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The investigation of the defect structures for Co^{2+} in ZnO microwires, thin films and bulks

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ABSTRACT

The defect structures for Co^{2+} in ZnO microwires, thin films and bulks are theoretically investigated by analyzing the electron paramagnetic resonance (EPR) parameters (zero-field splitting D, g factors $g_{//}$ and $g_{\perp}$ and hyperfine structure constants $A_{//}$ and $A_{\perp}$) for trigonally distorted tetrahedral $3d^7$ clusters in a consistent way. The impurities Co^{2+} are found to suffer the displacements (≈0.046, 0.044 and 0.045 Å) away from the ligand triangles along the C_3 axis in ZnO microwires, thin films and bulks, respectively, which considerably reduce the trigonal distortions of the Zn^{2+} sites in the hosts. Apart from the contributions from the conventional crystal-field (CF) mechanism, those from the charge-transfer (CT) mechanism are important and should be included in the EPR analysis. The defect structures and spectral properties of the three $ZnO:Co^{2+}$ systems are discussed.

1. Introduction

Over the past decades, zinc oxide (ZnO) has attracted considerable interest in many fields due to the unique electrical and optical properties as well as the high thermal and chemical stability [1–4]. As the promising candidates for the applications in optoelectronic devices such as light-emitting diodes, ultraviolet lasers, detectors and transparent electronics, ZnO of different types have been synthesized to tune the properties and applications suitable for different technological areas [5–7]. Unlike nano-size of ZnO sensing devices unable to survive under extreme environments, high-quality zinc oxide microwires [8,9] are capable to optimize the sensing performance for diverse environments. Particularly, the multifunctionality of ZnO systems can be enhanced by some transition-metal dopants [10–13]. Among these dopants, divalent cobalt (Co^{2+}) is an important impurity because of the highly localized spin and intense coupling with the host valence bands and lattices. Besides, the $Zn_{1-x}Co_xO$ films also suggest a possibility of the application in the electrical resistivity and room temperature ferromagnetism of the diluted magnetic semiconductors [14–16]. Despite the studies [13,17] on the magnetic and electrical properties of Co-doped ZnO, few systematical works have been focused on the structural and spectroscopic properties of these systems. As is known, electron paramagnetic resonance (EPR) is a powerful technique to probe the local structures and spectroscopic behaviors for transition-metal impurities. For example, the EPR spectra were measured for $ZnO:Co^{2+}$ microwires, thin films and bulks, respectively [13,18,19], which yielded the close EPR parameters (zero-filed splitting D, g factors $g_{//}$ and $g_{\perp}$ and hyperfine structure constants $A_{//}$ and $A_{\perp}$) with similar anisotropies $g_{//} > g_{\perp} > 2$ and $|A_{//}| > |A_{\perp}|$ of ground $^4A_2$ state for a trigonally distorted tetrahedral Co^{2+} cluster [20]. To the best of our knowledge, there is no systematic theoretical study of the defect structures and EPR spectra for these $ZnO:Co^{2+}$ systems until now. Since the information of local structures and spectroscopic behaviors can be helpful to understand the properties of the materials with transition-metal dopants, a comprehensive investigation of the EPR parameters and defect structures for Co^{2+} in the three types of ZnO are of specific scientific and practical significance.

In this paper, the EPR parameters and the local structures are theoretically investigated for Co^{2+} in various ZnO systems in a consistent way, by establishing the high-order perturbation formulas of the EPR parameters for a trigonally distorted tetrahedral $3d^7$ cluster. In addition to the contributions from the conventional crystal-field (CF) mechanism, those from the charge-transfer (CT) mechanism are also taken into account in view of the covalency. By analyzing the EPR spectra of the Co^{2+} centres, the information of the defect structures is obtained, and the similarity and differences in the spectroscopic properties and local structures among these systems are also discussed.

