative contributions relevant to κ and the much smaller positive contributions relevant to g -shifts. Of course, the present calculated A_{\perp} with the much smaller magnitudes remain to be further verified with additional EPR experiments.

4. Summary

The local structures and EPR parameters for Cu^{2+} in TAW glasses at distinct modifier concentrations x are theoretically investigated using the perturbation formulas of these parameters. Subject to the Jahn-Teller effect, the impurity Cu^{2+} centers are found to experience moderate tetragonal elongations ($\tau \approx 1.78 - 2.77\%$). Based on merely three adjusted coefficients a , b , and ω , the relevant model parameters (Dq , k , τ , and κ) are expressed in terms of the Fourier type functions of the modifier concentration. The observed concentration variations of the d-d transition bands and the EPR parameters are suitably interpreted in a uniform way. And the mechanisms of the above concentration dependences of these quantities are illustrated by the modifications of the local structure and the electron cloud distribution around the Cu^{2+} dopant with the concentration x .

Acknowledgments

This work is financially supported by the Innovation Seedling Project of Sichuan Province (No.2018100) and a major project of CDNU (No.CS18ZDZ0511).

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