EPR Theoretical Study of Local Molecular Structure and Thermal Expansion Coefficient for Octahedral Mn^{2+} Centers in Zinc Fluosilicate

Ai-Jie Mao,[†] Xiao-Yu Kuang,*[,†,‡] Hui Wang,[†] and Cheng Lu[†]

Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China, and International Centre for Materials Physics, Academia Sinica, Shenyang 110016, China

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A theoretical method for studying the inter-relation between electronic and molecular structure has been proposed by diagonalizing the complete energy matrices for a d^5 configuration ion in a trigonal ligand field and considering the second-order and fourth-order EPR parameters D and $(a - F)$ simultaneously. As for $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ and $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$ complex molecules, the local lattice distortion and local thermal expansion coefficient for the octahedral Mn^{2+} centers in zinc fluosilicate have been investigated, respectively. The calculations indicate that the local lattice structure around an octahedral Mn^{2+} center has an expansion distortion, whether the Mn^{2+} ion is doped in $ZnSiF_6{\cdot}6H_2O$ or $ZnSiF_6{\cdot}6D_2O$. Moreover, the total tendency of the local lattice expansion distortion will be more and more obvious with the temperature rising, apart from some slight variations at $T = 60$ K for the $ZnSiF_6{\cdot}6H_2O$. By simulating the two low-symmetry EPR parameters D and $(a - F)$ simultaneously, the local lattice structure parameters R and θ have been determined to vary from 2.204 Å to 2.256 Å and from 53.417° to 52.710°, respectively, in the temperature range 19−297 K for $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ and to vary from 2.215 Å to 2.255 Å and from 53.346° to 52.714°, respectively, in the temperature range 50−300 K for $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$. Subsequently the dependence of local thermal expansion coefficients on the temperature is studied and the corresponding theoretical values of the local thermal expansion coefficients are reported firstly. Some characteristics of local thermal expansion coefficients of Mn^{2+} in $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ and $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$ systems are also analyzed.

I. Introduction

The inter-relation between electronic and molecular structure is central to understanding chemical and physical processes. The transition-metal complex molecules may display various spin ground states, such as high-spin, low-spin, or intermediate-spin states, depending on the relative strength of the ligand field energy and the mean spin-pairing energy. In some special cases, i.e., when the ligand field splitting energy becomes comparable with the mean spin-pairing energy, the spin transition phenomena, such as high-spin ↔ low-spin transition, high-spin ↔ intermediate-spin transition, or intermediate-spin ↔ low-spin transition, can be observed.[1−10] In order to understand the various characteristics of transition-metal complex molecules, it is important to establish the inter-relation between electronic and molecular structure. In the present paper, a theoretical method for determining the inter-relation for a d^5 configuration ion in a trigonal ligand field is proposed by diagonalizing the complete energy matrices and simulating the second-order and fourth-order EPR parameters D and $(a - F)$ simultaneously. By this method, the local lattice distortion and local thermal expansion coefficient for the octahedral Mn^{2+} centers in $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ and $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$ complex molecules are determined, respectively.

