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Studies of the spin Hamiltonian parameters and local structure for ZnO:Cu^{2+}

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ABSTRACT

The spin Hamiltonian parameters (the *g* factors and the hyperfine structure constants) and local structure for ZnO:Cu^{2+} are theoretically studied from the perturbation formulas of these parameters for a $3d^9$ ion under trigonally distorted tetrahedra. The ligand orbital and spin–orbit coupling contributions are taken into account from the cluster approach due to the significant covalency of the $[CuO_4]^{6-}$ cluster. According to the investigations, the impurity Cu^{2+} is suggested not to locate on the ideal Zn^{2+} site in ZnO but to undergo a slight outward displacement (≈0.01 Å) away from the ligand triangle along C_3 axis. The calculated spin Hamiltonian parameters are in good agreement with the observed values. The validity of the above impurity displacement is also discussed.

1. Introduction

Zinc oxide (ZnO) containing Cu^{2+} has been widely investigated due to the unique green luminescence [1–3], ferromagnetism [4–6] and catalytic properties [7–9]. These properties usually closely correlate to local structures around Cu^{2+} in this material, which can be studied with the aids of electron paramagnetic resonance (EPR). Decades ago, Broser and Schulz [10] performed the EPR investigations on ZnO:Cu^{2+}, and the spin Hamiltonian parameters (the *g* factors, $g_{//}$ and $g_\perp$ and the hyperfine structure constants $A_{//}$ and $A_\perp$) for the trigonal Cu^{2+} center were also measured. Up to now, however, the above EPR experimental findings have not been theoretically explained, and information about local structure for Cu^{2+} in ZnO was not obtained yet.

Since information about local structures around impurity ions in ZnO would be helpful to understand properties of this material with transition-metal dopants, theoretical studies of the local structure and the EPR spectra for ZnO:Cu^{2+} are of fundamental and practical significance. In this work, the formulas of the spin Hamiltonian parameters for a $3d^9$ ion in trigonally distorted tetrahedra are established including the ligand orbital and spin–orbit coupling contributions based on the cluster approach. The formulas are then applied to the studied trigonal Cu^{2+} center in ZnO, by considering the suitable impurity displacement along C_3 axis.

2. Calculations

For a $Cu^{2+}(3d^9)$ ion under trigonally distorted tetrahedral environments, its lower cubic irreducible representation $^2T_2$ may split into three Kramers doublets due to combination of the spin–orbit coupling and the trigonal crystal-field interactions [11,12].

Previous studies of the EPR spectra for $3d^9$ ions in trigonally distorted tetrahedra were largely based on the conventional crystal-field model [11,12], by adopting various adjustable parameters (e.g., metal spin–orbit coupling coefficient or/and trigonal splitting and orbital reduction factor). However, these studies usually failed to connect with the immediate structures around impurities, which are generally dissimilar to those of the host cation sites due to some possible local lattice distortions. In addition, the ligand orbital and spin–orbit coupling contributions were also neglected. Normally, $3d^9$ ions under tetrahedral environments (e.g., ZnO and other II–VI semiconductors) exhibit strong covalency and hence significant admixtures between impurity and ligand orbitals. This means that the previous treatments [11,12] can lead to some errors due to neglecting of the ligand contributions and local lattice distortions and that these formulas are necessary to be optimized. Thus, the improved formulas of the spin Hamiltonian parameters for $3d^9$ ions under trigonally distorted tetrahedra can be obtained by considering the ligand orbital and spin–orbit

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coupling contributions from the cluster approach, i.e.,

$$
\begin{aligned}
g_{//} &= 2|(1+k)\cos^2\delta - \sin^2\delta|,\\
g_{\perp} &= 2|\frac{k'\sin 2\delta}{\sqrt{2}} + \sin^2\delta|,\\
A_{//} &= P\kappa\cos 2\delta + 2N_\mathrm{t}P\left[\frac{-2N_\mathrm{t}}{7} - 6\cos^2\delta + \frac{3\sin 2\delta}{(7\sqrt{2})}\right],\\
A_{\perp} &= P\kappa\sin^2\delta - 2N_\mathrm{t}^2P\left[\frac{\sin^2\delta}{7} + \frac{11\sin 2\delta}{(14\sqrt{2})}\right],
\end{aligned}
\tag{1}
$$

with

$$
\delta = \frac{1}{2}\tan^{-1}\frac{\sqrt{2}\zeta'}{\zeta/2-\nu}. \tag{2}
$$

Here, ζ and ζ' are the spin–orbit coupling coefficients, and k and k' are the orbital reduction factors, which can be determined from the cluster approach. P is the dipolar hyperfine structure parameter of the $3d^9$ ion. κ is the core polarization constant. ν is the trigonal field parameter, depending upon the local structure of the impurity center. In the cluster approach, the one-electron wave functions for the tetrahedral $3d^9$ cluster can be written as:

$$
\begin{aligned}
\psi_\mathrm{t} &= N_\mathrm{t}^{1/2}(\phi_\mathrm{dt} - \lambda_\sigma\chi_{\mathrm{p}\sigma} - \lambda_\mathrm{s}\chi_\mathrm{s} - \lambda_\pi\chi_{\mathrm{p}\pi\mathrm{t}}),\\
\psi_\mathrm{e} &= N_\mathrm{e}^{1/2}\left(\phi_\mathrm{de} - \sqrt{3}\lambda_\pi\chi_{\mathrm{p}\pi\mathrm{e}}\right).
\end{aligned}
\tag{3}
$$