2. Theoretical calculations

Although the various $ZnO:Co^{2+}$ systems were synthesized with different methods and conditions, the impurities Co^{2+} tend to similarly occupy the trigonally distorted tetrahedral Zn^{2+} sites and exhibit analogous EPR spectra [13,18,19]. Due to the mismatching substitu-

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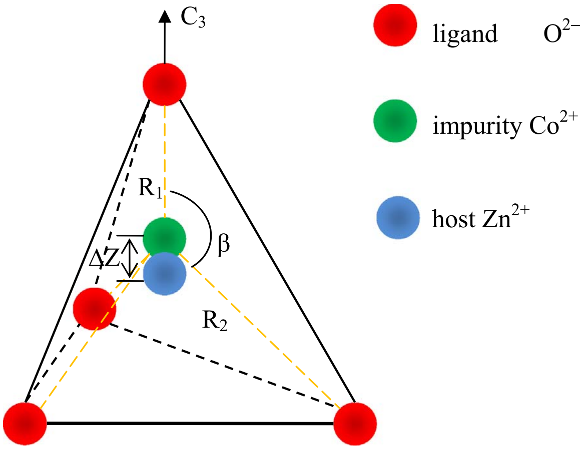

Fig. 1. Local structures of the trigonal Co^{2+} centres in ZnO:Co^{2+} microwires, thin films and bulks. The impurity Co^{2+} undergoes an outward displacement ΔZ away from the ligand triangle along the C$_3$ axis.

tion of the smaller host Zn^{2+} by the larger impurity Co^{2+}, local tension may be induced around the impurity centres. Moreover, the electronegativity difference of the systems declines from 1.9 of Zn^{2+}-O^{2-} bond in the hosts to 1.7 of Co^{2+}-O^{2-} one in the impurity centres, indicating the increasing covalent interactions in the Co^{2+} centres. As a result, the impurity Co^{2+} may not occupy exactly the host Zn^{2+} sites but undergo a displacement ΔZ along the C$_3$ axis so as to release the above local tension due to the size mismatch and the increasing covalent interactions (see Fig. 1).

Based on the Macfarlane's perturbation-loop method [2,11], the fourth order perturbation formulas of the EPR parameters for 3d^7 ions in trigonal tetrahedra can be established by introducing both the conventional CF (relevant to the CF excited states) and the CT mechanisms (relevant to the CT excited states) in view of the covalency:

$$D = D^{CF} + D^{CT}.$$
$$g_{\parallel} = g_{\parallel}^{CF} + g_{\parallel}^{CT}, \qquad g_{\perp} = g_{\perp}^{CF} + g_{\perp}^{CT}.$$
$$A_{\parallel} = A_{\parallel}^{CF} + A_{\parallel}^{CT}, \qquad A_{\perp} = A_{\perp}^{CF} + A_{\perp}^{CT}. \tag{1}$$

with

$$\begin{aligned}
D^{CF} &= 2\zeta_{CF}'^{2}(1/E_1^2 - 1/E_3^2)\nu/9 - \sqrt{2}\nu\zeta_{CF}'\zeta_{CF}'(2/(3E_1E_4) + 1/(E_2E_3)\\
&\quad + 1/(E_3E_4) + 4\sqrt{2}B/(E_1E_4E_5))\\
&\quad - \sqrt{2}\zeta_{CF}'^{2}\,\nu B(4/(E_3E_4E_5) + 9/(2E_2^2E_3)),\\
D^{CT} &= 35\upsilon(\zeta_{CT}'/E_n)^2/6.\\
g_{\parallel}^{CF} &= g_s + 8\zeta_{CF}'k_{CF}'/(3E_1) - 2\zeta_{CF}'(2k_{CF}'\zeta_{CF} - k_{CF}\zeta_{CF}' + 2g_s\zeta_{CF}')/(9E_1^2)\\
&\quad + 4\zeta_{CF}\zeta_{CF}'^{2}(k_{CF} - 2g_s)/(9E_3^2)\\
&\quad - 2\zeta_{CF}'^{2}\,(k_{CF} + g_s)/(3E_3^2)\\
&\quad + 4k_{CF}'\zeta_{CF}\zeta_{CF}'[1/(9E_1E_3) - 1/(3E_1E_2) + 1/(3E_2E_3)]\\
&\quad - 8k_{CF}'\,\zeta_{CF}'\nu/(9E_1^2) + 4\sqrt{2}\nu'(k_{CF}'\zeta_{CF} + k_{CF}\zeta_{CF}')/(3E_1E_4),\\
g_{\parallel}^{CT} &= 8k_{CT}'\,\zeta_{CT}'/(3E_n) - 106\sqrt{2}\upsilon k_{CT}'\zeta_{CT}'/(E_n^2).\\
g_{\perp}^{CF} &= g_{\parallel}^{CF} + 4k_{CF}'\,\zeta_{CF}'\,\nu/(3E_1^2) - 4\sqrt{2}\nu'(k_{CF}'\zeta_{CF} + 2k_{CF}\zeta_{CF}')/(3E_1E_4),\\
g_{\perp}^{CT} &= 8k_{CT}'\,\zeta_{CT}'/(3E_n) + 53\sqrt{2}\upsilon k_{CT}'\,\zeta_{CT}'/(E_n^2).\\
A_{\parallel}^{CF} &= P_{CF}'(g_{\parallel}^{CF} - g_s) - P_{CF}\kappa,\\
A_{\parallel}^{CT} &= 8P_{CT}'\,\kappa\zeta_{CT}'/(3E_n) - P_{CT}\kappa/2 + 106\sqrt{2}P_{CT}'\,\upsilon\zeta_{CT}'\,k_{CT}'/(E_n^2).\\
A_{\perp}^{CF} &= P_{CF}'(g_{\perp}^{CF} - g_s) - P_{CF}\kappa k_{CF}'\,\zeta_{CF}'\,\nu/(3E_1^2) - 4\sqrt{2}\nu'(k_{CF}'\,\zeta_{CF} + 2k_{CF}\zeta_{CF}')/\\
&\quad (3E_1E_4),\\
A_{\perp}^{CT} &= 8P_{CT}'\kappa\zeta_{CT}'/(3E_n) - P_{CT}\kappa/4 + 323P_{CT}'\,\upsilon\zeta_{CT}'\,k_{CT}'/(E_n^2).
\end{aligned} \tag{2}$$

