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Theoretical investigation of the local lattice structure of Mn^{2+} ion doped in tetragonal K_2ZnF_4 crystal

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Abstract. The complete energy matrices(252×252) for a d^5configuration ion in a tetragonal ligand-field has been constructed on the basis of the complete set of basis $|L, S, M_L, M_S\rangle$ of d^5configuration (252 dimension), and the relationship between the low-symmetry EPR parameters b_2^0, b_4^0 and the local distortion parameters has been established based on the complete energy matrices. As an application, we have studied the EPR parameters and the local lattice structure of Mn^{2+} ion doped in tetragonal K_2ZnF_4 system. The calculation indicated that the local lattice structure around a tetragonal Mn^{2+} ion center has an expansion distortion. Simultaneously, the local lattice structure parameters $R_1 = 2.0727$ Å, $R_2 = 2.0801$ Å at room temperature (295 K) and $R_1' = 2.0439$ Å, $R_2' = 2.05478$ Å at low temperature (4.2 K) are determined.

PACS. 71.70.Ch Crystal and ligand fields – 76.30.-v Electron paramagnetic resonance and relaxation

1 Introduction

The inter-relation between electronic and molecular structure is central to understanding physical and chemical processes. Transition-metal ions doped in most crystals are well known that strongly influence the electrical and optical properties of the system. In order to describe the various characteristics of transition-metal cluster, it is important to establish the relation between electronic and molecular structure. In the present work, the complete energy matrices (252×252) for a d^5configuration ion in a tetragonal ligand-field has been constructed on the basis of the complete set of basis of d^5 configuration (252 dimension), and the relationship between the low-symmetry EPR parameters b_2^0, b_4^0 and the local distortion parameters has been established based on the complete energy matrices. By this method, the local lattice structure for the Mn^{2+} ion doped in tetragonal K_2ZnF_4 system will be determined. As a typical ionic crystal, the fluoroperovskites doped with transition metal ions (Mn^{2+}, Fe^{3+}, Cr^{3+}, etc.) have been studied experimentally and theoretically by many workers [1–10]. For example, the EPR spectrum of Mn^{2+} ion doped in K_2ZnF_4system, which is very sensitive to distortion of the local lattice structure around the paramagnetic ion, had been measured by Folen at room temperature (295 K) [7] and Schrama at low temperature (4.2 K) [8], and the results show that the local lattice around the Mn^{2+} ion has tetragonal symmetry(D_{4h}). In order to understand the influence of impurity ion on the materials' property, the local lattice structure around the impurity ion in host crystal should be elucidated. To describe the ground-state splitting of d^5 configuration ion in a tetragonal ligand-field, the spin Hamiltonian should include EPR parameters b_2^0, b_4^0 and b_4^4 simultaneously. In this paper, the EPR zero-field-splitting parameters and the local structure distortion of Mn^{2+} ion centers in K_2ZnF_4 crystal will be studied with use of the complete energy matrices for a d^5configuration ion in a tetragonal ligand-field. The local lattice structure around a tetragonal Mn^{2+} center in the crystal is determined and the EPR parameters b_2^0, b_4^0 and b_4^4 also get a satisfactory explanation.

2 Theoretical model

2.1 EPR parameters in a tetragonal ligand-field

The EPR spectra of d^5configuration Mn^{2+} ion in a tetragonal ligand-field may be analyzed by employing the spin Hamiltonian [11,12]

$$\hat{H}_s = g\beta \boldsymbol{H} \cdot \boldsymbol{S} + \frac{1}{3} b_2^0 O_2^0 + \frac{1}{60}(b_4^0 O_4^0 + b_4^4 O_4^4) \qquad (1)$$

where $O_k^q\,(S_x, S_y, S_z)$ are the standard Stevens spin operators [13] and the Z axis is taken to be along the C_4 axis; b_n^m are EPR zero-field splitting parameters, among which b_4^4 corresponds to a fourth-order spin operator and stands for