Here γ (=t and e) denotes the irreducible representations of T_d group. ϕ_dt and ϕ_de are the d-orbitals of the $3d^9$ ion, and $\chi_{\mathrm{p}\sigma}$, $\chi_{\mathrm{p}\pi\mathrm{t}}$, $\chi_{\mathrm{p}\pi\mathrm{e}}$ and χ_s are the p- and s-orbitals of ligands. N_γ is the normalization factor, and λ_σ, λ_π and λ_s are the orbital admixture coefficients. From Eq. (1), we have the normalization conditions

$$
\begin{aligned}
&N_\mathrm{t}(1+\lambda_\pi^2+\lambda_\sigma^2-2\lambda_\pi\lambda_\sigma-2\lambda_\mathrm{s}S_\mathrm{s}-2\lambda_\pi S_\sigma)=1,\\
&N_\mathrm{e}(1+3\lambda_\pi^2+6\lambda_\pi S_\pi)=1,
\end{aligned}
\tag{4}
$$

and the approximation relationships

$$
\begin{aligned}
N^2 &\approx (1+6\lambda_\pi S_\pi+9\lambda_\pi^2S_\pi^2)(1+3\lambda_\pi^2+6\lambda_\pi S_\pi)^{-2}\\
N^2 &\approx (1+2\lambda_\pi S_\pi+2\lambda_\sigma S_\sigma+2\lambda_\mathrm{s}S_\mathrm{s}+2\lambda_\pi S_\pi\lambda_\sigma S_\sigma+2\lambda_\pi S_\pi\lambda_\mathrm{s}S_\mathrm{s}\\
&\quad +\lambda_\pi^2S_\pi^2+\lambda_\sigma^2S_\sigma^2+\lambda_\mathrm{s}^2S_\mathrm{s}^2)(1+\lambda_\pi^2+\lambda_\sigma^2+\lambda_\mathrm{s}^2\\
&\quad +2\lambda_\pi S_\pi+2\lambda_\sigma S_\sigma+2\lambda_\mathrm{s}S_\mathrm{s})^{-2}.
\end{aligned}
\tag{5}
$$

Here S_π, S_σ and S_s are the group overlap integrals between the d-orbitals of the $3d^9$ ion and p- or s-orbitals of the ligands. N is the average covalency factor, characteristic of the covalency (or orbital admixtures) between the central metal and ligand ions. In general, the admixture coefficients increase with increasing the group overlap integrals, and one can approximately apply the proportional relationship for the admixture coefficients and the related group overlap integrals, i.e., $\lambda_\sigma/\lambda_\mathrm{s} \approx S_\sigma/S_\mathrm{s}$ within the same σ component.

Thus, the spin–orbit coupling coefficients and the orbital reduction factors in Eq. (4) can be determined from the cluster approach:

$$
\begin{aligned}
\zeta &= N_\mathrm{t}\left[\zeta_\mathrm{d}^0 + \left(\sqrt{2}\lambda_\pi\lambda_\sigma - \frac{\lambda_\pi^2}{2} - \sqrt{2}A\lambda_\pi\lambda_\mathrm{s}\right)\zeta_\mathrm{p}^0\right],\\
\zeta' &= (N_\mathrm{t}N_\mathrm{e})^{1/2}\left[\zeta_\mathrm{d}^0 + \left(\frac{\lambda_\pi\lambda_\sigma}{\sqrt{2}} + \frac{\lambda_\pi^2}{2} - \frac{A\lambda_\pi\lambda_\mathrm{s}}{\sqrt{2}}\right)\zeta_\mathrm{p}^0\right],\\
k &= N_\mathrm{t}\left(1-\frac{\lambda_\pi^2}{2}+\sqrt{2}\lambda_\pi\lambda_\sigma-2\lambda_\sigma S_\sigma-2\lambda_\mathrm{s}S_\mathrm{s}-2\lambda_\pi S_\pi-\sqrt{2}A\lambda_\pi S_\mathrm{s}\right),\\
k' &= (N_\mathrm{t}N_\mathrm{e})^{1/2}\left(1+\frac{\lambda_\pi^2}{2}+\frac{\lambda_\pi\lambda_\sigma}{\sqrt{2}}-4\lambda_\pi S_\pi-\lambda_\sigma S_\sigma-\lambda_\mathrm{s}S_\mathrm{s}-\frac{A\lambda_\pi S_\mathrm{s}}{\sqrt{2}}\right).
\end{aligned}
\tag{6}
$$

Here A denotes the integral $R\langle ns|\partial/\partial y|np_y\rangle$, with the metal-ligand distance R. ζ_d^0 and ζ_p^0 are the spin–orbit coupling coefficients of the free $3d^9$ and ligand ions, respectively. Obviously, when taking $S_\lambda = \lambda_\gamma = 0$, the above formulas return to those based on the conventional crystal-field model in the absence of the ligand contributions [11,12].

