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Local structure distortion and spin Hamiltonian parameters of oxide-diluted magnetic semiconductor Mn-doped ZnO*

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The local structure distortion, the spin Hamiltonian (SH) parameters, and the electric fine structure of the ground state for $Mn^{2+}(3d^5)$ ion in ZnO crystals are systematically investigated, where spin–spin (SS), spin–other–orbit (SOO) and orbit–orbit (OO) magnetic interactions, besides the well-known spin–orbit (SO) coupling, are taken into account for the first time, by using the complete diagonalization method. The theoretical results of the second-order zero-field splitting (ZFS) parameter D, the fourth-order ZFS parameter (a-F), the Zeeman g-factors: $g_{//}$ and $g_{\perp}$, and the energy differences of the ground state: δ_1 and δ_2 for Mn^{2+} in Mn^{2+}: ZnO are in good agreement with experimental measurements when the three O^{2-} ions below the Mn^{2+} ion rotate by 1.085° away from the [111]-axis. Hence, the local structure distortion effect plays an important role in explaining the spectroscopic properties of Mn^{2+} ions in Mn^{2+}: ZnO crystals. It is found for Mn^{2+} ions in Mn^{2+}: ZnO crystals that although the SO mechanism is the most important one, the contributions to the SH parameters, made by other four mechanisms, i.e. SS, SOO, OO, and SO∼SS∼SOO∼OO mechanisms, are significant and should not be omitted, especially for calculating ZFS parameter D.

Keywords: Mn^{2+}: ZnO crystal, spin Hamiltonian (SH) parameter, local structure distortion, magnetic interaction

PACC: 7510D, 7630F, 7170C, 7170E

1. Introduction

ZnO, a II–VI semiconductor, is a well-known piezoelectric and electro-optic material with a wide direct band gap (3.37ev).[1] Doing ZnO with transitional metal elements leads to its many interesting properties. Currently, much experimental and theoretical research[2−5] is focused on dilute magnetic semiconductors (DMS) based on ZnO doped with transitional metal (TM) ions such as Mn, Fe, and Co, since the predicted room temperature ferromagnetism in DMS may be useful in spintronics. TM ions such as Mn^{2+} and Fe^{2+} are active ions in DMS materials. These impurity ions in the materials play a major role because they can modify properties of the materials. Obviously, an understanding of the local structure and the electric fine structure of the ground state for Mn^{2+} in Mn^{2+}: ZnO crystals is very important. However, the information about the local structure and the electronic structure of the ground state Mn^{2+} in ZnO is lacking. The spin-Hamiltonian (SH) parameter[6−8] is a physical parameter which can describe the magnetic and spectroscopic properties of TMs in crystal material such as DMS materials. And it can reflect very sensitively even small variations in coordination of the paramagnetic centres,[9−11] so that the study of the SH parameters of TM ions in crystals can provide a microscopic insight into crystal structure, order-disorder or phase transitions, pressure behaviour as well as the observed magnetic and spectroscopic properties.[12−15]

To probe the local structure distortion, the SH parameters and the electric fine structure of the ground state Mn^{2+} in Mn^{2+}: ZnO crystals, the relationship between the SH parameters and the crystal structure of Mn^{2+} in ZnO has been established on the basis of the superposition model[16] and the complete diagonalization method (CDM).[17,18] By investigating the SH parameters including the zero-field splitting parameters (D, a-F) and Zeeman g factors ($g_{//}$, $g_{\perp}$) as well as the electric fine structure of the ground state Mn^{2+} in Mn^{2+}: ZnO crystals, the local struc-

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ture distortion and the microscopic origins of the spin-Hamiltonian parameters for Mn^{2+} ions in ZnO materials are investigated. It is shown that there exists a slight local structure distortion for Mn^{2+} ions in ZnO materials