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a cubic component of the tetragonal ligand-field; b_2^0, b_4^0 are, respectively, the second- and fourth-order spin operators, and denote a component of the crystalline electronic field that is axially symmetric about the C_4 axis. Solving the Hamiltonian (1) within the basis of states $\left|S=\frac{5}{2},M_s\right\rangle$, we obtain the energy eigenvalues of ground-state ${}^6A_1$for a zero magnetic field as follows:

$$\begin{aligned} E\left(\pm\tfrac{1}{2}\right) &= -\tfrac{8}{3}b_2^0+2b_4^0, \\ E\left(\pm\tfrac{3}{2}\right) &= \tfrac{4}{3}b_2^0-b_4^0\mp\left[(2b_2^0+2b_4^0)^2+\tfrac{1}{5}(b_4^4)^2\right]^{\frac{1}{2}}, \\ E\left(\pm\tfrac{5}{2}\right) &= \tfrac{4}{3}b_2^0-b_4^0\pm\left[(2b_2^0+2b_4^0)^2+\tfrac{1}{5}(b_4^4)^2\right]^{\frac{1}{2}}. \end{aligned} \tag{2}$$

Then, the zero-field splitting energies, $\varDelta E_1$ and $\varDelta E_2$ in the ground state ${}^6A_1$ can be explicitly expressed as a function of the EPR parameters b_2^0, b_4^0 and b_4^4:

$$\begin{aligned} \varDelta E_1 &= 4b_2^0-3b_4^0\pm\left[(2b_2^0+2b_4^0)^2+\tfrac{1}{5}(b_4^4)^2\right]^{\frac{1}{2}}, \\ \varDelta E_2 &= 4b_2^0-3b_4^0\mp\left[(2b_2^0+2b_4^0)^2+\tfrac{1}{5}(b_4^4)^2\right]^{\frac{1}{2}}. \end{aligned} \tag{3}$$

Herein, the upper signs and lower signs of "±" and "∓" in equations (2) and (3) correspond to $b_2^0 \geq 0$ and $b_2^0 < 0$, respectively. The EPR zero-field-splitting axial parameters b_2^0 and b_4^0 are due to the associated effect of the low-symmetry crystal field and the spin-orbit-coupling interaction among the sextet, quartets, and doublets; they are very sensitive to distortion of the octahedron [14,15], and can be determined by the splitting energy $\varDelta E_1$ and $\varDelta E_2$ which can be obtained by diagonalizing the complete energy matrices. It should be remarked that the parameters b_k^q are related to the D, a and Fused conventionally in the literature by the ralations [5,11,12]:

$$b_2^0 = D,\ b_4^0 = \frac{a}{2}+\frac{F}{3},\ b_4^4 = \frac{5}{2}a. \tag{4}$$

2.2 The complete energy matrices of the d^5 configuration in tetragonal ligand-field

The complete set of basis functions of d^5 configuration should include 252 basic Slater determinants $\varPhi_i$ such as $\varPhi_1 = |2^+,1^+,0^+,-2^+,-1^+|,\cdot\cdot\cdot,\varPhi_{252} = |2^-,1^-,0^-,-2^-,-1^-|$. Then, we can get the wave fuctions $|L,S,M_L,M_S\rangle_i$of d^5 configuration according to the expression:

$$|L,S,M_L,M_S\rangle_i = \sum_j C_j\varPhi_j. \tag{5}$$

The perturbation Hamiltonian for a d^5 configuration ion in a tetragonal ligand-field can be written as:

$$\hat{H} = \hat{H}_{ee}+\hat{H}_{so}+\hat{H}_{cf} = \sum_{i<j} e^2/r_{i,j}+\zeta\sum_i l_i\cdot s_i+\sum_i V_i \tag{6}$$

where $\hat{H}_{ee}$ denotes the electron-electron interactions,$\hat{H}_{so}$ denotes the spin-orbit coupling interactions, and $\hat{H}_{cf}$ denotes the ligand-field potentials. ζ is the spin-orbit coupling coefficient and V_i is the ligand-field potential:

$$\begin{aligned} V_i &= \gamma_{00}Z_{00}+\gamma_{20}r_i^2Z_{20}(\theta_i,\phi_i)+\gamma_{40}r_i^4Z_{40}(\theta_i,\phi_i) \\ &\quad+\gamma_{44}^c r_i^4Z_{44}^c(\theta_i,\phi_i)+\gamma_{44}^s r_i^4Z_{44}^s(\theta_i,\phi_i) \end{aligned} \tag{7}$$