When a Cu^{2+} ion is doped into ZnO, it can occupy substitutionally Zn^{2+} site and conserve the original trigonal (C_{3V}) symmetry [10], with one bond length $R_1 \approx 1.978$ Å along C_3 axis and three bond lengths $R_2 \approx 1.965$ Å and the corresponding bond angle $\theta \approx 109.24°$ related to C_3 axis [13]. The trigonal field parameter can be calculated from the local geometrical relationship of this $[CuO_4]^{6-}$ cluster, by using the superposition model [14]:

$$
\begin{aligned}
\nu = {}& (-3/7)\bar{A}_2(R)[2(R/R_1)^{t_2} + 3(3\cos^2\theta - 1)(R/R_2)^{t_2}]\\
& -(20/63)\bar{A}_4(R)[8(R/R_1)^{t_4} + 3(35\cos^4\theta - 30\cos^2\theta + 3)(R/R_2)^{t_4}]\\
& -(20\sqrt{2}/3)\bar{A}_4(R)\sin^3\theta\cos\theta(R/R_2)^{t_4}
\end{aligned}
\tag{7}
$$

where $\bar{A}_2(R)$ and $\bar{A}_4(R)$ are the intrinsic parameters (with the reference or average distance R). For $3d^n$ ions in tetrahedra, the relationships $\bar{A}_4(R) \approx (27/16)$Dq (where Dq is the cubic field parameter) and $\bar{A}_2(R) \approx 10.8\bar{A}_4(R)$ are proved to be valid in many crystals [14–16]. Thus, the trigonal distortion (or the local structure) of the studied system is correlated to the trigonal field parameter and hence to the spin Hamiltonian parameters, particularly the anisotropy Δg ($=g_\perp - g_{//}$).

From the optical spectra for Cu^{2+} in ZnO, the cubic field parameter $\mathrm{Dq} \approx 570\ \mathrm{cm}^{-1}$ and the covalency factor $N \approx 0.67$ can be obtained [17]. From the average distance $\bar{R}[=(R_1+3R_2)/4]$ and the Slater-type SCF functions [18,19], the group overlap integrals $S_\pi \approx 0.005$, $S_\sigma \approx -0.227$, $S_\mathrm{s} \approx 0.224$ and the integral $A \approx 1.2813$ are calculated. From Eqs. (4)–(6), the parameters $\zeta \approx 439\ \mathrm{cm}^{-1}$, $\zeta' \approx 520\ \mathrm{cm}^{-1}$, $k \approx 0.407$ and $k' \approx 0.473$ can be determined by using the free-ion values ζ_d^0 (Cu^{2+}) $\approx 829\ \mathrm{cm}^{-1}$ [20] and ζ_p^0 (O^{2-}) $\approx 151\ \mathrm{cm}^{-1}$ [21]. The dipolar hyperfine structure parameters are P ($^{63}Cu^{2+}$) $\approx 388 \times 10^{-4}\ \mathrm{cm}^{-1}$ and P ($^{65}Cu^{2+}$) $\approx 416 \times 10^{-4}\ \mathrm{cm}^{-1}$ [22]. The core polarization constant is usually obtained from the relationship $\kappa \approx -2\chi/(3\langle r^{-3}\rangle)$ [11]. Here χ is 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 $\chi \approx -3.4$ a.u. [18] for Cu^{2+} in some oxides (e.g., TiO_2), one can obtain $\kappa \approx 0.45$ for the studied ZnO:Cu^{2+}.

Substituting the above values into Eq. (1), the spin Hamiltonian parameters (Cal.^{a}) are calculated and shown in Table 1. It can be found that the g factors show poor agreement with the experimental data, especially the anisotropy Δg is more than twice of the exact result. This means that the trigonal distortion (i.e., the parameter ν) based on Cu^{2+} locating on the ideal Zn^{2+} site in ZnO is somewhat overestimated. Since the ionic radius (≈0.76 Å [23]) of Cu^{2+} is slightly larger than that (≈0.74 Å [23]) of Zn^{2+}, the impurity may not occupy exactly the host Zn^{2+} site but suffer a tiny displacement ΔR along C_3 axis due to size mismatching substitution. Thus, the new local structural parameters R_1', R_2' and β' should be adopted in Eq. (7) due to the impurity displacement ΔR. Substituting these parameters into Eq. (1) and matching the theoretical spin Hamiltonian parameters to the observed values, we have

$$
\Delta R \approx 0.01\ \text{Å}. \tag{8}
$$

Note that the displacement direction away from the ligand triangle along C_3 axis is defined as positive. The corresponding theoretical results (Cal.^{c}) are shown in Table 1. For comparisons, the calculated values (Cal.^{b}) based on the local structural parameters due to ΔR in Eq. (8) and neglecting of the ligand orbital and spin–orbit coupling contributions (i.e., $\zeta = \zeta' = N\zeta_\mathrm{d}^0$ and $k = k' = N$,