2. Theoretical background

Recently, a Complete Diagonalization Method/ Microscopic Spin Hamiltonian (CDM/MSH) program (Visual Basic version),[19] where the spin–spin (SS), the spin–other–orbit (SOO), and the orbit–orbit (OO) magnetic interactions are also taken into account besides the well-known spin–orbit (SO) magnetic interaction, has been developed for the microscopic calculation of the ZFS parameter D, the g-factors ($g_{//}$ and $g_{\perp}$) and the optical spectra for $3d^3$ ions in an axially symmetric crystal field (CF) including the tetragonal symmetry type I (C_{4v}, D_{2d}, D_4, D_{4h}) and the trigonal symmetry type I (C_{3v}, D_3, D_{3d}) as a function of CF parameters. The CDM/MSH program and the Crystal Field Analysis/Microscopic Spin Hamiltonian (CFA/MSH) computer package have obtained the same results if the microscopic states for $3d^3$ ions are all considered in the axial symmetry including trigonal symmetry and tetragonal symmetry. The CFA/MSH computer package in free ion irreducible representation basis for a spherical symmetry group is based on the Visual Basic version of CFA package developed by Yeung and Rudowicz,[20,21] and Rudowicz *et al.*[22] The CDM/MSH program in irreducible representation basis of the axially symmetric point group for $3d^{3/7}$ ions is based on our developed Fortran version.[23,24] The present version of the CDM/MSH program has been extended to the case where included are $3d^5$ ions in an axially symmetric crystal field including the tetragonal symmetry type I (C_{4v}, D_{2d}, D_4, D_{4h}) and the trigonal symmetry type I (C_{3v}, D_3, D_{3d}). The CDM/MSH program can be used to study not only the energy levels and the full configuration mixed wavefunctions but also the SH parameters including Zero-field splitting (ZFS) parameters D and (a-F) as well as Zeeman g factors $g_{//}$ and $g_{\perp}$. The SH parameters are known to reflect very sensitively even small variations in coordination of the TM impurity ions in crystal materials. Thus the theoretical studies of the SH and CF parameters can provide a microscopic insight into the crystal structure and the structural disorder.

In the intermediate crystal field coupling scheme, the Hamiltonian of a $3d^5$ ion can be written as

$$H = H_{ee}(B, C) + H_{CF}(B_{kq}) + H_m, \tag{1}$$

where H_{ee} is the electrostatic interaction, H_{CF} is the CF potential, H_m is the magnetic interaction. In general, $H_{ee} > H_{CF} > H_m$ for $3d^N$ ions. The magnetic interaction H_m can be written as

$$\begin{aligned} H_m = {} & H_{SO}(\zeta) + H_{SS}(M_{ss}^{(k)}) + H_{SOO}(M_{soo}^{(k)}) \\ & + H_{OO}(M_{oo}^{(k)}), \end{aligned} \tag{2}$$

where H_{SO} is the SO magnetic interaction, H_{SS} is the SS magnetic interaction, H_{SOO} is the SOO magnetic interaction, and H_{OO} is the OO magnetic interaction. All symbols appearing in expressions (1) and (2) have their own conventional meanings. It is found[25] that for d^N configurations, $M_{ss}^{(k)} = M_{soo}^{(k)} \equiv M_{oo}^{(k)} \equiv M^{(k)}$ for $k = 0$ and 2. The explicit forms of expressions (1) and (2) have been given in Refs.[26, 27].

The number of states of five particles on a 3d-level is 252 in total. These states can be labelled by the conventional quantum numbers for total spin and angular momentum. The CDM/MSH program constructs a complete 252×252 energy matrix for the $3d^5$ ions at trigonal symmetry sites and, for the first time, includes the SS, SOO, and OO magnetic interactions[27−29] that were omitted in the previous studies. The complete energy matrix in trigonal symmetry can be separated into three small matrices, i.e. $E^{/}\alpha^{/}(84 \times 84)$, $E^{/}\beta^{/}(84 \times 84)$, and $E^{//}(84 \times 84)$. Details concerning the choice of the basis and the calculation of the pertinent matrix elements may be found in Refs.[23, 24, 26, 30] The Hamiltonian matrices obtained in this way are the functions of the Racah parameters B and C, CF parameter B_{kq} (in the Wybourne notation),[27] SO constant ξ_d, and SS, SOO and OO parameters $M^{(0)}$ and$M^{(2)}$. Provided that the values of these microscopic parameters are available, the diagonalization of the full Hamiltonian matrices yields the energy levels and eigenvectors. Under the trigonally symmetric crystal field, the ground state $3d^5(^6S)$ eigenvector obtained in this way is a mixture of 252 states of $3d^5$.

