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Theoretical studies of the EPR g factors and optical spectra of copper bearing turquoise mineral

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ABSTRACT

In this paper, the EPR g factors g_i (i=x, y, z) of the Cu^{2+} ions in turquoise are theoretically studied by using the third-order perturbation formulas of the g factors for a $3d^9$ ion in rhombically elongated octahedron. In these formulas, the contributions from the ligand orbital and spin-orbit coupling interaction and the admixture of d-orbitals in the ground state wave function are taken into account. The results show that although the admixture of the $|d_{z2}>$ state to the ground state wave function is small, it should not be neglected in theoretical explanations of the g factors of the studied system. The calculated results are in good agreement with the observed values. The results are discussed.

Key words: Electron paramagnetic resonance (EPR), turquoise, Cu^{2+}, optical spectra

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INTRODUCTION

It is well known that electron paramagnetic resonance (EPR) is a useful technique to study the properties of transition metal ions in crystals for the reason that it can give valuable information about the environmental symmetry produced by the ligands around the metal ion and get information about the electric fields of these ions. Among the TM ions, copper (Cu^{2+}) is a model system with a single 3d hole, corresponding to only one ground state and one excite state under ideal octahedral crystal-fields. Thus, Cu^{2+} is usually applied as probes to provide useful information of the local structures for the studied systems by means of EPR technique [1-7]. For example, the EPR experiment was performed for turquoise $[CuAl_6(PO_4)_4(OH)_8\cdot 4H_2O]$ and the EPR parameters g factors and the optical spectra were also measured for the Cu^{2+} ion [7].Until now, however, no satisfactory interpretation to the above experimental results has been made. The g factors were theoretically studied by the simple second-order perturbation formulas based on three adjusted parameters (i.e., reduction parameters k_1, k_2, k_3) in Ref.[7], and the contributions to g factors from the spin-orbit coupling coefficient of the ligand were neglected. Moreover, the contribution from admixture of d-orbitals was ignored which has been proved to be important for Cu^{2+} ion in rhombic octahedron [8-10]. In order to investigate the g factors to a better extent, in this work the g factors of Cu^{2+} ion in turquoise are theoretically studied by the high-order perturbation formulas of g factors for a $3d^9$ ion under rhombically elongated octahedron. In the calculations, the contributions from the ligand orbital and spin-orbit interactions are included, and the admixture of d-orbitals in the ground state wave function for the Cu^{2+} ions in turquoise are also taken into account. The results are discussed.

MATERIALS AND METHODS

Turquoise cell contains one formula of $CuAl_6(PO_4)_4(OH)_8\cdot 4H_2O$ so that each Cu^{2+} ion is in an inversion centre with four OH 1.92 Å(2) and 2.11 Å(2) and two H_2O 2.42 Å ligands in an elongated rhombic octahedron [7]. For a Cu^{2+}

ion ($3d^9$) in rhombically elongated octahedron, the ground state ^2E_g in cubic field would be separated into two singlets $^2A_{1g}(\theta)$ and $^2A_{1g}'(\varepsilon)$, with the latter lying lowest, while the higher cubic orbital triplet $^2T_{2g}$ would be split into three singlets $^2B_{1g}(\zeta)$, $^2B_{2g}(\eta)$ and $^2B_{3g}(\xi)$[10]. Since the states $^2A_{1g}(\theta)$ and $^2A_{1g}'(\varepsilon)$ belong to the same representation of rhombic symmetry group, the ground state will be neither $^2A_{1g}(\theta)$ or $^2A_{1g}'(\varepsilon)$ but an admixture of both and can be expressed as follow:

$$|\varphi\rangle = a|d_{x2-y2}\rangle + b|d_{z2}\rangle \tag{1}$$

Here a and b are the mixing coefficients which satisfy the normalization condition

$$a^2+b^2=1 \tag{2}$$

Generally speaking, the $|d_{x2-y2}\rangle$ state is dominant and so a>>b [9]. For many Cu^{2+} in crystals, the value of a is about 0.99 [8-10] and can be reasonably adopted here.

In the two-SO-parameter model, one-electron basis function for an octahedral $3d^n$ cluster can be written as: [11]

$$\psi_t = N_t^{1/2}(\varphi_t - \lambda_t \chi_{pt}) \qquad \psi_e = N_e^{1/2}(\varphi_e - \lambda_e \chi_{pe} - \lambda_s \chi_s) \tag{3}$$