where r_i, θ_i and φ_i are spherical coordinates of the ith electron. Z_{lm},Z_{lm}^c and Z_{lm}^s are defined as

$$\begin{aligned} Z_{l0} &= Y_{l0}, \\ Z_{lm}^c &= (1/\sqrt{2})[Y_{l,-m}+(-1)^mY_{l,m}], \\ Z_{lm}^s &= (i/\sqrt{2})[Y_{l,-m}-(-1)^mY_{l,m}]. \end{aligned} \tag{8}$$

The $Y_{l,m}$ in equation (8) are the spherical harmonics. γ_{l0},γ_{lm}^c and γ_{lm}^s are associated with the local lattice structure around d^5 configuration ion by the relations:

$$\begin{aligned} \gamma_{l0} &= -\tfrac{4\pi}{2l+1}\sum_{\tau=1}^{n}\tfrac{eq_\tau}{R_\tau^{l+1}}Z_{l0}(\theta_\tau,\varphi_\tau), \\ \gamma_{lm}^c &= -\tfrac{4\pi}{2l+1}\sum_{\tau=1}^{n}\tfrac{eq_\tau}{R_\tau^{l+1}}Z_{lm}^c(\theta_\tau,\varphi_\tau), \\ \gamma_{lm}^s &= -\tfrac{4\pi}{2l+1}\sum_{\tau=1}^{n}\tfrac{eq_\tau}{R_\tau^{l+1}}Z_{lm}^s(\theta_\tau,\varphi_\tau) \end{aligned} \tag{9}$$

where θ_τ and φ_τ are angular coordinates of the ligand. τ and q_τ represent the τth ligand ion and its effective charge, respectively. R_τ denotes the impurity-ligand distance.

Therefore, we can get the complete energy matrices $\langle L',M_L',S',M_S'|\,\hat{H}\,|L,M_L,S,M_S\rangle(252\times252)$ of d^5configuration in tetragonal ligand-field. The energy matrix elements are the function of the Racah parameters B and C, Trees correction α, Racah correction β, the spin-orbit coupling coefficient ζ and the ligand-field parameters that are in the following forms [16]:

$$\begin{aligned} B_{20} &= \left(\tfrac{5}{4\pi}\right)^{1/2}\gamma_{20}\langle r^2\rangle, \\ B_{40} &= \left(\tfrac{9}{4\pi}\right)^{1/2}\gamma_{40}\langle r^4\rangle, \\ B_{44}^c &= \left(\tfrac{9}{8\pi}\right)^{1/2}\gamma_{44}^c\langle r^4\rangle, \\ B_{44}^s &= i\left(\tfrac{9}{8\pi}\right)^{1/2}\gamma_{44}^s\langle r^4\rangle. \end{aligned} \tag{10}$$

For the tetragonal Mn^{2+} centers in $K_2ZnF_4:Mn^{2+}$ crystal, the local symmetry is D_{4h} point group. Based on the superposition model, when we consider the Z-axis as C_4 axis, the ligand-field parameter B_{44}^s will vanish and the other terms may be derived as

$$\begin{aligned} B_{20} &= 2A_2\left(\tfrac{1}{R_2^3}-\tfrac{1}{R_1^3}\right), \\ B_{40} &= \tfrac{1}{2}A_4\left(\tfrac{3}{R_2^5}+\tfrac{4}{R_1^5}\right), \\ B_{44}^c &= \left(\sqrt{\tfrac{35}{8}}\right)\tfrac{A_4}{R_1^5} \end{aligned} \tag{11}$$

where

$$A_2 = -eq_\tau\left\langle r^2\right\rangle, A_4 = -eq_\tau\left\langle r^4\right\rangle \text{ and } A_2/A_4 = \left\langle r^2\right\rangle/\left\langle r^4\right\rangle \tag{12}$$

where R_1 stands for the bond length of Mn^{2+}–F^- in the plane which perpendicular to the chosen Z axis, R_2 is the bond length of Mn^{2+}–F^- along the Z axis (see Fig. 1). The A_2,A_4 values which are almost the constants for the $(MnF_6)^{4-}$ cluster, can be obtained from the optical spectra and the Mn^{2+}-F^- bond length of the MnF_2 crystal. In the earlier works, the crystal structure and optical spectra of MnF_2 have been detailedly reported [17–19], so from the optical spectra we determine the covalency factor $N = 0.98496$ and $A_4 = 20.7868$ a.u. for $(MnF_6)^{4-}$