The free-ion ^6S ground term of $3d^5$ ions (e.g. Mn^{2+}) is not spilt by the C_{3v} symmetry CF, whereas the magnetic interaction (expression (2)) split this state into the spin states $E^{/}(\tilde{M}s = \pm 1/2)$, $E^{/}(\tilde{M}s = \pm 5/2)$ and $E^{//}(\tilde{M}s = \pm 3/2)$, where $\tilde{M}s$ denotes the effective spin. The process can be described in Fig.1.

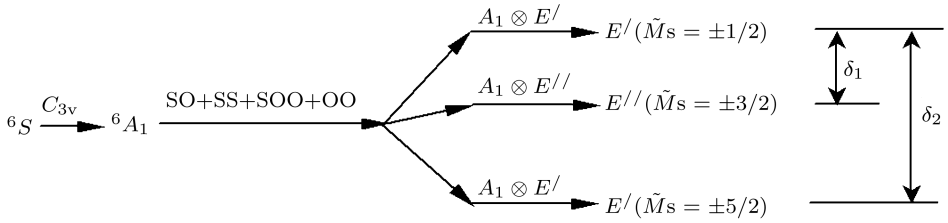


Fig.1. Schematic splitting of the ground term of $3d^5$ ions in the C_{3v} symmetry CF.

The effective spin Hamiltonian for $3d^5$ ions at trigonal symmetry sites, which takes into account the ZFS term and the Zeeman term, can be written as[6,31]

$$\begin{aligned} H_S =& \mu_B g_{//} B_z S_z + \mu_B g_\perp (B_x S_x + B_y S_y) \\ &+ D\left[S_z^2 - \frac{1}{3}S(S+1)\right] \\ &+ \frac{1}{6}a[S_\xi^4 + S_\eta^4 + S_\zeta^4 \\ &- \frac{1}{5}S(S+1)(3S^2+3S-1)] \\ &+ \frac{1}{180}F[35S_z^4 - 30S(S+1)S_z^2 \\ &+ 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2], \end{aligned} \quad (3)$$

where $g_{//}$ and $g_\perp$ are Zeeman g-factors, the D, a, and F are ZFS parameters.

For trigonal symmetry, the diagonalization of the matrix of expression (1) yields the actual fine-structure energy levels e_i (i = 1, 2, 3) of the ground orbital singlet ($S = 5/2$), i.e. the actual ZFS for $3d^5$ ions at trigonal symmetry sites. On the other hand, in the zero magnetic field, i.e. $B = 0$, the eigenvalues of the effective SH (expression (3)) matrix within the effective spin states $|S = 5/2, M_S\rangle$ can be solved as[32]

$$\begin{aligned} \varepsilon_1 =& \frac{1}{3}D - \frac{1}{2}(a-F) \\ &+ \frac{1}{6}\{(18D + a - F)^2 + 80a^2\}^{1/2}, \end{aligned} \quad (4a)$$

$$\varepsilon_2 = -\frac{2}{3}D + (a-F), \quad (4b)$$

$$\begin{aligned} \varepsilon_3 =& \frac{1}{3}D - \frac{1}{2}(a-F) \\ &- \frac{1}{6}\{(18D + a - F)^2 + 80a^2\}^{1/2}, \end{aligned} \quad (4c)$$

where ε_1, ε_2, and ε_3 are the doublets, corresponding to the spin states φ_j (j = 1, 2, 3), respectively. These spin states can be expressed as[32]

$$\varphi_1 = \cos\gamma|\pm 5/2\rangle \mp \sin\gamma|\mp 1/2\rangle, \quad (5a)$$

$$\varphi_2 = |\pm 3/2\rangle, \quad (5b)$$

$$\varphi_3 = \sin\gamma|\pm 5/2\rangle \pm \cos\gamma|\mp 1/2\rangle, \quad (5c)$$

where $\gamma = (1/2)\arctan[\sqrt{80}a/(a - F + 18D)]$.

