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Theoretical studies of the spin Hamiltonian parameters for the two tetragonal Cu^{2+} centers in the calcined catalysts CuO–ZnO

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The spin Hamiltonian parameters for the two Cu^{2+} centers $A1$ and $A2$ in the calcined catalysts CuO–ZnO are theoretically investigated using the high order perturbation formulas of these parameters for a $3d^9$ ion in tetragonally elongated octahedra. In the above formulas, the tetragonal field parameters Ds and Dt are determined from the superposition model, by considering the relative axial elongation of the oxygen octahedron around the Cu^{2+} due to the Jahn-Teller effect. Based on the calculations, the relative elongation ratios of about 5% and 3% are obtained for the tetragonal Cu^{2+} centers $A1$ and $A2$, respectively. The theoretical spin Hamiltonian parameters are in good agreement with the observed values for both systems. The larger axial elongation in center $A1$ is ascribed to the more significant low symmetrical (tetragonal) distortion of the Jahn-Teller effect. The local structures characterized by the above axial elongations are discussed.

Key words: *EPR, Cu^{2+}, CuO–ZnO, defect structures*

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1. Introduction

The calcined catalysts CuO–ZnO are the systems widely applied in the fields of CO oxidation [1–6]. The catalytic properties can be closely related to the electronic states and local structures of Cu in ZnO, which may be conveniently investigated with the aid of electron paramagnetic resonance (EPR) technique. Cu^{2+} ($3d^9$) is usually treated as a model system with one equivalent $3d$ hole, having a ground state and a single excited state under ideal octahedral crystal-fields [7]. In CuO–ZnO catalysis, two non-equivalent Cu^{2+} locate on slightly tetragonally (D_{4h}) elongated octahedra, with four coplanar Cu^{2+}–O^{2-} bond lengths shorter than the axial ones [8–11]. The properties of the above structure may play an important role in the catalytic behaviour of these systems. That is why their local structure features are worth being further investigated. For example, the EPR experiments were carried out for the calcined catalysts CuO–ZnO, and the spin Hamiltonian parameters (the anisotropic g factors $g_{\parallel}$ and $g_{\perp}$ and the hyperfine structure constants $A_{\parallel}$ and $A_{\perp}$) were also measured for the two signals $A1$ and $A2$ [12]. The signals $A1$ and $A2$ are attributable to isolated Cu^{2+} ions automically dispersed in the lattice of ZnO and located in tetragonally distorted octahedral cavities [12]. The observed EPR spectra reveal positive g anisotropy Δg ($= g_{\parallel} - g_{\perp}$) and a much larger $A_{\parallel}$ in magnitude than $A_{\perp}$, characteristic of a $3d^9$ ion under a tetragonally elongated octahedron. This point is quite similar to the case of Cu^{2+}/Al_2O_3 systems [13]. According to references [12, 14], the difference between signals $A1$ and $A2$ may be ascribed to the two slightly different types of Cu^{2+} in different positions and unlike local environments in the CuO–ZnO systems. Specifically, the higher $g_{\parallel}$ and lower $A_{\parallel}$ values for center $A2$ can originate from

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the samples suffering stronger axial interaction [12, 14]. However, the above experimental results have not been theoretically explained so far, and the data on the local structures of the Cu^{2+} centers have not been obtained yet. Since the analysis of the EPR spectra can provide useful data on the electronic states and local structures for Cu^{2+} in the calcined catalysts CuO–ZnO, which would be helpful in understanding the properties of the catalysts, further studies on the above EPR experimental results are of particular scientific and practical significance. In this work, the spin Hamiltonian parameters are theoretically investigated for the two Cu^{2+} centers $A1$ and $A2$ in the calcined catalysts CuO–ZnO using the high order perturbation formulas of these parameters for a $3d^9$ ion in tetragonally elongated octahedra. In the above formulas, the tetragonal field parameters Ds and Dt are determined from the superposition model, by considering the relative axial elongation (in terms of the relative elongation ratio ρ of the axial Cu^{2+}–O^{2-} bond lengths related to the average bond length) of the oxygen octahedron around the Cu^{2+} due to the Jahn-Teller effect. The calculation results and the local structures of the Cu^{2+} centers are discussed.

