

An Investigation for the Spin Hamiltonian Parameters and the Local Structure for Co^{2+} in ZnWO_4

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Abstract. Based on the perturbation formulae of the spin Hamiltonian parameters (SHPs), i.e., g factors g_x , g_y , g_z , and hyperfine structure constants A_x , A_y , A_z , for a $3d^7$ ion in rhombically distorted octahedra, the defect structure and the experimental EPR spectra are theoretically investigated for the rhombic Co^{2+} centre in ZnWO_4 . Due to the Jahn-Teller effect, the impurity ion Co^{2+} on host Zn^{2+} site is found to undergo the local rhombic elongation distortion, characterized by the axial elongation ΔZ (≈ 0.157 Å) of the impurity-ligand bonds and the perpendicular distortion angle $\Delta\phi$ ($\approx 3.5^\circ$) related to an ideal octahedron. Compared with host Zn^{2+} site in ZnWO_4 , the Co^{2+} centre exhibits a more regular oxygen octahedron. All the calculated SHPs show good agreement with the observed values. The present work may be helpful to understand the local structures and properties of metal tungstate with transition-metal dopants.

1. Introduction

As a stable and hard metal tungstate, ZnWO_4 is attractive in microwave, acoustic, catalytic, magnetic and phase-change optical recording properties and widely used in optical fibers, humidity sensors, photoluminescence and scintillation materials [1–4]. More important, this material containing transition-metal dopants exhibits novel performances such as catalyst [5–7], electrochemistry [8,9], lasing efficiency enhancement [10] and bright green upconversion luminescence emission [11]. For example, Co^{2+} doped ZnWO_4 is also an extension of the use of ruby as a maser material [12]. Usually, the properties of function materials have close relationships with the features of local environments (e.g., coordination number, occupation, local symmetry, strength of crystal-fields) in the vicinity of the doped impurities. The involved local features of impurities can be effectively revealed by use of electron paramagnetic resonance (EPR) technique. The EPR experiments have been performed for Co^{2+} doped ZnWO_4 , and the spin Hamiltonian parameters (SHPs)

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(g factors g_x , g_y , g_z and hyperfine structure constants A_x , A_y , A_z) were measured for the rhombic Co^{2+} centre [12], with the properties of $g_x, g_y < g_z$ and $A_x, A_y < A_z$. But, up to now, there are no theoretical explanations to the above EPR results. In this work, the SHPs for the rhombic Co^{2+} centre in ZnWO_4 are studied from the perturbation formulae of these parameters for a $3d^7$ ion under rhombically distorted octahedra. The calculated results and the local structure of the impurity centre are discussed.

2. Calculations

ZnWO_4 has wolframite structure with C_{2h} point group symmetry and P2/c space group [13]. When impurity Co^{2+} is doped into ZnWO_4 , it may substitute for host Zn^{2+} and undergo local lattice distortion due to size mismatch. The formulae of g factors and hyperfine structure constants for a $3d^7$ ion in rhombic distorted octahedra can be written as follows [14]:

$$\begin{aligned}
 &g_x \\
 &= \left\{ 4 \left[\left(\frac{\alpha}{\alpha'} \right)^2 + \frac{2k\alpha}{(x+2)} \left(\frac{\alpha'}{\alpha''} \right) + \frac{12}{x(x+2)} \right] + \left(\frac{\alpha}{\alpha'} \right)^2 v_{4x} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}} \frac{4v_{7x}}{(x+2)} \right\} / H \\
 &g_y \\
 &= \left\{ 4 \left[\left(\frac{\alpha}{\alpha''} \right)^2 + \frac{2k\alpha}{(x+2)} \left(\frac{\alpha''}{\alpha'} \right) + \frac{12}{x(x+2)} \right] + \left(\frac{\alpha}{\alpha''} \right)^2 v_{4y} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{\alpha}{(\alpha'\alpha'')^{1/2}} \frac{4v_{7y}}{(x+2)} \right\} / H \\
 &g_z = 2 + \left\{ 4(k\alpha + 2) \left[\frac{3}{x^2} - \frac{4}{(x+2)^2} \right] + \left[\frac{9}{x^2} - \frac{4}{(x+2)^2} \right] (v_{1x} + v_{1y}) - \frac{\alpha(v_{3x} + v_{3y})}{(\alpha'\alpha'')^{1/2}} \left(\frac{3}{x} - \frac{4}{x+2} \right) \right\} / H
 \end{aligned} \tag{1}$$