Electron paramagnetic resonance (EPR) is regarded as an effective method to study the local geometry and local properties (such as local thermal expansion coefficient and local compressibility) in the vicinity of impurity. As for the $M^{II}M^{IV}F_6{\cdot}6H_2O$ (M^{II} = Zn, Mg, Co, Ni, Fe; M^{IV} = Si, Ti, Sn) series, $ZnSiF_6{\cdot}6H_2O$ was the first complex of this series to be studied by using Mn^{2+} as a probe.[11] Subsequently a lot of studies have appeared in which different transition metal ions (Mn^{2+}, V^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+}) were doped in complexes having a structure similar to that of $ZnSiF_6{\cdot}6H_2O$ (such as $ZnSiF_6{\cdot}6D_2O$, $ZnZrF_6{\cdot}6H_2O$, $CoZrF_6{\cdot}6H_2O$, $NiSiF_6{\cdot}6H_2O$).[12−23] Especially the studies of some characteristics of the Mn^{2+} ion doped in $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ (or $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$) system are distinctly important and interesting.[19−23] For example, the EPR spectra of the $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ and $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$ systems, which are very sensitive to the local lattice structure distortions, have been measured by Wan et al.[19] and Drumheller et al.,[23] respectively. Li et al.[21] have studied local geometry and local compressibilities for the Mn^{2+} ion in the complex $ZnSiF_6{\cdot}6H_2O$ on the basis of the second-order EPR parameter. Their results indicate that the local lattice structure around an octahedral Mn^{2+} center at low temperature (4.2 K) has a compressed distortion. It is well-known that the spin-Hamiltonian of d^5 configuration ion in a trigonal ligand field should include three different EPR parameters a, D, and $(a - F)$. The parameter a relates to a fourth-order spin operator and represents a cubic component of the crystalline electric field. The parameters D and $(a - F)$ are respectively associated with the second-order and fourth-order spin operators and represent a component of the crystalline

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* Corresponding author. Mailing address: Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China. E-mail: scu_kxy@163.com.

[†] Sichuan University.

[‡] Academia Sinica.

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electric field that is axially symmetric about the C_3 axis. Since both the EPR parameters D and $(a - F)$ relate to the axial ligand field, we thus believe that only considering the second-order EPR parameter D to determine the local structure is insufficient. Generally, we suggest that, in addition to the second-order EPR parameter D, the fourth-order EPR parameter $(a - F)$ should also be taken into account in the determination of the distortion of the local lattice structure of Mn^{2+} in $ZnSiF_6 \cdot 6H_2O$ (or $ZnSiF_6 \cdot 6D_2O$). Since the properties (e.g., charge, mass, and radius) of the Mn^{2+} ion are different from those of the host ion Zn^{2+}, the local lattice structure and the local thermal expansion coefficient in the vicinity of Mn^{2+} ion are often unlike those in the host complex. Moreover, up to now a theoretical explanation for the local thermal expansion coefficients has not been made. This may be ascribed to the lack of the effective calculation formulas related to the structure data for a d^5 configuration ion in a trigonal ligand field. In the present work, by analyzing the EPR spectra of $ZnSiF_6 \cdot 6H_2O{:}Mn^{2+}$ in the temperature range 19−299 K and $ZnSiF_6 \cdot 6D_2O{:}Mn^{2+}$ in the temperature range 50−300 K , respectively, the local lattice distortion and local thermal expansion coefficient for the $ZnSiF_6 \cdot 6H_2O{:}Mn^{2+}$ and $ZnSiF_6 \cdot 6D_2O{:}Mn^{2+}$ systems have been determined on the basis of the complete energy matrices for a d^5 configuration ion in a trigonal ligand field.

II. Theoretical Methods

The EPR spectra of Mn^{2+} ions in sites of trigonal symmetry can be described by the following spin Hamiltonian:[24]

$$\hat{H}_S = g\beta\hat{H}\cdot\hat{S} + D[S_z^{\ 2} - (1/3)S(S+1)] + (1/6)a[S_\xi^{\ 4} + S_\eta^{\ 4} + S_\zeta^{\ 4} - (1/5)S(S+1)(3S^2+3S-1)] + (1/180)F[35S_z^{\ 4} - 30S(S+1)S_z^{\ 2} + 25S_z^{\ 2} - 6S(S+1) + 3S^2(2S+1)^2] \quad (1)$$

where a, D, and $(a - F)$ are EPR parameters. From eq 1 the splitting energy levels in the ground state $^6A_1$ for a zero-magnetic field can be written as

$$E(\pm 1/2) = (1/3)D - (1/2)(a-F) - (1/6)[(18D + a - F)^2 + 80a^2]^{1/2}$$
$$E(\pm 3/2) = -(2/3)D + (a - F)$$
$$E(\pm 5/2) = (1/3)D - (1/2)(a-F) + (1/6)[(18D + a - F)^2 + 80a^2]^{1/2} \quad (2)$$