The equivalences of the actual energies e_i in expression (1) and the effective energies ε_j in expressions (4a)–(4c) have been utilized in the projection method to derive the SH expressions for the ZFS parameters. For trigonal symmetry, the number of available ZFS transitions obtained from the complete diagonalization method (CDM) is two, whereas that of the non-zero ZFS parameters is three. Since the number of available ZFS transitions is insufficient to determine all non-zero ZFS parameters, an approximation has to be made. If the value of parameter $\tan(2\gamma)$ is very small, the ZFS parameters D and a-F are obtained as follows:

$$D = \frac{1}{28}(5\delta_2 - \delta_1), \quad (6a)$$

$$a - F = \frac{3}{14}(3\delta_1 - \delta_2), \quad (6b)$$

where the energy differences δ_1 and δ_2 (see Fig.1) can be expressed as

$$\delta_1 = \varepsilon_2(|\tilde{M}s = \pm 3/2\rangle) - \varepsilon_3(|\tilde{M}s = \pm 1/2\rangle), \quad (7a)$$

$$\delta_2 = \varepsilon_1(|\tilde{M}s = \pm 5/2\rangle) - \varepsilon_3(|\tilde{M}s = \pm 1/2\rangle). \quad (7b)$$

The experimental data[33,34] yield a very small value of $\tan(2\gamma)(\cong -0.014)$ for Mn^{2+} in ZnO crystals, Thus, expressions (6a) and (6b) provide a good approximation. It can be seen from expressions (6a) and (6b) that the ZFS parameters D and a-F can be obtained as long as the energy differences δ_1 and δ_2 in expressions (6a) and (6b) are known by using the CDM.

By means of the matrix element equivalence[19] between the effective Zeeman term in expression (3) and the real physical Zeeman interaction term, the following formulae are obtained:

$$g_{//} = 2\{k\langle\psi_{+1/2}|L_0^{(1)}|\psi_{+1/2}\rangle + g_e\langle\psi_{+1/2}|S_0^{(1)}|\psi_{+1/2}\rangle\}, \tag{8a}$$

$$g_{\perp} = \frac{\sqrt{2}}{3}\{k(\langle\psi_{+1/2}|L_{-1}^{(1)}|\psi_{-1/2}\rangle - \langle\psi_{+1/2}|L_{+1}^{(1)}|\psi_{-1/2}\rangle) + g_e(\langle\psi_{+1/2}|S_{-1}^{(1)}|\psi_{-1/2}\rangle - \langle\psi_{+1/2}|S_{+1}^{(1)}|\psi_{-1/2}\rangle)\}, \tag{8b}$$

where k is the orbital reduction factor for the orbital angular momentum L. The matrix elements of the irreducible tensor operators in expressions (8a) and (8b) are obtained by using the Wigner–Eckart theorem.[22,35,36] The $\psi_{\pm 1/2}$ denote the eigenfunctions of the ground state, which can be obtained by diagonalizing the complete Hamiltonian matrix. They can be written as

$$|\psi_{1/2}\rangle = \sum_{i=1}^{84} a_i\,|\varphi_i\rangle = a_1\left|{}^6S, \frac{1}{2}\right\rangle + a_2\left|{}^6S, -\frac{5}{2}\right\rangle + \text{smaller contributions arising from the } \ S = \frac{3}{2}, \tag{9a}$$

$$|\psi_{-1/2}\rangle = \sum_{i=1}^{84} b_i\,|\varphi_i\rangle = b_1\left|{}^6S, -\frac{1}{2}\right\rangle + b_2\left|{}^6S, \frac{5}{2}\right\rangle + \text{smaller contributions arising from the } \ S = \frac{3}{2}, \tag{9b}$$

where $a_1 \gg a_2$ and $b_1 \gg b_2$.