2. Calculation

In the calcined catalysts CuO–ZnO, the original Cu^{2+} in the form of CuO may be located in the center of oxygen octahedra. As a Jahn-Teller ion, Cu^{2+} will suffer the Jahn-Teller effect via stretching the two Cu^{2+}–O^{2-} bonds along the C_4 axis and contracting the other four bonds in the perpendicular plane, which reduces the local symmetry to tetragonal (an elongated octahedron). This point has been illustrated in various studies on Cu^{2+} in oxygen octahedra [15]. Thus, the local structures of the Cu^{2+} centers can be characterized by the relative tetragonal elongation ratio (labeled as ρ) in the $[CuO_6]^{10-}$ clusters. For a Cu^{2+} ($3d^9$) ion in tetragonally elongated octahedra, the lower ^2E_g irreducible representation may be separated into two orbital singlets $^2B_{1g}$ and $^2A_{1g}$, with the former lying lowest [7, 15]. Meanwhile, the upper $^2T_{2g}$ representation would split into an orbital singlet $^2B_{2g}$ and a doublet ^2E_g [7, 15]. The perturbation formulas of the spin Hamiltonian parameters for a tetragonally elongated $3d^9$ cluster can be expressed as [16]:

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

where $g_s \approx 2.0023$ is the spin-only value. Parameter k is the orbital reduction factor, which is equivalent to the covalency factor N. Parameter κ is the core polarization constant. ζ_d and P are, respectively, the spin-orbit coupling coefficient and the dipolar hyperfine structure parameter for the $3d^9$ ion in crystals. 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 [16]:

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

Here Dq is the cubic field parameter, and Ds and Dt are the tetragonal field parameters.

For the Jahn-Teller elongated $[CuO_6]^{10-}$ clusters, the parallel and perpendicular bond lengths can be expressed in terms of the relative tetragonal elongation ratio ρ and the reference distance R as: $R_{\parallel} \approx R(1 + 2\rho)$ and $R_{\perp} \approx R(1 - \rho)$. Thus, the cubic and tetragonal field parameters are determined from the superposition model [16] and the geometrical relationship of the Cu^{2+} centers:

$$\begin{aligned}
Dq &\approx (3/4)\bar{A}_4(1-\rho)^{-t_4}, \\
Ds &\approx (2/7)\bar{A}_2\left[(1-\rho)^{-t_2} - (1+2\rho)^{-t_2}\right], \\
Dt &\approx (16/21)\bar{A}_4\left[(1-\rho)^{-t_4} - (1+2\rho)^{-t_4}\right].
\end{aligned} \tag{3}$$

Here $t_2 \approx 3$ and $t_4 \approx 5$ are the power-law exponents in view of the ionic nature of the bonds [17]. $\bar{A}_2$ and $\bar{A}_4$ are the rank-2 and rank-4 intrinsic parameters, respectively. For octahedral $3d^n$ clusters, the relationships $\bar{A}_4 \approx (3/4)Dq$ and $\bar{A}_2 \approx 10.8\bar{A}_4$ [17–19] are proved valid in many crystals and are reasonably applied here. Thus, the g factors, especially the anisotropy $\Delta g(= g_{\|} - g_{\perp})$ is connected with the tetragonal field parameters and hence with the local structure (i.e., the relative tetragonal elongation ratio ρ) of the systems studied.

