

UDC 541.67:541.49:546.562

STUDIES ON THE *g*-FACTORS OF THE COPPER(II)—OXYGEN COMPOUNDSG.-L. Li<sup>1,2</sup>, S.-Y. Wu<sup>1</sup>, M.-Q. Kuang<sup>1</sup>, X.-F. Hu<sup>1</sup>, Y.-Q. Xu<sup>1</sup><sup>1</sup>*Department of Applied Physics, School of Physical Electronics, University of Electronic Science and Technology of China, Chengdu, P. R. China*

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Received October, 17, 2015

The *g* factors for Cu<sup>2+</sup> in meta-zeunerite (Cu(UO<sub>2</sub>)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O), kroehnkite (Na<sub>2</sub>Cu(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O), copper benzoate (Cu(PhCO<sub>2</sub>)<sub>2</sub>·3H<sub>2</sub>O) and diaboletite (Pb<sub>2</sub>Cu(OH)<sub>4</sub>Cl<sub>2</sub>) of the tetragonal phase are uniformly treated by high order perturbation formulas for 3*d*<sup>9</sup> ions in tetragonally elongated octahedra. The calculation results are in good agreement with the observed values and systematically analyzed in view of the local structures around Cu<sup>2+</sup>. The *g* anisotropies Δ*g* (= *g*<sub>||</sub> – *g*<sub>⊥</sub>) are largely ascribed to the local tetragonal elongations of the Cu<sup>2+</sup> sites, characterized by the relative elongation ratios (*R*<sub>||</sub> – *R*<sub>⊥</sub>)/ $\bar{R} \approx 19\%$ , 21%, 27% and 30% for meta-zeunerite, kroehnkite, copper benzoate and diaboletite, respectively. The anomalous valley (minimum) of relative *g* anisotropy for copper benzoate is attributed to the modification of the Cu<sup>2+</sup> electronic states due to the phenyl ring. The ligand orbital contributions are found to be significant due to covalency, and should be taken into account. The present study would be helpful to the unified investigations of structures and properties of the copper oxygen compounds.

DOI: 10.15372/JSC20170408

**Keywords:** electron paramagnetic resonance (EPR), local structures, Cu(UO<sub>2</sub>)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O, Na<sub>2</sub>Cu(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, Cu(PhCO<sub>2</sub>)<sub>2</sub>·3H<sub>2</sub>O, Pb<sub>2</sub>Cu(OH)<sub>4</sub>Cl<sub>2</sub>.

## INTRODUCTION

The copper (II)—oxygen compounds have become a significant theme in the fields of electrochemistry [ 1—4 ], spectroscopy [ 5—8 ], geochemistry [ 9 ], magnetism [ 10, 11 ], and crystal structural research [ 12 ]. Normally, their behavior and properties are sensitively dependent upon electronic states and local structures of paramagnetic Cu<sup>2+</sup> and can be efficiently probed by means of electron paramagnetic resonance (EPR) technique. For example, EPR experiments were employed for tetragonal Cu(UO<sub>2</sub>)<sub>2</sub>(AsO<sub>4</sub>)<sub>2</sub>·3H<sub>2</sub>O, Na<sub>2</sub>Cu(SO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, Cu(PhCO<sub>2</sub>)<sub>2</sub>·3H<sub>2</sub>O, and Pb<sub>2</sub>Cu(OH)<sub>4</sub>Cl<sub>2</sub>, and the anisotropic Cu<sup>2+</sup> *g* factors *g*<sub>||</sub> and *g*<sub>⊥</sub> were also measured [ 13 ]. Unfortunately, these experimental results [ 13 ] have not been satisfactorily explained until now, except for the *g* factors which were tentatively analyzed from the simple second-order formulas [ 13 ]. Nevertheless, the ligand contributions were neglected, and the local structures of the Cu<sup>2+</sup> sites were not involved in the analysis [ 13 ]. In order to overcome these shortcomings and investigate the *g* factors of these copper oxygen compounds to a better extent, high order perturbation formulas for the *g* factors in tetragonally elongated octahedral 3*d*<sup>9</sup> Cu<sup>2+</sup> are adopted in the present treatment, and the local structures (low-symmetry distortions) of the Cu<sup>2+</sup> sites are quantitatively included using the superposition model.