3. Spin-Hamiltonian parameters for Mn^{2+} in ZnO

In order to investigate the SH parameters and the electric structure of the ground state for the Mn^{2+} ions at Zn sites in ZnO, we need the values of parameters B, C, ξ, B_{20}, B_{40}, B_{43}, $M^{(0)}$, $M^{(2)}$ and k defined in Section 2. For Mn^{2+} ions in ZnO crystal, the values of the following parameters had been obtained from optical spectra: $B = 720\,\mathrm{cm}^{-1}$, $C = 2710\,\mathrm{cm}^{-1}$, and the cubic CF parameter $Dq = -650\,\mathrm{cm}^{-1}$, which were adopted in an earlier study.[37] The SS or SOO or OO parameters $M^{(0)} = 1.4358\mathrm{cm}^{-1}$ and $M^{(2)} = 0.7846\,\mathrm{cm}^{-1}$ for $Mn^{2+}(3d^5)$ ions from atomic data[38] are adopted in our calculations. To evaluate the orbital reduction factor k and the spin–orbit coupling constant ξ_d, we use the relation[39,40] $N^2 \approx (\sqrt{B/B_0} + \sqrt{C/C_0})/2$, where $B_0 = 960\,\mathrm{cm}^{-1}$ and $C_0 = 3325\,\mathrm{cm}^{-1}$[41] are the Racah parameters of a free Mn^{2+} ion. Thus, we obtain $k \approx N^2 \approx 0.884$ and, using the free Mn^{2+} ion value $\xi_0 = 347\,\mathrm{cm}^{-1}$[41] yields $\xi_d \approx N^2\xi_0 = 307\,\mathrm{cm}^{-1}$. Having fixed the values of the microscopic parameters B, C, ξ_d, $M^{(0)}$, $M^{(2)}$ and k, the theoretically predicted SH parameters, i.e. D, a, F, $g_{//}$ and $g_{\perp}$, become functions of only the CF parameters B_{20}, B_{40}, and B_{43}, which in turn may be directly related to the local structure of the Mn^{2+} in ZnO crystals. Hence, the theoretical SH and structural parameters can be modelled via the CF parameters. This enables us to study theoretically the local structure distortion around Mn^{2+} centres in ZnO crystals.

3.1. Local structure model and CF parameters

Pure ZnO crystal has a hexagonal wurtzite structure,[42] where metal ion Zn^{2+} is surrounded by an almost-regular tetrahedron of oxygen ions. The metal site has a trigonal symmetry (C_{3v}) as indicated in Fig.2. The Mn ion is understood to occupy the Zn site without changing the wurtzite structure.[5,33,43] To obtain the CF parameters B_{20}, B_{40}, and B_{43}, we establish the relationships between the CF parameters and crystal structure parameters by using the superposition model (SPM).[16] For a tetrahedron with symmetry C_{3v}, the CF parameters are derived as

$$\begin{aligned}
B_{20} &= 2\bar{A}_2\left(\frac{R_0}{R_1}\right)^{t_2} + 3\left(\frac{R_0}{R_2}\right)^{t_2}(3\cos^2\theta - 1),\\
B_{40} &= 8\bar{A}_4\left(\frac{R_0}{R_1}\right)^{t_4} + 3\left(\frac{R_0}{R_2}\right)^{t_4}\\
&\quad\times(35\cos^4\theta - 30\cos^2\theta + 3),\\
B_{43} &= 6\sqrt{35}\bar{A}_4\left(\frac{R_0}{R_2}\right)^{t_4}\sin^3\theta\cos\theta,
\end{aligned} \tag{10}$$

where R_i is the metal-ligand distance, θ is the angle between the R_2 and the [111]-axis (see Fig.2), and R_0 is the reference distance. t_k is the power-law exponent and $\bar{A}_k$ is the intrinsic parameter.[16] For ionic crystals, we take the power-law exponents $t_2 = 3$, and $t_4 = 5$.[16] $\bar{A}_4$ can be found from the relation for the cubic CF parameter Dq to be about $-27Dq/16$, i.e. $\bar{A}_4 \approx -27Dq/16$, and the ratio $\bar{A}_2/\bar{A}_4$ tends to a constant value for the iron-group ions.[44–46] Hence, we take $\bar{A}_2/\bar{A}_4 \approx 10.8$.[46]

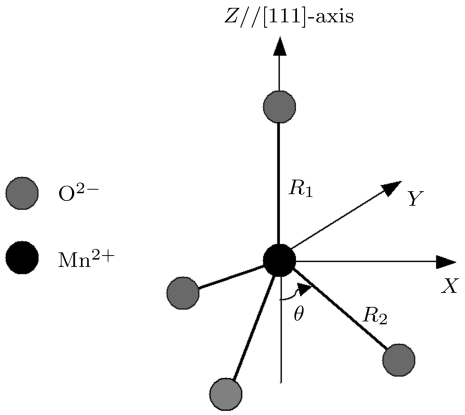


Fig.2. Local structure model of Mn^{2+} ion in Mn^{2+}: ZnO crystal.