According to the optical spectra for Cu^{2+} in some oxides [20, 21], the values $\bar{A}_4 \approx 800$ cm^{-1} and $N \approx 0.82$ can be obtained. The spin-orbit coupling coefficient ζ_d and the dipolar hyperfine structure parameter are acquired for the systems studied using the free-ion data $\zeta_d^0 \approx 829$ cm^{-1} [22] and $P_0 \approx 416 \times 10^{-4}$ cm^{-1} [23]. The core polarization constant is taken as the expectation value 0.3 [22] for $3d^n$ ions in crystals. Thus, only the relative tetragonal elongation ratio ρ is unknown in the formulas of the spin Hamiltonian parameters. Substituting these values into equation (1) and fitting the calculated results to the experimental data, one can obtain

$$\rho \approx 5\% \quad \text{and} \quad 3\% \tag{4}$$

for the two centers $A1$ and $A2$, respectively. The corresponding theoretical results are shown in table 1.

Table 1. The g factors and the hyperfine structure constants (in 10^{-4} cm^{-1}) for the two tetragonal Cu^{2+} centers in the calcined catalysts CuO–ZnO.

		$g_{\|}$	$g_{\perp}$	$A_{\|}$	$A_{\perp}$
$A1$	Cal.	2.329	2.070	−142.5	18.8
	Expt. [12]	2.325	2.075	−140.1	18.7
$A2$	Cal.	2.367	2.083	−139.4	17.3
	Expt. [12]	2.366	2.085	−130.7	18.7

3. Discussion

Table 1 reveals that the calculated spin Hamiltonian parameters for the two centers $A1$ and $A2$ in the calcined catalysts CuO–ZnO based on the relative tetragonal elongation ratios in equation (4) are in good agreement with the observed values. Thus, the experimental EPR spectra [12] for both systems are satisfactorily interpreted in this work, and the local structure information is obtained.

1. The EPR spectra for the Cu^{2+} centers can be characterized by the positive anisotropy Δg. The anisotropy largely depends upon the tetragonal distortion (i.e., the tetragonal field parameters Ds and Dt) arising from the relative tetragonal elongation ratio ρ ($\approx 3\% - 5\%$). Further, the tetragonal elongations are of the Jahn-Teller nature via relaxation of the parallel bond lengths and contraction of the perpendicular ones. Similar tetragonal elongation of the oxygen octahedra was also reported for Cu^{2+} on the Al^{3+} site in $LaSrAlO_4$ [15]. The relative elongation ratio ρ in the $A1$ center larger than in the $A2$ center may be attributed to the more significant Jahn-Teller distortion in the former. Thus, one can expect that the two centers $A1$ and $A2$ may be distorted in different ways. The difference in the Jahn-Teller distortion strength is likely due to the $[CuO_6]^{10-}$ clusters at different octahedral cavities and hence differ from local environments in the CuO–ZnO systems. Similar difference in the Jahn-Teller distortion was also reported for the two trigonal Ti^{3+} (with the same spin $S = 1/2$) centers at non-equivalent octahedral Al^{3+} sites in $LaMgAl_{11}O_{19}$ corresponding to two different sets of EPR spectra [24].

2. The hyperfine structure constants for the Cu^{2+} centers are close to each other, which can be illustrated by the similar spectral parameters and the core polarization constant. However, the parallel component ($A_{\|}$) is smaller in $A2$ center than that in $A1$ center. From equation (1)

it is seen that $A_{\parallel}$ is effected by $g_{\parallel} - g_{\rm s}$, while $A_{\perp}$ remains almost the same because $g_{\perp}$ shows the similar values for both centers. Thus, the larger $g_{\parallel}$ in $A2$ center may somewhat cancel the negative isotropic term (proportional to the core polarization constant) and then leads to the lower magnitude of $A_{\parallel}$. The signs of the experimental hyperfine structure constants were not given in [12]. Nevertheless, the theoretical studies in this work indicated negative signs of hyperfine structure constants $A_{\parallel}$.