Here the subscript $\gamma = e$ or t represents the irreducible representation of O_h group. φ_γ is the d-orbital of the d^n ion. $\chi_{p\gamma}$ and χ_s are the *p*- orbital and *s*- orbital of ligand. N_γ and λ_γ (or λ_s) are, respectively, the normalization factors and the orbital mixing coefficients, they can be determined from the normalization conditions [11]:

$$N_t(1 - 2\lambda_t S_{dpt} + \lambda_t^2) = 1 \qquad N_e(1 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds} + \lambda_e^2 + \lambda_s^2) = 1 \tag{4}$$

and the approximate relationships[11]:

$$N^2 = N_t^2[1 + \lambda_t^2 S_{dpt}^2 - 2\lambda_t S_{dpt}]$$
$$N^2 = N_e^2[1 + \lambda_e^2 S_{dpe}^2 + \lambda_s^2 S_{ds}^2 - 2\lambda_e S_{dpe} - 2\lambda_s S_{ds}] \tag{5}$$

Here N is the average covalency factor, characteristic of the covalency effect of the central ion in crystals. $S_{dp\gamma}$ (and S_{ds}) are the group overlap integrals. In general, the orbital mixing coefficients increase with increasing the group overlap integrals, and one can approximately adopt proportionality relationship $\lambda_e / S_{dpe} \approx \lambda_s / S_s$ between the orbital mixing coefficients and the related group overlap integrals within the same irreducible representation e_g. Thus, from Eq.(3), the spin-orbit coupling coefficients and the orbital reduction factors can be derived:

$$\zeta = N_t(\zeta_d + \lambda_t^2 \zeta_p/2) \qquad \zeta' = (N_t N_e)^{1/2}(\zeta_d - \lambda_t \lambda_e \zeta_p/2)$$
$$k = N_t(1 + \lambda_t^2/2) \qquad k' = (N_t N_e)^{1/2}[1 - \lambda_t(\lambda_e + \lambda_s A)/2] \tag{6}$$

here ζ_d and ζ_p are the spin-orbit coupling coefficients of the free $3\,d^n$ and ligand ions. For present system, we have $\zeta_d(Cu^{2+}) \approx 829\ cm^{-1}$[8], $\zeta_p(O^{2-}) \approx 151\ cm^{-1}$[12]. A denotes the integral $R\left\langle ns \middle| \frac{\partial}{\partial y} \middle| np_y \right\rangle$, where R ($\approx$ (1.92+2.11+2.42)/3≈2.15Å [7]) is the impurity -ligand distance of present system. From the distance R, the group overlap integrals $S_{dpt} \approx 0.0035$, $S_{dpe} \approx 0.0138$, $S_{ds} \approx 0.0107$ and $A \approx 1.4536$ are calculated by using the SCF functions [13, 14].

According to the perturbation theory and Eq(1) and Eq(3), the third-order perturbation formulas of g factors based on the two-SO-parameter model for d^9 ions in rhombic symmetry can be expressed as[8]:

$$g_x = g_s + \frac{2(a+\sqrt{3}b)^2 k'\zeta'}{E_4} - \frac{2a(a+\sqrt{3}b)^2 k'\zeta k'}{E_2 E_4} + \frac{(a^2-3b^2)k'\zeta' k'}{E_3 E_4} - \frac{2a^2 g_s \zeta'^2}{E_2^2}$$
$$- \frac{(a-\sqrt{3}b)^2 g_s \zeta'^2}{2E_3^2} + \frac{2a(a-\sqrt{3}b)k\zeta'^2}{E_2 E_3}$$
$$g_y = g_s + \frac{2(a-\sqrt{3}b)^2 k'\zeta'}{E_3} - \frac{2a(a-\sqrt{3}b)^2 k'\zeta k'}{E_2 E_3} + \frac{(a^2-3b^2)k'\zeta' k'}{E_3 E_4} - \frac{2a^2 g_s \zeta'^2}{E_2^2}$$
$$- \frac{(a+\sqrt{3}b)^2 g_s \zeta'^2}{2E_4^2} + \frac{2a(a+\sqrt{3}b)k\zeta'^2}{E_2 E_4}$$

$$g_z = g_s + \frac{8a^2k'\zeta'}{E_2} - \frac{2a(a-\sqrt{3}b)k'\zeta k'}{E_2E_3} - \frac{2a(a+\sqrt{3}b)k'\zeta k'}{E_2E_4} - \frac{(a-\sqrt{3}b)^2 g_s\zeta'^2}{2E_3^2}$$
$$- \frac{(a+\sqrt{3}b)^2 g_s\zeta'^2}{2E_4^2} - \frac{(a^2-3b^2)k'\zeta\zeta'}{E_3E_4} \qquad (7)$$

In above formulas, g_s (≈2.0023) is the spin-only value. k', k, ζ, ζ' are the orbital reduction factors and the spin-orbit coupling coefficients as mentioned before, respectively. The denominators E_i (i=2-4) denote the energy separations between the excited $^2B_{1g}(\zeta)$、$^2B_{2g}(\eta)$ 、$^2B_{3g}(\xi)$ and the ground $^2A_{1g}'(\varepsilon)$ state, and can be expressed in terms of the cubic field parameter D_q and the rhombic field parameters D_s, D_t, D_ξ and D_η.