Then the ground-state splitting ΔE_1 and ΔE_2 can be expressed as a function of the parameters a, D, and $(a - F)$:

$$\Delta E_1 = \pm\frac{1}{3}[(a - F + 18D)^2 + 80a^2]^{1/2}$$
$$\Delta E_2 = \frac{3}{2}(a-F) - D \pm \frac{1}{6}[(a - F + 18D)^2 + 80a^2]^{1/2} \quad (3)$$

Herein, the signs “+” and “−” correspond to $D \geq 0$ and $D < 0$, respectively. Kuang has shown that the low-symmetry EPR parameters D and $(a - F)$ are almost independent of the EPR cubic parameter a for Fe^{3+} in Al_2O_3.[25] Yu has given explicit expressions of the EPR parameters a, D, and F by using the high order perturbation method:[26]

$$D = \frac{1}{28}[5W(5/2,5/2) - W(3/2,3/2) - 4W(1/2,1/2)]$$
$$F = \frac{-3}{2\sqrt{5}}W(5/2,-1/2) + \frac{3}{14}[W(5/2,5/2) + 2W(1/2,1/2) - 3W(3/2,3/2)]$$
$$a = \frac{-3}{2\sqrt{5}}W(5/2,-1/2) \quad (4)$$

Where $W(M_s, M_s')$ denotes perturbation matrix elements, from eq 4, we can see that the $(a - F)$ parameter is not related to the cubic parameter a, so we can take a cubic approximation in the calculation of the EPR parameter a and determine low-symmetry EPR parameters D and $(a - F)$ by eq 3 as well as ΔE_1, ΔE_2 from diagonalizing the complete energy matrices.

The energy matrices for a d^5 configuration ion with C_3^* symmetry have been established based on the following perturbation Hamiltonian:[25]

$$\hat{H} = \hat{H}_{ee} + \hat{H}_{so} + \hat{H}_{LF} = \sum_{i<j} e^2/r_{i,j} + \zeta\sum_i l_i \cdot s_i + \sum_i V_i \quad (5)$$

where $\hat{H}_{ee}$ denotes the electron−electron interaction, $\hat{H}_{so}$ denotes the spin−orbit coupling interaction, $\hat{H}_{LF}$ denotes the ligand-field interaction, ζ is the spin−orbit coupling coefficient, and V_i is the ligand-field potential:

$$V_i = \gamma_{00}Z_{00} + \gamma_{20}r_i^{\ 2} + \gamma_{40}r_i^{\ 4}Z_{40}(\theta_i,\varphi_i) + \gamma_{43}^c r_i^{\ 4}Z_{43}^c(\theta_i,\varphi_i) + \gamma_{43}^s r_i^{\ 4}Z_{43}^s(\theta_i,\varphi_i) \quad (6)$$

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

$$Z_{l0} = Y_{l0}$$
$$Z_{lm}^c = (1/\sqrt{2})[Y_l,-m + (-1)^m Y_l,m]$$
$$Z_{lm}^s = (i/\sqrt{2})[Y_l,-m - (-1)^m Y_l,m] \quad (7)$$

The $Y_{l,m}$ in eq 6 are the spherical harmonics. γ_{l0}, γ_{lm}^c, and γ_{lm}^s are associated with the local lattice structure around the d^5 configuration ion by the relations

$$\gamma_{l0} = -\frac{4\pi}{2l+1}\sum_{\tau=1}^{n}\frac{eq_\tau}{R_\tau^{l+1}}Z_{l0}(\theta_\tau,\varphi_\tau)$$
$$\gamma_{lm}^c = -\frac{4\pi}{2l+1}\sum_{\tau=1}^{n}\frac{eq_\tau}{R_\tau^{l+1}}Z_{lm}^c(\theta_\tau,\varphi_\tau)$$
$$\gamma_{lm}^s = -\frac{4\pi}{2l+1}\sum_{\tau=1}^{n}\frac{eq_\tau}{R_\tau^{l+1}}Z_{lm}^s(\theta_\tau,\varphi_\tau) \quad (8)$$

where θ_τ and φ_τ are angle coordinates of the ligand. τ and q_τ represent the τth ligand ion and its effective charge, respectively. R_τ represents the impurity−ligand distance.