Here the energy denominators E_1, E_2, E_3, E_4 and E_5 represent the energy differences between the CF excited states $^4T_2(t_2{}^4e^3)$, $^2T_{2a}\,(t_2{}^3e^4)$, $^2T_{2b}\,(t_2{}^4e^3)$, $^4T_{1a}\,(t_2{}^3e^4)$ and $^4T_{1b}\,(t_2{}^4e^3)$, respectively, and the ground state $^4A_2(t_2{}^3e^4)$ [2,11]:

$$\begin{aligned}
E_1 &= 10D_q,\\
E_2 &= 15B + C,\\
E_3 &= 9B + 3C + 10D_q,\\
E_4 &= 12B + 10D_q,\\
E_5 &= 3B + 20D_q.
\end{aligned} \tag{3}$$

Here B and C are the Racah parameters for the 3d^7 ions in the various systems, and Dq is the cubic CF parameter. E_n is the energy separation between the CT excited state $^4T_2{}^n$ and the CF ground state $^4A_2(t_2{}^3e^4)$, which is usually determined from the optical electronegativities χ (L) and χ (M) of ligand and central metal ions [21]:

$$E_n \approx 30000[\chi(L) - \chi(M)]\,cm^{-1} \tag{4}$$

ν and ν' are the trigonal CF parameters. The spin-orbit (SO) coupling coefficients and the orbital reduction factors for the CF mechanism can be expressed as [22]:

$$\begin{aligned}
\zeta_{CF} &= N_t^a\{\zeta_d^0 + [\sqrt{2}\lambda_\pi^a\lambda_\sigma^a - (\lambda_\pi^a)^2/2 - \sqrt{2}w\,\lambda_\pi^a\lambda_s^a]\zeta_p^0\},\\
\zeta_{CF}' &= (N_t^aN_e^a)^{1/2}\{\zeta_d^0 + [\lambda_\pi^a\lambda_\sigma^a/\sqrt{2} + (\lambda_\pi^a)^2/2 - w\,\lambda_\pi^a\lambda_s^a/\sqrt{2}]\,\zeta_p^0\},\\
k_{CF} &= N_t^a[1 - (\lambda_\pi^a)^2/2 + \sqrt{2}\lambda_\pi^a\lambda_\sigma^a - 2\lambda_\sigma^aS_\sigma - 2\lambda_s^aS_s - 2\lambda_\pi^a\,S_\pi - \sqrt{2}w\lambda_\pi^a\lambda_s^a],\\
k_{CF}' &= (N_t^bN_e{}^a)^{1/2}[1 + (\lambda_\pi^a)^2/2 + \lambda_\pi^a\lambda_\sigma^a/\sqrt{2} - 4\lambda_\pi^aS_\pi - \lambda_\sigma^aS_\sigma - \lambda_s^aS_s - w\,\lambda_\pi^a\lambda_s^a/\sqrt{2}],\\
P_{CF} &= N_t^aP_0, \quad P_{CF}' = (N_t^aN_e^a)^{1/2}P_0.
\end{aligned} \tag{5}$$