3.2. Spin-Hamiltonian parameters and local structure distortion

Owing to the differences in mass and ionic radius between Mn^{2+} and Zn^{2+}, the mutual interaction between the Mn^{2+} ion and the surrounding O^{2-} ions in the doped ZnO crystals must differ from that between Zn^{2+} ion and O^{2-} ions in the host crystals. Thus the bond-lengths, R_1 and R_2, and the bond-angle, θ, in the doped crystals must differ from those ($R_{H1} = 0.1992\,nm$, $R_{H2} = 0.1976\,nm$ $\theta_0 = 71.86$)[47] in the host crystals. The values of R_1 and R_2 in the doped crystals can be estimated from the approximate formula $R_i \approx R_{Hi} + (R_i - R_h)/2$[48,49] where r_i and r_h are the ionic radii for the impurity and the host ion, respectively. We adopt the values: $R_{H1} = 0.1992\,nm$, $R_{H2} = 0.1976\,nm$, $r_i(Mn^{2+}) = 0.080\,nm$[50] and $r_h(Zn^{2+}) = 0.074\,nm$.[51] The reference distance R_0 is approximated as $R_0 \approx (R_1 + R_2)/2$. Having fixed the values of R_0, R_1 and R_2, the theoretically predicted SH parameters D, a-F, $g_{//}$ and $g_\perp$ as well as the energy differences become functions of only the bond-angle θ. Hence, the investigation of the SH parameters and electric structure of the ground state Mn^{2+} in ZnO crystals can give a better insight into the variation of these parameters with the bond-angle θ. In general, the 'local structure distortion' is described by the distortion angle, namely, $\Delta\theta = \theta - \theta_0$.

The SH parameter D and the energy differences δ_1 and δ_2 predicted in this way are plotted in Figs.3 and 4 as a function of distortion angle $\Delta\theta$, respectively. The experimental[33,34] values $D = -235.5 \times 10^{-4}\,cm^{-1}$, $\delta_1 = -462.01 \times 10^{-4}\,cm^{-1}$, and $\delta_2 = -1411.33 \times 10^{-4}\,cm^{-1}$ which are plotted as horizontal lines in Figs.3 and 4 for Mn^{2+} in ZnO crystals provide a direct comparison among the various options considered in the present calculations. The theoretical results of D, δ_1, δ_2, a-F, $g_{//}$, and $g_\perp$ for the three cases considered are listed in Table 1 together with the experimental data for Mn^{2+}: ZnO. It is found that the second-order ZFS parameter D and the energy differences: δ_1 and δ_2 are very sensitive to the change in distortion angle $\Delta\theta$, whereas the fourth-order ZFS parameter (a-F) and the Zeeman g-factors: $g_{//}$ and $g_\perp$ are insensitive to the change in distortion angle $\Delta\theta$. Ignoring the structural distortions yields remarkably smaller values of D, δ_1 and δ_2 than the experimental ones (see row (A) of Table 1). It is found that $D_{cal.}/D_{exp.} = 0.39$, $(\delta_1)_{cal.}/(\delta_1)_{exp.} = 0.38$, and $(\delta_2)_{cal.}/(\delta_2)_{exp.} = 0.39$. On the other hand, for the same symmetry but with the structural distortions included, the predicted the second-order ZFS parameter D, the fourth-order ZFS parameter (a-F), the Zeeman g-factors: $g_{//}$ and $g_\perp$, and the energy differences: δ_1 and δ_2 are much closer to the experimental ones (see row (C) in Table 1) for

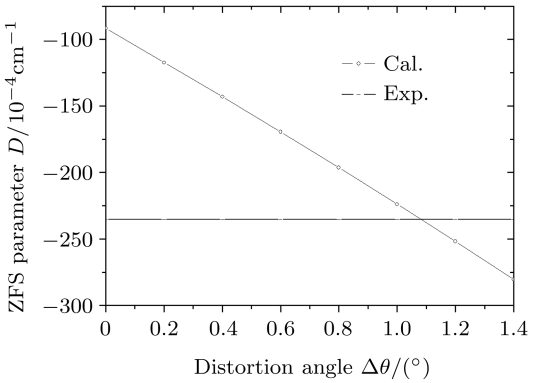


Fig.3. Zero-field splitting parameter D of Mn^{2+} ions in ZnO crystal as a function of distortion angle $\Delta\theta$.