3. The studied Cu^{2+} centers in the calcined catalysts CuO–ZnO are ascribed to the octahedral $[CuO_6]^{10-}$ clusters embedded in the ZnO host. Although ZnO exhibits some covalency, the Cu^{2+} centers are mainly ionic, characterized by the covalency factor N (≈ 0.82). In addition, the spin-orbit coupling coefficient ($\approx 151\ \text{cm}^{-1}$) [25] of the ligand oxygen is much smaller than that ($\approx 829\ \text{cm}^{-1}$) [18] of the central ion Cu^{2+}. Thus, contributions to the spin Hamiltonian parameters from the ligand orbital and spin-orbit coupling interactions can be regarded as very small and negligible for simplicity.

4. The calculation errors of the present work can be discussed as follows. First, the approximation of the theoretical model (i.e., crystal-field model) and formulas may lead to some errors. Second, the spectral parameters Dq (or $\bar{A}_4$) and N obtained from those for Cu^{2+} in some oxides can effect the final results. As Dq varies by 10% , the relative elongations ratio ρ and the spin Hamiltonian parameters would be modified by about 0.5% , because the tetragonal distortion (or ρ) and the resultant Δg [see equation (3)] have a little relation to Dq. While N changes by 10% , the final ρ and spin Hamiltonian parameters deviate by only 0.4% , suggesting that covalency affects mainly the average of the g factors and brings forward a few effects on ρ and Δg. Third, the errors can also be introduced from the approximation of the relationship $\bar{A}_2 \approx 10.8\bar{A}_4$ [17–19], which would slightly modify the tetragonal field parameters. The errors are estimated to be no more than 1% for ρ and the spin Hamiltonian parameters when the ratio $\bar{A}_2/\bar{A}_4$ varies within the widely accepted range of 9–12. Finally, the uncertainty of the core polarization constant κ used in the present calculations of the hyperfine structure constants may lead to some errors. Since this value is the expectation result for transition-metal ions in crystals, the effects of the above errors on the hyperfine structure constants may be regarded as very small or negligible.

4. Summary

The spin Hamiltonian parameters and the local structures of the tetragonal Cu^{2+} centers $A1$ and $A2$ in the calcined catalysts CuO–ZnO are theoretically investigated from the perturbation formulas for a $3d^9$ ion in tetragonally elongated octahedra. The oxygen octahedra around Cu^{2+} are found to suffer the relative tetragonal elongation ratios of about 3% and 5% due to the Jahn-Teller effect for centers $A1$ and $A2$, respectively. The axial elongation for center $A1$ larger than for center $A2$ can be attributed to the more significant tetragonal Jahn-Teller distortion in the former.

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Теоретичні дослідження параметрів спінового гамільтоніану для двох тетрагональних центрів Cu^{2+} в кальцинованих каталізаторах CuO–ZnO

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Параметри спінового гамільтоніану для двох центрів Cu^{2+}, $A1$ і $A2$, у кальцинованих каталізаторах CuO–ZnO досліджуються теоретично, використовуючи формули теорії збурень високого порядку для цих параметрів для іона $3d^9$ у тетрагонально видовжених октаедрах. В цих формулах параметри тетрагонального поля Ds і Dt визначаються з суперпозиційної моделі, шляхом розгляду відносного аксійного видовження октаедра кисню навколо Cu^{2+} відповідно до ефекту Яна-Теллера. Базуючись на цих розрахунках, отримано коефіцієнти відносного видовження приблизно 5% і 3% для тетрагональних Cu^{2+} центрів $A1$ і $A2$, відповідно. Параметри теоретичного спінового гамільтоніану добре узгоджуються зі спостережуваними величинами для обох систем. Більше аксійне видовження в центрі $A1$ приписується до вагомішої низько симетричної (тетрагональної) дисторсії ефекту Яна-Телера. Обговорюються локальні структури, що характеризуються вище згаданим аксійним видовженням.

Ключові слова: *EPR, Cu^{2+}, CuO–ZnO, дефектні структури*