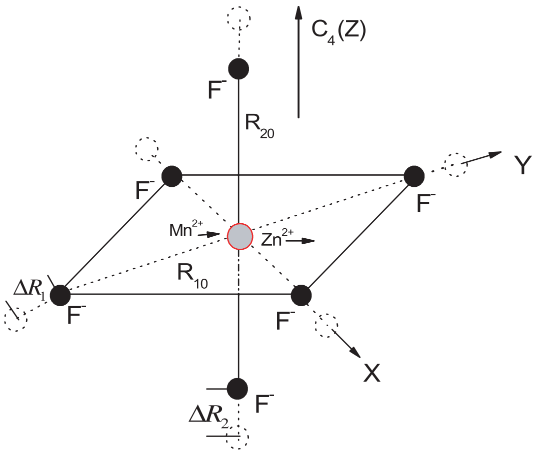

Fig. 1. Local structure distortion of Mn^{2+} in the K_2ZnF_4:Mn^{2+} system. R_{10} and R_{20} are the structure parameters of K_2ZnF_4. R_1 and R_2 are the structure parameters when Mn^{2+} substitutes for Zn^{2+}. ΔR_1 and ΔR_2 denote the structure distortion.

Table 1. The observed and calculated optical spectra for Mn^{2+} in MnF_2 for $N = 0.98496$, $A_4 = 20.7868$ a.u., the bond length of MnF_2: $R_1 = 2.102$ Å, $R_2 = 2.132$ Å [18,19], all values in units of cm^{-1}.

Energy levels	Observed [17]	Calculated
${}^4T_1\,(G)$	19 200	19 200
${}^4T_2\,(G)$	23 100	23 335
${}^4A_1\,(G)\,,{}^4E\,(G)$	25 200	25 200
${}^4T_2\,(D)$	28 200	28 667
${}^4E\,(D)$	30 170	30 345
${}^4T_1\,(P)$	32 800	32 948

cluster (see Tab. 1). Meanwhile, from the parametric radial wave faction, we estimate the ratio $\langle r^2\rangle/\langle r^4\rangle = 0.1193$ [20], and get the value of $A_2 = 2.47986$ a.u. With use of equations (11) and (12), the relationship between the local lattice structure of tetragonal Mn^{2+} centers in K_2ZnF_4:Mn^{2+} system and its EPR parameters can be established by employing the complete energy matrices.

3 Calculations

In K_2ZnF_4crystal Zn^{2+} ion is surrounded by six F^- ions, the local symmetry belongs to the space group D_{4h} [21]. Of these six ligands, the four equatorial ligands are equivalent and the two axial fluorine ligands are equivalent, too. When the Mn^{2+}ion doped in K_2ZnF_4, it will substitute for Zn^{2+} ion. The local lattice structure displays tetragonal distortion, which can be described by use of ΔR_1 and ΔR_2 as shown in Figure 1. If one takes R_{10}, R_{20} to represent the Zn^{2+}-F^- bond length of the four equatorial ligands and two axial fluorine ligands, respectively. Then, the local structure parameters R_1, R_2 for Mn^{2+} replaced Zn^{2+} ion in K_2ZnF_4:Mn^{2+} system can be written as:

$$R_1 = R_{10} + \Delta R_1, \quad R_2 = R_{20} + \Delta R_2 \tag{13}$$

where $R_{10} = 2.0045$ Å and $R_{20} = 1.966$ Å [7]. Based on Curie's covalence theory [22], the Racah parameters B and C, Trees correction α, Seniority correction β and the spin-orbit coupling coefficient ζ depend on the free-ion parameters B_0, C_0, α_0, β_0 and ζ_0. The relations are