## THEORETICAL

When a  $3d^9$  ( $\text{Cu}^{2+}$ ) ion is in a tetragonally elongated octahedron, the  $g$  round  ${}^2E_g$  level splits into two orbital singlets  ${}^2A_{1g}(|z^2\rangle)$  and  ${}^2B_{1g}(|x^2 - y^2\rangle)$ , with the latter lying lowest. The excited  ${}^2T_{2g}$  state can be separated, too, into an orbital singlet  ${}^2B_{2g}(|xy\rangle)$  and a doublet  ${}^2E_g(|xy\rangle, |yz\rangle)$  [14]. As mentioned before, simple second-order  $g$  formulas were applied in the previous theoretical analysis without involving the local structures of the paramagnetic  $\text{Cu}^{2+}$  sites. In fact, these copper oxygen compounds may exhibit significant covalency due to relatively short Cu—O bond lengths, and then the ligand orbital contributions should be considered in the EPR analysis. Therefore, high order perturbation  $g$  formulas for a tetragonally elongated octahedral  $3d^9$  ion containing ligand orbital and spin-orbit coupling contributions should be adopted. Thus, we have [15]

$$\begin{aligned} g_{\parallel} &= g_s + 8k'\zeta'/E_1 + k\zeta'^2/E_2^2 + 4k'\zeta\zeta'/(E_1E_2) + g_s\zeta'^2[1/E_1^2 - 1/(2E_2^2)] - k\zeta\zeta'^2(4/E_1 - 1/E_2)/E_2^2 - \\ &\quad - 2k'\zeta\zeta'^2[2/(E_1E_2) - 1/E_2^2]/E_1 - g_s\zeta\zeta'^2[1/(E_1E_2^2) - 1/(2E_2^3)], \\ g_{\perp} &= g_s + 2k'\zeta'/E_2 - 4k\zeta'^2/(E_1E_2) + k'\zeta\zeta'(2/E_1 - 1/E_2)/E_2 + 2g_s\zeta'^2/E_1^2 + \zeta\zeta'(k\zeta' - k'\zeta)/(E_1E_2^2) - \\ &\quad - \zeta\zeta'(1/E_2 - 2/E_1)(2k\zeta'/E_1 + k'\zeta/E_2)/(2E_2) - g_s\zeta\zeta'^2[1/E_1^2 - 1/(E_1E_2) + 1/E_2^2]/(2E_2). \end{aligned} \quad (1)$$

Here  $g_s$  ( $\approx 2.0023$ ) is the pure spin  $g$  value.  $E_1$  and  $E_2$  are the energy separations between the excited  ${}^2B_{2g}$  and  ${}^2E_g$  and the ground  ${}^2B_{1g}$  states, which can be expressed in terms of the cubic field parameter  $Dq$  and the tetragonal field parameters  $Ds$  and  $Dt$ :  $E_1 \approx 10Dq$  and  $E_2 \approx 10Dq + 3D_s - 5D_t$ . The spin-orbit coupling coefficients  $\zeta$  and  $\zeta'$  and the orbital reduction factors  $k$  and  $k'$  can be determined from the cluster approach [15]

$$\begin{aligned} \zeta &= N_t(\zeta_d^0 + \lambda_t^2\zeta_p^0 / 2), \quad \zeta' = (N_tN_e)^{1/2}(\zeta_d^0 - \lambda_t\lambda_e\zeta_p^0 / 2), \\ k &= N_t(1 + \lambda_t^2 / 2), \quad k' = (N_tN_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A / 2)], \end{aligned} \quad (2)$$

Here  $\zeta_d^0$  and  $\zeta_p^0$  are the spin-orbit coupling coefficients of free  $3d^9$  ion and ligand, respectively.  $A$  denotes the integral  $R\langle n_s | \partial/\partial y | np_y \rangle$  with the reference metal-ligand distance  $R$ .  $N_\gamma$  ( $\gamma = t$  and  $e$  stands for the irreducible representations  $T_{2g}$  and  $E_g$  of group  $O_h$ ) and  $\lambda_\gamma$  (or  $\lambda_s$ ) are, respectively, the normalization factors and the orbital admixture coefficients. They are usually obtained from the normalization conditions [15]

$$\begin{aligned} N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) &= 1, \\ N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) &= 1. \end{aligned} \quad (3)$$

and the approximate relationships [15]

$$\begin{aligned} N^2 &= N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}], \\ N^2 &= N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}]. \end{aligned} \quad (4)$$