$$\begin{aligned}
 &A_x \\
 &= \\
 &P \left\{ (-\kappa/2) \left[\left(\frac{\alpha^2}{\alpha'\alpha''} \right) + \frac{12}{x(x+2)} \right] + \frac{8k\alpha}{x+2} - \left(\frac{\alpha^2}{\alpha'\alpha''} \right) W_z - \frac{32W_{xy}}{(x+2)^2} - \frac{12W_x}{x(x+2)} + \frac{4\alpha W_{xz}}{(x+2)(\alpha'\alpha'')^{1/2}} \right\} / H \\
 &+ P' \left\{ \left(\frac{\alpha}{\alpha'} \right)^2 v_{4x} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{4\alpha v_{7x}}{(x+2)(\alpha'\alpha'')^{1/2}} \right\} / H
 \end{aligned}$$

$$\begin{aligned}
 &A_y \\
 &= P \left\{ (-\kappa/2) \left[\left(\frac{\alpha^2}{\alpha'\alpha''} \right) + \frac{12}{x(x+2)} \right] + \frac{8k\alpha}{x+2} - \left(\frac{\alpha^2}{\alpha'\alpha''} \right) W_z - \frac{32W_{xy}}{(x+2)^2} - \frac{12W_y}{x(x+2)} + \frac{4\alpha W_{yz}}{(x+2)(\alpha'\alpha'')^{1/2}} \right\} / H \\
 &+ P' \left\{ \left(\frac{\alpha}{\alpha'} \right)^2 v_{4y} + \frac{8v_5}{(x+2)^2} + \frac{12v_6}{x(x+2)} - \frac{4\alpha v_{7y}}{(x+2)(\alpha'\alpha'')^{1/2}} \right\} / H
 \end{aligned}$$

$$\begin{aligned}
 &A_z \\
 &= P \left\{ (-\kappa/2) \left[2 + 8 \left(\frac{3}{x^2} - \frac{4}{(x+2)^2} \right) \right] + 4k\alpha \left(\frac{3}{x^2} - \frac{4}{(x+2)^2} \right) + (W_x + W_y) \left(\frac{9}{x^2} - \frac{4}{(x+2)^2} \right) + \frac{\alpha^2 W_z}{\alpha'\alpha''} \right\} / H \\
 &- P \frac{2\alpha(W_{xz} + W_{yz}) \left(\frac{3}{x} - \frac{4}{x+2} \right)}{Z(\alpha'\alpha'')^{1/2}} + P' \left\{ (v_{1x} + v_{1y}) \left(\frac{9}{x^2} - \frac{4}{(x+2)^2} \right) - \frac{\alpha(v_{3x} + v_{3y}) \left(\frac{3}{x} - \frac{4}{x+2} \right)}{(\alpha'\alpha'')^{1/2}} \right\} / H
 \end{aligned}$$

Here $H = \left(\frac{\alpha}{\alpha' \alpha''}\right) + \frac{6}{x^2} + \frac{8}{(x+2)^2}$. κ is the core polarization constant. x can be determined from the energy splittings $\Delta (=E\{^4B_1[{}^4T_1(F)]\} - E\{^4B_3[{}^4T_1(F)]\})$ and $\delta (=E\{^4B_2[{}^4T_1(F)]\} - E\{^4B_3[{}^4T_1(F)]\})$ of 4T_1 ground state in rhombic crystal-fields by the expression $\Delta = \frac{\zeta \alpha' \alpha''}{3} \left[\frac{3}{\alpha x} + \frac{4\zeta}{\alpha \zeta (x+2) + 6\delta} \right] - \frac{\zeta \alpha}{6} (x+3)$. The splittings Δ and δ can be calculated from the d-d transition energy matrices for $3d^7$ ion in rhombic symmetry. The related parameters f_i , q_i , α^i , v_{ij} and W_{ij} in the above formulae are related to the admixtures of the ground and excited states in rhombic symmetry and can be found in Ref. [14].

Based on the cluster approach, the spin-orbit coupling coefficients ζ , ζ' , the orbital reduction factors k , k' and the dipole hyperfine structure parameters P and P' for $3d^7$ ion can be written as [14,15]

$$\begin{aligned} \zeta &= N_t (\zeta_d^0 + \lambda_t^2 \zeta_p^0 / 2), & \zeta' &= (N_t N_e)^{1/2} (\zeta_d^0 - \lambda_t \lambda_e \zeta_p^0 / 2), \\ k &= N_t (1 + \lambda_t^2 / 2), & k' &= (N_t N_e)^{1/2} (1 - \lambda_t \lambda_e / 2) \\ P &= N_t P_0, & P' &= (N_t N_e)^{1/2} P_0, \end{aligned} \quad (2)$$

where ζ_d^0 and ζ_p^0 are the spin-orbit coupling coefficients of a free $3d^7$ and ligand ions, respectively. P_0 is the dipolar hyperfine structure parameter of the free $3d^7$ ion. N_t and λ_t are, respectively, the normalization factors and the orbital admixture coefficients. They can be determined from the normalization conditions and the approximate relationships [14,15]

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

Here N is the covalency factor, and S_{dpy} (and S_{ds}) are the group overlap integrals. The orbital admixture coefficients and the group overlap integrals have the proportionality relationship $\lambda_e / S_{dpe} \approx \lambda_s / S_{ds}$.