$$B = N^4B_0, C = N^4C_0, \ \alpha = N^4\alpha_0, \ \beta = N^4\beta_0, \ \zeta = N^2\zeta_0 \tag{14}$$

where N is the average covalency parameter. The values of the free-ion parameters for Mn^{2+} ion have been obtained as [20]

$$B_0 = 911\ \text{cm}^{-1},\ C_0 = 3273\ \text{cm}^{-1},\ \alpha_0 = 65\ \text{cm}^{-1},$$
$$\beta_0 = -131\ \text{cm}^{-1},\ \zeta_0 = 336.6\ \text{cm}^{-1}. \tag{15}$$

Table 2. The ground-state splittings $\Delta E_1, \Delta E_2$and the EPR parameters b_2^0 and b_4^0 for K_2ZnF_4:Mn^{2+} system as a function of ΔR_1 and ΔR_2 at room temperature, where $10^4\Delta E_1$, $10^4\Delta E_2$, $10^4b_2^0$ and $10^4b_4^0$ are in units of cm^{-1}. In the calculation, $10^4b_4^4 = 14.0\ \text{cm}^{-1}$ takes the experimental value.

ΔR_1 (Å)	ΔR_2 (Å)	$10^4\Delta E_1$	$10^4\Delta E_2$	$10^4b_2^0$	$10^4b_4^0$
0.0672	0.1141	242.9	64.6	41.0	3.44
	0.1131	214.2	54.9	36.2	3.47
	0.1121	185.4	45.2	31.4	3.48
	0.1111	156.5	35.4	26.6	3.50
0.0682	0.1151	241.5	64.2	40.8	3.43
	0.1141	**212.9**	**54.6**	**36.0**	**3.44**
	0.1131	184.3	44.9	31.2	3.46
	0.1121	155.5	35.2	26.6	3.47
0.0692	0.1161	240.0	63.8	40.5	3.41
	0.1151	211.7	54.3	35.8	3.42
	0.1141	183.2	44.6	31.1	3.45
	0.1131	154.6	34.9	26.3	3.47
Expt. [7]		212.8	54.6	36	3.43

Using these parameters, the relationship between the low-symmetry EPR parameters b_2^0 , b_4^0 and the local distortion ΔR_1 and ΔR_2 can be established based on the complete energy matrices. By diagonalizing the complete energy matrices, the ground-state splitting of Mn^{2+} center in K_2ZnF_4:Mn^{2+}system at room temperature ($T = 295$ K) and at low temperature ($T = 4.2$ K) are calculated and the results are given in Tables 2 and 3.

From Tables 2 and 3 we can clearly see that the experimental findings of the EPR parameters b_2^0 and b_4^0 can be satisfactorily explained by the distortion parameters $\Delta R_1 = 0.0682$ Å, $\Delta R_2 = 0.1141$ Å at $T = 295$ K and $\Delta R_1' = 0.0394$ Å, $\Delta R_2' = 0.08878$ Å at $T = 4.2$ K for the K_2ZnF_4:Mn^{2+} system. This $\Delta R > 0$ indicated that the local lattice structure around tetragonal Mn^{2+} center in K_2ZnF_4:Mn^{2+}system has an expansion distortion. The expansion distortion may be attributed to the fact that the radius of Mn^{2+} ion is bigger than that of Zn^{2+} ion [23] and Mn^{2+}ion pushes the fluorine ligands outward. From our calculation, the local lattice structure parameters $R_1 = 2.0727$ Å, $R_2 = 2.0801$ Å at room temperature (295 K) and $R_1' = 2.0439$ Å, $R_2' = 2.05478$ Å at low temperature (4.2 K) for Mn^{2+} doped in K_2ZnF_4:Mn^{2+} system have been determined. The result suggests the expansion distortion is different at $T = 295$ K and 4.2 K. The local lattice structure parameters $R_1 = 2.0727$ Å,

Table 3. The ground-state splittings $\Delta E_1, \Delta E_2$and the EPR parameters b_2^0 and b_4^0 for K_2ZnF_4:Mn^{2+} system as a function of ΔR_1 and ΔR_2 at 4.2 K, where $10^4\Delta E_1$, $10^4\Delta E_2$, $10^4 b_2^0$ and $10^4 b_4^0$ are in units of cm^{-1}. In the calculation, $10^4 b_4^4 = 15.0\ cm^{-1}$ takes the experimental value.