According to the perturbation Hamiltonian (5), for a d^5 configuration ion three 84 × 84 energy matrices have been constructed in terms of the irreducible representations $\Gamma_4(\Gamma_5)$ and Γ_6 of the C_3^* point group.[25] The matrix elements are functions of the Racah parameters B and C, the spin−orbit coupling coefficient ζ, and the crystal-field parameters B_{20}, B_{40},

B_{43}^c and B_{43}^s, which are generally expressed as

$$B_{20} = \left(\frac{5}{4\pi}\right)^{1/2}\gamma_{20}\langle r^2\rangle$$

$$B_{40} = 3\left(\frac{1}{4\pi}\right)^{1/2}\gamma_{40}\langle r^4\rangle$$

$$B_{43}^c = \frac{3}{2}\left(\frac{1}{2\pi}\right)^{1/2}\gamma_{43}^c\langle r^4\rangle$$

$$B_{43}^s = i\frac{3}{2}\left(\frac{1}{2\pi}\right)^{1/2}\gamma_{43}^s\langle r^4\rangle \tag{9}$$

For the octahedral Mn^{2+} center in $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ and $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$ complexes, the local structure symmetry belongs to the $R\bar{3}$ space group. Based on the superposition model, the ligand-field parameter B_{43}^s will vanish and the rest can be written as[27]

$$B_{20} = 3G_2(\tau)(3\cos^2\theta_\tau - 1)$$

$$B_{40} = \frac{3}{4}G_4(\tau)(35\cos^4\theta_\tau - 30\cos^2\theta_\tau + 3)$$

$$B_{43}^c = \frac{3\sqrt{35}}{2}G_4(\tau)\sin^3\theta_\tau\cos\theta_\tau \tag{10}$$

where $G_2(\tau)$ and $G_4(\tau)$ are written as

$$G_2(\tau) = -q_\tau e G^2(\tau)$$

$$G_4(\tau) = -q_\tau e G^4(\tau)$$

$$G^k(\tau) = \int_0^{R_\tau} R_{3d}{}^2(r)\, r^2 \frac{r^k}{R_\tau{}^{k+1}}\,dr + \int_{R_\tau}^{\infty} R_{3d}{}^2(r)\, r^2 \frac{R_\tau{}^k}{r^{k+1}}\,dr \tag{11}$$

The R in eq 9 and θ in eq 8 are the Mn−M (M = H_2O or D_2O) distance and the angle between Mn−M and the C_3 axis, respectively. τ and q_τ represent the τth ligand and its effective charge, respectively. According to the van Vleck approximation for the $G^k(\tau)$ integral,[28] we may get the following relations:

$$G_2(P_i) = \frac{A_2}{R_{P_i}{}^3} \quad \text{and} \quad G_4(P_i) = \frac{A_4}{R_{P_i}{}^5} \tag{12}$$

where

$$A_4 = -eq_\tau\langle r^4\rangle, \quad A_2 = -eq_\tau\langle r^2\rangle, \quad \text{and} \quad A_2 = \frac{\langle r^2\rangle}{\langle r^4\rangle}A_4$$

The ratio $\langle r^2\rangle/\langle r^4\rangle = 0.119\,328$ for Mn^{2+} may be obtained from the parametric radial wave function.[29] A_4 is a constant for the (MnO_6) octahedron, and its value can be determined from the optical spectra and the Mn−O bond length of the $MnCO_3$ crystal.[30] By this way, we derive $A_4 = 26.7375$ au and $A_2 = 3.1905$ au for the (MnO_6) octahedron and we will take them in the following calculation. With the use of eq 8 and eq 10, the relationship between the molecular structure parameters R and θ and the EPR parameters D and $(a - F)$ can be established by means of the complete energy matrices.