The host Zn^{2+} site in $ZnWO_4$ is surrounded by a considerably (by about 0.31 Å) elongated oxygen octahedron with obvious perpendicular (planar) rhombic angular distortion [13]. Nevertheless, substitution of Zn^{2+} by Co^{2+} may lead to quite different local environment around the impurity. Importantly, the Jahn-Teller ion Co^{2+} at octahedral crystal-fields can suffer the Jahn-Teller effect (i.e., the phenomenon of removal of the degeneracy of energy levels and results in lower symmetry and energy via the vibrational interactions [16,17]). For example, the $[CoO_6]^{10-}$ cluster may experience a local axial elongation ΔZ along Z-axis and the planar angular variation $\Delta\phi$. According to the superposition model [18] and the geometrical relationship of the studied Co^{2+} centre, the rhombic field parameters can be expressed as follows:

$$\begin{aligned} D_s &\approx (2/7) \bar{A}_2 ((R/R_1)^2 + (R/R_2)^2 + (R/R_3)^2 + (R/R_4)^2 - 2(R/R_5)^2 - 2(R/R_6)^2), \\ D_t &\approx \\ &(-1/21) \bar{A}_4 ((R/R_1)^4 \cos(4\phi_1) + (R/R_2)^4 \cos(4\phi_2) + (R/R_3)^4 \cos(4\phi_3) + (R/R_4)^4 \cos(4\phi_4) \\ &\quad - 2(R/R_5)^4 - 2(R/R_6)^4), \end{aligned} \quad (4)$$

$$D_\xi \approx$$

$$(1/7)\bar{A}_2((R/R_1)^{12} \cos(2\phi_1) - (R/R_2)^{12} \cos(2\phi_2) + (R/R_3)^{12} \cos(2\phi_3) - (R/R_4)^{12} \cos(2\phi_4))$$

$D_\eta \approx$

$$(5/21)\bar{A}_4((R/R_1)^{14} \cos(2\phi_1) - (R/R_2)^{14} \cos(2\phi_2) + (R/R_3)^{14} \cos(2\phi_3) - (R/R_4)^{14} \cos(2\phi_4))$$

Here \bar{A}_2 and \bar{A}_4 are the intrinsic parameters related to the reference (average) cation-anion distance R ($\approx 2.114 \text{ \AA}$ [13]) of Zn^{2+} site in ZnWO_4 . For $3d^n$ ions in octahedral environments [19–21], the expressions $\bar{A}_4 \approx (27/16) Dq$ and $\bar{A}_2 \approx 12 \bar{A}_4$ have been proved valid and are reasonably utilized in this work. From the Slater-type self-consistent field functions [22,23] and R , the integrals $S_{dpt} \approx 0.096$, $S_{dpc} \approx 0.0328$, $S_{ds} \approx 0.262$ and $A \approx 1.3763$ are calculated. The spectral parameters Dq , B and C of the studied system can be obtained from those of similar octahedral Co^{2+} cluster in MgO [24], i.e.,

$$Dq \approx -860 \text{ cm}^{-1}, \quad B \approx 985 \text{ cm}^{-1}, \quad C \approx 3858 \text{ cm}^{-1} . \quad (5)$$

From the free ion values $B_0 \approx 1115 \text{ cm}^{-1}$ and $C_0 \approx 4366 \text{ cm}^{-1}$ [22] of Co^{2+} , one can obtain $N \approx 0.915$. Then the molecular orbital coefficients $N_t \approx 0.943$, $N_c \approx 0.951$, $\lambda_t \approx 0.257$ and $\lambda_c \approx 0.231$ from Eq. (3). Substituting the free-ion parameters $\zeta_d^0 \approx 533 \text{ cm}^{-1}$ [25] and $P_0 \approx 254 \times 10^{-4} \text{ cm}^{-1}$ [26] for Co^{2+} and $\zeta_p^0 \approx 151 \text{ cm}^{-1}$ for O^{2-} [27] into Eq. (2), we have

$$\begin{aligned} \zeta \approx 507 \text{ cm}^{-1}, \quad \zeta' \approx 500 \text{ cm}^{-1}, \quad k \approx 0.973, \\ k' \approx 0.892, \quad P \approx 239 \times 10^{-4} \text{ cm}^{-1}, \quad P' \approx 240.5 \times 10^{-4} \text{ cm}^{-1}. \end{aligned} \quad (6)$$

For Co^{2+} in Tutton salts, the core polarization constant $\kappa \approx 0.132$ [28] is obtained and also adopted here. There are only two unknown quantities (local axial elongation ΔZ and planar angular variation Δ) in the formulae of SHPs. Substituting the above parameters into Eq. (1) and fitting the calculated SHPs to the experimental data, one can obtain the optimal values

$$\Delta Z \approx 0.157 \text{ \AA}, \quad \Delta \phi \approx 3.5^\circ . \quad (7)$$

The corresponding SHPs (Cal. ^b) are shown in Table 1.