$$E_1=4D_s+5D_t$$
$$E_2=10D_q$$
$$E_3=10D_q+3D_s-5D_t-3D_\xi+4D_\eta$$
$$E_4=10D_q+3D_s-5D_t+3D_\xi-4D_\eta \qquad (8)$$

Fitting the energy separations to the optical spectra, these crystal field parameters (D_s≈850 cm^{-1}, D_t ≈ 952 cm^{-1}, *D . .*≈590 cm^{-1}, *D . .*≈149 cm^{-1}) are obtained and the optical spectrum band positions are collected in Table 1.

Substituting the related values into Eq.(7) and fitting the calculated g factors to the experimental data, the covalency factor N (≈ 0.91) can be obtained. The values $N_t \approx 0.9110$, $N_e \approx 0.9152$, $\lambda_t \approx 0.3161$, $\lambda_e \approx 0.2548$ and $\lambda_s \approx 0.1976$ are calculated from equations (4) and (5). The parameters $\zeta \approx 762.1$ cm^{-1}, $\zeta' \approx 751.4$ cm^{-1}, $k \approx 0.9565$ and $k' \approx 0.8349$ can be determined from equation (6) and the corresponding free-ion values. The theoretical g factors are shown in Table 1. For comparisons, the theoretical results of g factors based on the conventional formulas in the absence of the ligand orbital and spin-orbit coupling contributions (i.e., taking λ_γ=0, ζ_p =0, $\zeta'=\zeta=N\zeta_d$ and $k= k'=N$) and the formulas in the absence of the contribution from the admixture of d-orbitals (i.e, a=1 and b=0) are also obtained and collected in Table 1.

RESULTS AND DISCUSSION

From Table 1, one can find that the computed results based on the high-order perturbation formulas (Eq.7) by considering the ligand orbital and spin-orbit coupling interactions and the admixture of d-orbitals show better agreement with the experimental data than those in the absence of the above contributions. This means that the contributions to the g factors from the ligand orbital and spin-orbit coupling interactions and the admixture of d-orbitals are important and cannot be ignored in the analyses of the g factors for Cu^{2+} in turquoise.

Table 1. The optical spectrum band positions (in cm^{-1}) and g factors for Cu^{2+} ions in turquoise

	calculation			Expt[7]
	Cal^a	Cal^b	Cal^c	
$^2A_1'\rightarrow{}^2A_1$	--	--	8160	8160
$^2A_1'\rightarrow{}^2B_1$	--	--	14970	14970
$^2A_1'\rightarrow{}^2B_2$	--	--	16006	--
$^2A_1'\rightarrow{}^2B_3$	--	--	18354	18354
g_x	2.108	2.072	2.101	2.119
g_y	2.045	2.078	2.037	2.043
g_z	2.349	2.355	2.319	2.313

[a] *calculations by using equation (7) and including the admixture of d-orbitals but neglecting the ligand orbital contributions*

[b] *Calculations by using equation (7) and including the ligand orbital contributions but neglecting the admixture of d-orbitals.*

[c] *Calculations by using equation (7) and including the ligand contributions and the admixture of d-orbitals.*

(1)The covalency factor N (≈0.91) adopted in this work is close to Cu^{2+} centers in other crystals with the similar ligand (i.e, N≈0.88 for $[Cu(H_2O)_6]^{2+}$) [15-17] and can be regarded as valid. In addition, the validity of the covalency factor N can be further demonstrated by the relationship:

$N^2=1-h(L)k(M)$[18], here the parameter h(L) is the characteristic of the ligand O^{2-} and k(M) is the characteristic of the central metal ion Cu^{2+}. From the data $h(O^{2-})\approx1$ [18] and $k(Cu^{2+})\approx0.26$[18], the value $N \approx 0.86$ is obtained and is close to that (≈0.91) adopted in this work.

(2)From Table 1, one can find that the contributions from the admixture of d-orbitals are more important than those from the ligand orbital and spin-orbit interactions. According to our calculations, inclusion of the contribution from the admixture of d-orbitals leads to the variations of about 0.013, 0.0201 and 0.0202 for the calculated g_x, g_y and g_z, respectively. While those from the ligand orbital and spin-orbit coupling interaction is merely about 0.0036, 0.0038 and 0.0198 for the theoretical g_x, g_y and g_z, respectively.

CONCLUSION

In this work, the optical spectra and EPR parameters g factors for the rhombic Cu^{2+} ion in turquoise are theoretically investigated from the high-order perturbation formulas of g factors. It is found that the contribution to g factors from the admixture of d-orbitals is more important than that from the ligand orbital and spin-orbit coupling interaction.

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