These relevant quantities for the CT mechanism are [22]:

$$\begin{aligned}
\zeta_{CT} &= (N_t^bN_t^a)^{1/2}\left[\zeta_d^0 + \left(\frac{\lambda_\pi^a\lambda_\sigma^b + \lambda_\pi^b\lambda_\sigma^a}{\sqrt{2}} - \frac{\lambda_\pi^a\lambda_\pi^b}{2} - \sqrt{2w}\,\lambda_s^a\lambda_\pi^b\right)\zeta_p^0\right],\\
\zeta_{CT}' &= (N_t^bN_e^a)^{1/2}\left[\zeta_d^0 + \left(\frac{\lambda_\pi^a\lambda_\sigma^b}{\sqrt{2}} + \frac{\lambda_\pi^a\lambda_\pi^b}{2} - w\lambda_s^a\lambda_\pi^b/\sqrt{2}\right)\zeta_p^0\right],\\
k_{CT} &= (N_t^bN_t^a)^{1/2}[1 - \frac{\lambda_\pi^a\lambda_\pi^b}{2} + \frac{\lambda_\pi^a\lambda_\sigma^b + \lambda_\pi^b\lambda_\sigma^a}{\sqrt{2}} - (\lambda_s^a + \lambda_s^b)S_s - (\lambda_\sigma^a + \lambda_\sigma^b)S_\sigma\\
&\quad - (\lambda_\pi^a + \lambda_\pi^b)S_\pi - \sqrt{2}w\lambda_s^a\lambda_\pi^b],\\
k_{CT}' &= (N_t^bN_e^a)^{1/2}\left[1 + \frac{\lambda_\pi^a\lambda_\pi^b}{2} + \frac{\lambda_\pi^a\lambda_\sigma^b}{\sqrt{2}} - 3\lambda_\pi^aS_\pi - \lambda_\pi^bS_\pi - \lambda_\sigma^bS_\sigma - \lambda_s^bS_s\right.\\
&\quad \left. - w\lambda_s^a\lambda_\pi^b/\sqrt{2}\right],\\
P_{CT} &= N_t^aN_t^bP_0, \quad P_{CT}' = (N_t^bN_e^a)^{1/2}P_0.
\end{aligned} \tag{6}$$

where $\zeta_d{}^0$ and $\zeta_p{}^0$ are the SO coupling coefficients of the free 3d^7 and ligand ions, respectively. $N_\gamma{}^x$ and $\lambda_j{}^x$ stand for the normalization coefficients and the orbital admixture factors. The subscripts γ (= t and e) are the irreducible representations T$_2$ and E of T$_d$ group, j (=π, σ and s) labels the various components of the metal 3d and ligand orbitals, and the superscripts x (= a and b) denote the anti-bonding and bonding orbitals, respectively. S_j are the group overlap integrals between the corresponding components of metal 3d and ligand p or s orbitals, with the approximate proportionality relationship $\lambda_\sigma{}^a/S_\sigma \approx \lambda_s{}^a/S_s$ for the same σ component. w denotes the integral $R\langle ns|\frac{\partial}{\partial y}|np_y\rangle$ and R is the reference impurity-ligand distance. The relevant molecular orbital coefficients $N_\gamma{}^x$ and $\lambda_j{}^x$ can be determined from the cluster approach [22] by using the normalization conditions for both anti-bonding and bonding orbitals, the orthogonalization relationships between the anti-bonding and bonding orbitals and the approximation relationships for the anti-bonding orbitals related to the covalency factor N.

For the host Zn^{2+} sites in ZnO microwires, thin films and bulks, there are one oxygen ligand in the C$_3$ axis with the bond length R$_1$ and three oxygen forming the ligand triangle with the bond length R$_2$ and the bond angle β between R$_2$ and the C$_3$ axis (see Fig. 1). From the superposition model [23–25], the trigonal CF parameters can be