TABLE 1 THE G FACTORS G_i AND HYPERFINE STRUCTURE CONSTANTS A_i (IN UNITS OF 10^{-4} CM^{-1}) FOR THE RHOMBIC CO^{2+} CENTRE IN ZNWO_4 .

	g_x	g_y	g_z	A_x	A_y	A_z
Cal. ^a	3.04	4.83	5.29	59.39	258.1	269.7
Cal. ^b	2.434	3.30	6.74	29.7	69.9	149
Expt. [12]	2.390	3.41	6.77	23.3	70	210

For comparison, the results (Cal. ^a) based on the host structural data (i.e., $R_{1H} \approx R_{3H} \approx 2.026 \text{ \AA}$, $R_{2H} \approx R_{4H} \approx 2.090 \text{ \AA}$, $R_{5H} \approx R_{6H} \approx 2.227 \text{ \AA}$; $\phi_{1H} \approx 53.17^\circ$, $\phi_{2H} \approx 141.85^\circ$, $\phi_{3H} \approx 306.83^\circ$, $\phi_{4H} \approx 228.17^\circ$ [13]) of Zn^{2+} in ZnWO_4 (i.e., omission of the local lattice distortion) are also collected in Table 1.

3. Discussions

From Table 1, one can find that the calculated g factors and hyperfine structure constants show reasonable agreement with the experimental data, except that A_z is smaller than the observed value. For $3d^7$ ions in rhombic distorted octahedra, g factors and hyperfine structure constants normally exhibit similarly consistently anisotropies related to the local structures of the impurity centres. In fact, the ratios are $A_x/g_x \approx 22.8 \times 10^{-4}$ and $12.6 \times 10^{-4} \text{ cm}^{-1}$, $A_y/g_y \approx 46.0 \times 10^{-4}$ and $37.6 \times 10^{-4} \text{ cm}^{-1}$ and $A_z/g_z \approx 42.5 \times 10^{-4}$ and $37.5 \times 10^{-4} \text{ cm}^{-1}$ for the similar rhombic Co^{2+} centres in NaF [29] and AgCl [30], respectively. Thus, the ratio $A_x/g_x \approx 12.2 \times 10^{-4} \text{ cm}^{-1}$, $A_y/g_y \approx 21.2 \times 10^{-4} \text{ cm}^{-1}$ and $A_z/g_z \approx 22.1 \times 10^{-4} \text{ cm}^{-1}$ based on the present calculations for Co^{2+} in ZnWO_4 show the comparable ratios for y and z components with the above two systems and can be regarded as suitable. However, the ratio A_z/g_z ($\approx 31.0 \times 10^{-4} \text{ cm}^{-1}$ [12]) based on the experimental data for $\text{ZnWO}_4:\text{Co}^{2+}$ are much (about 50%) larger than A_y/g_y ($\approx 20.5 \times 10^{-4} \text{ cm}^{-1}$ [12]), reflecting unsuitably higher magnitude of A_z . So, further experimental verification for the hyperfine structure constants would be helpful.

The moderate axial anisotropies $\Delta g [= g_z - (g_x + g_y)/2]$ and $\Delta A [= A_z - (A_x + A_y)/2]$ of g and A factors may be attributed to the moderate axial elongation of the system, characterized by the intermediate axial elongation ΔZ . The relatively smaller perpendicular anisotropies $\delta g (= g_x - g_y)$ and $\delta A (= A_x - A_y)$ originate mainly from the planar angular distortion, characterized by the deviation of the angle ϕ from that ($= 45^\circ$) in regular octahedra. So, the oxygen octahedron transforms from considerable elongation (i.e., large $\Delta Z \approx 0.31 \text{ \AA}$) in host Zn^{2+} site to slight elongation (i.e., small $\Delta Z \approx 0.157 \text{ \AA}$) in the impurity Co^{2+} center. And the four nearly planar $\text{Co}^{2+} - \text{O}^{2-}$ bonds experience the angular variations $\Delta\phi$ via bending the bonds, yielding a more regular $[\text{CoO}_6]^{10-}$ octahedron.

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