Here  $N$  is the average covalency factor, characteristic of the covalency of the systems.  $S_{dpy}$  (and  $S_{ds}$ ) are the group overlap integrals. In general, the orbital admixture coefficients increase with increasing group overlap integrals, and one can reasonably apply the proportionality relationship  $\lambda_e/S_{dpe} \approx \lambda_s/S_{ds}$  for the same irreducible representation  $E_g$ .

This treatment has been applied to the studies of the tetragonal  $\text{Cu}^{2+}$  sites in  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \times 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$ . The tetragonal field parameters can be expressed from the superposition model [16] and local geometry as follows:

$$\begin{aligned} D_s &= 4\bar{A}_2(R)[(R/R_{\parallel})^{t_2} - (R/R_{\perp})^{t_2}]/7, \\ D_t &\approx 16\bar{A}_4(R)[(R/R_{\parallel})^{t_4} - (R/R_{\perp})^{t_4}]/21. \end{aligned} \quad (5)$$

Here  $t_2$  ( $\approx 3$ ) and  $t_4$  ( $\approx 5$ ) are the power-law exponents.  $\bar{A}_2(R)$  and  $\bar{A}_4(R)$  are the intrinsic parameters, with the reference distance taken as the average Cu—O bond length:  $R = \bar{R} = (R_{\parallel} + 2R_{\perp})/3$ . For coor-

Table 1

The local parallel and perpendicular copper(II) ligand bond lengths (in Å), covalency factor  $N$ , cubic field parameter  $Dq$  (in  $\text{cm}^{-1}$ ), the group overlap integrals, the normalization factors, the orbital admixture coefficients, the spin-orbit coupling coefficients (in  $\text{cm}^{-1}$ ) as well as the orbital reduction factors for  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$

System	$R_{\parallel}$	$R_{\perp}$	$\bar{R}$	$N$	$Dq$	$S_{dpt}$	$S_{dpe}$	$S_{ds}$	$A$
$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$	2.565	2.14	2.282	0.88	1300	0.0032	0.0126	0.0100	1.4855
$\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	2.41	1.97	2.117	0.86	1200	0.0061	0.0215	0.0171	1.3781
$\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$	2.51	1.94	2.130	0.84	1260	0.0058	0.0206	0.0164	1.3867
$\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$	2.75	2.07	2.297	0.91	1350	0.0030	0.0120	0.0095	1.4953
System	$N_t$	$N_e$	$\lambda_t$	$\lambda_e$	$\lambda_s$	$\zeta$	$\zeta'$	$k$	$k'$
$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$	0.881	0.885	0.371	0.295	0.234	740	725	0.942	0.778
$\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	0.862	0.870	0.406	0.325	0.258	725	709	0.933	0.746
$\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$	0.842	0.850	0.439	0.350	0.279	710	692	0.923	0.709
$\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$	0.911	0.915	0.316	0.252	0.199	762	751	0.956	0.833

dinated  $3d^n$  ions, the relationships  $\bar{A}_4(R) \approx (3/4)Dq$  and  $\bar{A}_2(R) \approx 10.8\bar{A}_4(R)$  [17–20] are valid for many systems, and are adopted here. Thus, the  $g$  factors, especially the anisotropy  $\Delta g$  ( $= g_{\parallel} - g_{\perp}$ ), are correlated with the tetragonal field parameters and hence with the local structures (e.g., the relative tetragonal elongation  $R_{\parallel} - R_{\perp}$ ) of the studied systems.