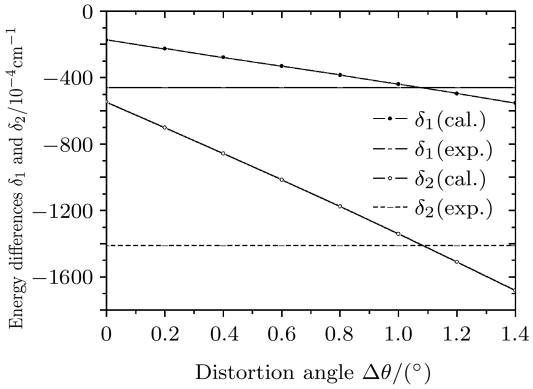


Fig.4. Energy differences δ_1 and δ_2 of the ground states for Mn^{2+} ions in ZnO crystal as a function of distortion.

the ground state Mn^{2+} in ZnO crystals. Our calculations reveal that the calculated parameters D, (a-F), $g_{//}$, $g_{\perp}$, δ_1 and δ_2 are in excellent agreement with the measured ones for the distortion angle $\Delta\theta = 1.085°$. This indicates that local structure distortions do occur and play a significant role in making contributions to the parameters D, (a-F), $g_{//}$, $g_{\perp}$, δ_1 and δ_2 of the ground state Mn^{2+} in ZnO crystals.

Table 1. SH parameters D, a-F, δ_1, δ_2 (all in units of $10^{-4}\,cm^{-1}$) and Zeeman g factor $g_{//}$, $g_{\perp}$ for Mn^{2+} ions in ZnO single crystal.

	δ_1	δ_2	D	a-F	$g_{//}$	$g_{\perp}$
(A)	–174.61	–547.17	–91.47	5.00	1.9999	2.0015
(B)	–524.69	–1595.28	–266.13	4.55	2.0016	2.0018
(C)	–463.57	–1412.77	–235.72	4.73	2.0015	2.0018
Expt.[33]	–462.01	–1411.33	–235.5	5.437	1.9984±0.0002	1.9998±0.0002
Expt.[34]	–441.21±20	–1349.21±60	–225.15±10	5.5	2.0012±0.0001	2.0012±0.0001

(A): without distortion but with SO, SS, SOO, and OO magnetic interactions,
(B): with both distortion and SO magnetic interaction,
(C): with distortion as well as SO, SS, SOO, and OO magnetic interactions.

3.3. The microscopic origin of ZFS parameters for ^{6}S state ion

In order to study the microscopic origin of ZFS parameters for ^{6}S state ions in a trigonal symmetry crystal field, we calculate the ZFS parameters D and (a-F) by using the CDM/MSH program. The results are listed in Table 2. In calculating, the parameters $B = 720\,cm^{-1}$, $C = 2710\,cm^{-1}$, $\xi_d = 307\,cm^{-1}$, $M^{(0)} = 1.4385\,cm^{-1}$, $M^{(2)} = 0.7846\,cm^{-1}$, $B_{20} = -3252.6\,cm^{-1}$, B_{40}= $10772.4\,cm^{-1}$, and $B_{43} = 10077.9\,cm^{-1}$ for Mn^{2+} in ZnO crystals are adopted. When the SO, SS, SOO, and OO interactions are all simultaneously taken into account, the SH parameters D, and (a-F) can be expected to arise from four mechanisms, i.e. SO, SS, SOO, and OO mechanisms, which can be denoted by Y_{SO}, Y_{SS}, Y_{SOO}, Y_{OO}, ($Y = D$, (a-F)), respectively. However, our investigations show that $Y_{Total} \neq Y_{SO} + Y_{SS} + Y_{SOO} + Y_{OO}$, (see Table 2). The result implies that there is a combined effect of the four magnetic interactions. The combined effect is accordingly called the combined SO∼SS∼SOO∼OO mechanism. The role of the combined SO∼SS∼SOO∼OO mechanism involving mixed transitions between the CF states due to these interactions can be accounted for by the difference

$$\begin{aligned} &Y_{SO\sim SS\sim SOO\sim OO} \\ &= Y_{Total} - (Y_{SO} + Y_{SS} + Y_{SOO} + Y_{OO}) \end{aligned} \quad (11)$$

for parameters D and (a-F). Hence the SH parameter Y_{Total}(= D, (a-F)) can be given as

$$\begin{aligned} Y_{Total} = {} & Y_{SO} + Y_{SS} + Y_{SOO} + Y_{OO} \\ & + Y_{SO\sim SS\sim SOO\sim OO}. \end{aligned} \quad (12)$$