ΔR_1 (Å)	ΔR_2 (Å)	$10^4\Delta E_1$	$10^4\Delta E_2$	$10^4 b_2^0$	$10^4 b_4^0$
0.0384	0.08878	407.3	116.4	68.6	4.13
	0.08778	373.8	105.1	63.0	4.15
	0.08678	340.1	93.7	57.4	4.19
	0.08578	306.2	82.3	51.7	4.21
0.0394	0.08978	404.8	115.7	68.1	4.10
	0.08878	**371.5**	**104.4**	**62.6**	**4.14**
	0.08778	337.9	93.1	57.0	4.16
	0.08678	304.2	81.8	51.4	4.17
0.0404	0.09078	402.3	114.9	67.7	4.09
	0.08978	369.2	103.8	62.2	4.10
	0.08878	335.8	92.6	56.6	4.12
	0.08778	302.3	81.3	51.1	4.14
Expt. [8]		371.5	104.4	62.6	4.15

Table 4. Predicted the d-d transition energy for K_2MnF_4 and K_2ZnF_4:Mn^{2+}at room temperature, all values in units of cm^{-1}.

Transition$^6A_1\,(S) \rightarrow$	K_2MnF_4	K_2ZnF_4:Mn^{2+}
$^4T_1\,(G)$	18 768	18 503
$^4T_2\,(G)$	23 077	22 914
$^4A_1\,(G)\,, {}^4E\,(G)$	25 200	25 199
$^4T_2\,(D)$	28 566	28 511
$^4E\,(D)$	30 339	30 344
$^4T_1\,(P)$	31 352	31 092

$R_2 = 2.0801$ Å are very close to $R = 2.086$ Å observed in K_2ZnF_4 crystal at room temperature [24]. This result seems to be reasonable, because the radius of Mn^{2+} ion is bigger than that of Zn^{2+} ion, when Mn^{2+} impurity substitutes the Zn^{2+} in K_2ZnF_4, the local structure will has an expansion distortion. Of course, a careful experimental investigations especially ENDOR experiment are required in order to clarify the distance around the Mn^{2+} in K_2ZnF_4 in detail.

Moreover, it is well known that the inter-relation between electronic and molecular structure is the central to understand chemical and physical processes — i.e. knowing the geometric structure of a given metal complexes may give us insight into its electronic structure. To our knowledge, the optical spectra of K_2ZnF_4:Mn^{2+} and K_2MnF_4 system have not been reported by experiments. So, we have predicted the d-d transition energy for K_2MnF_4 and K_2ZnF_4:Mn^{2+} system listed in Table 4 by considering local lattice structure. From Table 4, we can see clearly that the two systems have different electronic structure. It may be duo to the fact that the two systems have different geometric structure.

4 Conclusions

The complete energy matrices (252×252) for a d^5configuration ion in a tetragonal ligand-field has been constructed, and the relationship between the low-symmetry EPR parameters b_2^0, b_4^0 and the local distortion parameters has been established based on the complete energy matrices. As an application, the local lattice structure of Mn^{2+} ion doped in K_2ZnF_4:Mn^{2+}system has been studied by means of the complete energy matrices for a d^5 configuration ion in a tetragonal ligand-field. From our calculation, we can conclude that the EPR zero-field-splitting parameters b_2^0 and b_4^0 are insensitive to a change of the EPR cubic parameter b_4^4. Furthermore, the local structure parameters $R_1 = 2.0727$ Å, $R_2 = 2.0801$ Å at room temperature (295 K) and $R_1' = 2.0439$ Å, $R_2' = 2.05478$ Å at low temperature (4.2 K) for Mn^{2+} doped in K_2ZnF_4:Mn^{2+} system have been determined. Moreover, the EPR parameters b_2^0, b_4^0 and b_4^4 are also reasonably interpreted.

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