From the optical spectral analysis for  $\text{Cu}^{2+}$  in the oxides [13, 21], the cubic field parameters  $Dq$  and the covalency factors  $N$  are extracted for the studied systems. From the distance  $R$  and the Slater-type self-consistent field wave functions [24, 25], the group overlap integrals  $S_{dpt}$ ,  $S_{dpe}$ ,  $S_{ds}$  and the integral  $A$  are calculated. Based on the free-ion values  $\zeta_d^0 \approx 829 \text{ cm}^{-1}$  for  $\text{Cu}^{2+}$  [22] and  $\zeta_p^0 \approx 151 \text{ cm}^{-1}$  [23] for oxygen in  $\text{H}_2\text{O}$  (or  $\text{OH}^-$ ), the quantities  $\zeta$  (and  $\zeta'$ ) and  $k$  (and  $k'$ ) are required. These values are listed in Table 1.

Substituting these values into Eq. (1), the  $g$  factors (Cal.  $^c$ ) are calculated for the tetragonal  $\text{Cu}^{2+}$  sites in the copper oxygen compounds and listed in Table 2. In order to clarify the importance of covalency and the ligand contributions, the results (Cal.  $^a$ ) based on the simple second-order  $g$  formulas [13] and those (Cal.  $^b$ ) based on the conventional crystal-field model (i.e., taking  $\zeta' = \zeta = N\zeta_d^0$  and  $k' = k = N$  in Eq. (1)) are also collected in Table 2.

## DISCUSSION

Table 2 indicates that the  $g$  factors (Cal.  $^c$ ) for the tetragonal  $\text{Cu}^{2+}$  sites in the copper oxygen compounds show better agreement with the experimental data than those (Cal.  $^a$ ) based on simple second-order formulas and those (Cal.  $^b$ ) based on the conventional crystal field model. Therefore, the EPR experimental data for these systems are uniformly explained in this work.

1) The results (Cal.  $^a$ ) based on simple second-order formulas and those (Cal.  $^b$ ) based on the high order perturbation formulas in the absence of the ligand contributions are not as good as those (Cal.  $^c$ ) based on the high order perturbation formulas containing the ligand contributions. In particular, the averages of  $g$  factors and the  $g$  anisotropies  $\Delta g$  (in Cal.  $^a$  and Cal.  $^b$ ) are larger than the observed values. This means that high order perturbation formulas with ligand contributions, employed in the present study, are superior to the simple second-order ones (Cal.  $^a$ ) and those (Cal.  $^b$ ) based on the conventional crystal field model. This point can be further illustrated as the moderate orbital admixture coefficients ( $\approx 0.20 - 0.44$ ) and the significant anisotropies  $k/k' - 1$  ( $\approx 15 - 30\%$ ) for the orbital reduction factors based on the present cluster approach calculations, suggesting obvious anisotropic copper(II)-ligand orbital admixtures due to covalency. The significant covalency in the copper oxygen com-

T a b l e 2

The  $g$  factors and anisotropies  $\Delta g$  ( $= g_{\parallel} - g_{\perp}$ ) for  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$

System		$g_{\parallel}$	$g_{\perp}$	$\Delta g$
$\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$	Cal. <sup>a</sup>	2.3951	2.0856	0.3095
	Cal. <sup>b</sup>	2.3996	2.0690	0.3306
	Cal. <sup>c</sup>	2.3508	2.0720	0.2788
	Expt. [ 13 ]	2.3554	2.0676	0.2878
$\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	Cal. <sup>a</sup>	2.4762	2.0966	0.3797
	Cal. <sup>b</sup>	2.4143	2.0762	0.3381
	Cal. <sup>c</sup>	2.3574	2.0804	0.2770
	Expt. [ 13 ]	2.35	2.083	0.267
$\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$	Cal. <sup>a</sup>	2.4034	2.0756	0.3269
	Cal. <sup>b</sup>	2.3779	2.0764	0.3015
	Cal. <sup>c</sup>	2.3168	2.0815	0.2353
	Expt. [ 13 ]	2.313	2.084	0.229
$\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$	Cal. <sup>a</sup>	2.5038	2.0940	0.4098
	Cal. <sup>b</sup>	2.4104	2.0671	0.3433
	Cal. <sup>c</sup>	2.3745	2.0692	0.3053
	Expt. [ 13 ]	2.383	2.064	0.319

<sup>a</sup> Calculations based on the simple second-order formulas in the previous work [ 13 ].

<sup>b</sup> Calculations based on the high order perturbation formulas and omission of the ligand contributions.