Table 2. Contributions to ZFS parameters D and (a-F) from SO, SS, SOO, and OO magnetic interactions for ^{6}S state ions in a trigonal symmetry crystal field (all in units of $10^{-4}\,cm^{-1}$).

parameters	(A)	(B)	(C)	(D)	(E)	(F)	(G)	(H)
D	–266.13	–0.2	–0.37	0	–248.98	–251.55	–267.37	–235.72
(a-F)	4.55	0.03	0	0	5.14	4.1	4.58	4.73

(A) only with SO; (B) only with SS; (C) only with SOO; (D) only with OO; (E) with SO and SS; (F) with SO and SOO; (G)with SO and OO; (H) with SO, SS, SOO, and OO.

In order to show the importance of the other four mechanisms (i.e. SS, SOO, OO, and SO∼SS∼SOO∼OO) making contributions to the ZFS parameters compared with the SO interaction, it is convenient to define a percentage ratio as

$$\eta_X = \frac{|Y_{Total} - Y_{SO}|}{|Y_{Total}|} \times 100\%. \quad (13)$$

It is found from Table 2 that the contributions to the ZFS parameters, made by the other four mechanisms, i.e. SS, SOO, OO, and SO∼SS∼SOO∼OO mechanisms for Mn^{2+} in ZnO crystals, are 12.9% for D and 3.8% for (a-F). In a word, although the SO mechanism is the most important one, the contributions to the ZFS parameters, made by the other four mech-

anisms, are appreciable and should not be omitted, especially for calculating ZFS parameter D.

4. Summary

In the doped Mn^{2+}: ZnO crystals, the Mn^{2+} impurity ions are substituted for Zn^{2+}. The differences in mass and ionic radius between Mn^{2+} and Zn^{2+} induce the local structural distortion around the Mn^{2+} ions. To probe the local structure distortion and the electric fine structure of the ground state Mn^{2+} in ZnO crystals, the relationship between the SH parameters and the crystal structure of Mn^{2+}: ZnO is established on the basis of the superposition model and the complete diagonalization method (CDM). The calculated parameters, i.e. the second-order ZFS parameter D, the fourth-order ZFS parameter (a-F), the Zeeman g-factors: $g_{//}$ and $g_{\perp}$, and the energy differences: δ_1 and δ_2 of the ground state Mn^{2+} in Mn^{2+}: ZnO are shown to be in good agreement with experimental measurements when the three O^{2-} ions below the Mn^{2+} ion rotate by 1.085° away from the [111]-axis. Hence, the local structure distortion effect plays an important role in explaining the spectroscopic properties of Mn^{2+} ions in Mn^{2+}: ZnO crystals. It is worthwhile to point out that the information concerning the local structure distortion in Fe^{3+}: $KZnF_3$ has been gained from electron-nuclear double-resonance (ENDOR) experiments by Krebs and Jeck.[52] They have found that the front three ligand F^- ions around Fe^{3+} ion rotate $2.8° \pm 0.3°$ away from the [111]-axis while the rear three ligand F^- ions around Fe^{3+} ion rotate $1.1° \pm 0.3°$ toward it. Hence, the distortion angle $\Delta\theta = 1.085°$ predicted based on the investigations of the SH parameters and the electric fine structure of the ground state Mn^{2+} in Mn^{2+}: ZnO crystals is acceptable and can be verified by ENDOR studies. This finding has also been confirmed theoretically through the microscopic spin Hamiltonian approach.[53] A similar suggestion has been made for Fe^{3+} in α-LiO_3[48] and Cr^{2+} in ZnS crystals.[54] On the other hand, it is found for Mn^{2+} ions in Mn^{2+}: ZnO crystals that although the SO mechanism is the most important one, the contributions to the SH parameters, made by other four mechanisms, i.e. SS, SOO, OO, and SO∼SS∼SOO∼OO mechanisms, are appreciable and should not be omitted, especially for calculating ZFS parameter D. This work indicates that the CF theory including the SO, SS, SOO, and OO magnetic interactions can provide a satisfactory explanation for the SH parameters and the electric fine structure of $d^5(^6S)$ ions in trigonal crystal fields.

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