<sup>c</sup> Calculations based on the high order perturbation formulas and inclusion of the ligand contributions from the cluster approach.

pounds may be attributed to the  $\text{Cu}^{2+} 3d_{x^2-y^2} - \text{O}^{2-} 2p/2s$  orbital admixtures under tetragonal elongation distortion. So, the ligand contributions should be taken into account in the EPR analysis of the copper oxygen compounds. This idea about covalency is different from the conventional cases for  $\text{Cu}^{2+}$  in normal oxides, where covalency and ligand contributions are actually very small and can be regarded as negligible [ 26—28 ].

2) The local structures of the  $\text{Cu}^{2+}$  sites in these systems show evident tetragonal elongation distortions, characterized by the relative elongation ratios  $(R_{\parallel} - R_{\perp})/\bar{R} \approx 19\%$ ,  $21\%$ ,  $27\%$  and  $30\%$  for  $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2\text{Cu}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Pb}_2\text{Cu}(\text{OH})_4\text{Cl}_2$ . This approximately accounts for the relative anisotropies  $(g_{\parallel} - g_{\perp})/\bar{g} \approx 13\%$ ,  $12\%$ ,  $11\%$  and  $15\%$ , respectively. The valley (minimum) of the relative anisotropy for copper benzoate may reveal anomalous values of  $Dq$  and  $N$  for this system. From Eq. (1), the anisotropy largely depends upon the term  $2k'\zeta'(4/E_1 - 1/E_2)$  and hence upon the quantities  $k'$ ,  $\zeta'$ ,  $Dq$  and  $N$ , which consequently induce the valley of  $\Delta g$  for copper benzoate. The above anomaly for  $\text{Cu}(\text{PhCO}_2)_2 \cdot 3\text{H}_2\text{O}$  may be attributed to the modification of electronic states for  $\text{Cu}^{2+}$  due to the phenyl ring, as compared with the other three systems. For example, the previous study [ 3, 11 ] indicated that strong antiferromagnetic exchange interactions exist in the loop arrays.

3) There are some errors in the present calculations. There are three reasons for this. Firstly, the approximations of the theoretical model and formulas would result in some errors. Secondly, the errors come from the approximation of the relationship  $\bar{A}_2(R) \approx 10.8\bar{A}_4(R)$  [ 17—20 ] for the superposition model intrinsic parameters, which may affect the tetragonal field parameters and the final results.

If one takes the widely accepted range  $\bar{A}_2(R)/\bar{A}_4(R) \approx 9 \sim 12$ , the errors for the calculated  $g$  factors are estimated to be not more than 3 %. Thirdly, the calculations are based on the local structures of the  $\text{Cu}^{2+}$  sites in the copper oxygen compounds, while the influence of the Jahn—Teller effect is not taken into account. In fact, the Jahn—Teller effect may induce some modifications of the local bond lengths around the Jahn—Teller ion  $\text{Cu}^{2+}$  and thus lead to some errors in the resultant  $g$  factors.

### CONCLUSIONS

The  $g$  factors for the tetragonal  $\text{Cu}^{2+}$  sites in the copper oxygen compounds are theoretically investigated by utilizing high order perturbation formulas based on the cluster approach, and the anisotropies  $\Delta g$  ( $= g_{\parallel} - g_{\perp}$ ) are largely illustrated by the relative elongation ratios  $(R_{\parallel} - R_{\perp})/\bar{R}$  for these systems. The anomalous valley (minimum) of relative  $g$  anisotropy for copper benzoate is attributed to the modification of electronic states for  $\text{Cu}^{2+}$  due to the phenyl ring. The ligand contributions are found to be significant due to notable covalency and should be taken into account. This idea about covalency is different from the conventional cases for  $\text{Cu}^{2+}$  in normal oxides where covalency and ligand contributions can be regarded as very small and negligible. The present studies would be helpful to the unified investigations of structures and properties for the copper oxygen compounds.

This work was financially supported by "the Sichuan Province Academic and Technical Leaders Support Fund" (Y02028023601015), "the Fundamental Research Funds for the Central Universities" (ZYGX2014J136) and "the United Science and Technology Foundation of Guizhou Provincial Science and Technology Department and Xingyi Normal University for Nationalities" (LH [2014] 7404).

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