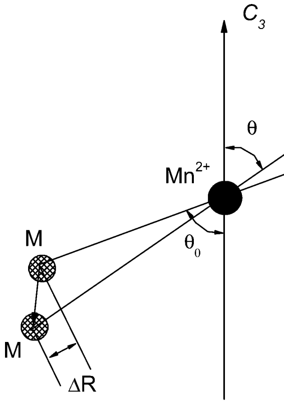

Figure 1. Local structure distortions of octahedral Mn^{2+} centers in $ZnSiF_6{\cdot}6H_2O$ and $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$ systems. M represent H_2O or D_2O ligand. R_0 and θ_0 are the structure parameters of host crystals, and R and θ are the structure parameters when Mn^{2+} replaces Zn^{2+}. ΔR and $\Delta\theta$ represent the structure distortion.

III. Calculation and Analysis

The EPR spectra of $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ and $ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$ systems have been reported by Wan et al.[19] and Drumheller et al.[23] In the following, we will study the local geometry and local thermal expansion coefficient for Mn^{2+} in $ZnSiF_6{\cdot}6H_2O$ by analyzing its EPR spectra. Ray et al.[31] have reported that the crystal structure of $ZnSiF_6{\cdot}6H_2O$ belongs to the $R\bar{3}$ space group and the Zn^{2+} ion is surrounded by a water molecule octahedron. When Mn^{2+} ion is doped in $ZnSiF_6{\cdot}6H_2O$, Mn^{2+} ion replaces the host Zn^{2+} ion and the local lattice structure around the octahedral Mn^{2+} center has a trigonal distortion. The trigonal distortion can be described by means of two parameters ΔR and $\Delta\theta$, as plotted in Figure 1, and we may approximately regard the water (H_2O and D_2O) as the oxygen ligand in the following calculation. Thus the local structure parameters R and θ for Mn^{2+} replacing Zn^{2+} in the $[MnM_6]^{2-}$ complex can be expressed as

$$R = R_0 + \Delta R$$

$$\theta = \theta_0 + \Delta\theta \tag{13}$$

where R_0 and θ_0 denote the Zn−M (M = H_2O, D_2O) bond length and the angle between the Zn−M bond and the C_3 axis, respectively, and $R_0 = 2.078$ Å, $\theta_0 = 54.67°$.[31] According to Curie et al.'s[32] covalence theory, we use the following relationship:

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

where B_0, C_0, α_0, β_0, ζ_0 are the free-ion parameters and their values have been reported ($B_0 = 918$ cm^{-1}, $C_0 = 3273$ cm^{-1}, $\zeta_0 = 347$ cm^{-1}, $\alpha_0 = 65$ cm^{-1}, $\beta_0 = -131$ cm^{-1},).[33] As for the Mn^{2+} ion in the $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ ($ZnSiF_6{\cdot}6D_2O{:}Mn^{2+}$) system, Mn^{2+} is surrounded by six water molecules, in fact the oxygen ions play an important role in ligands (H_2O, D_2O), so we may take a typical covalency parameter N ($N = 0.965$) as found in the $MgO{:}Mn^{2+}$ system.[33] Using those parameters, the low-symmetry EPR parameters D and $(a - F)$ as functions of ΔR and $\Delta\theta$ can be calculated by diagonalizing the complete energy matrices, and the results are listed in Table 1 and Table 2, respectively.

From Table 1 and Table 2 we can see that the EPR parameters D and $(a - F)$ in the temperature ranges 19−299 K and 50−300 K are in agreement with the experimental findings, and the corresponding local lattice distortion parameters ΔR and $\Delta\theta$ have been determined to vary from 0.126 Å to 0.178 Å and from −1.253° to −1.960°, for $ZnSiF_6{\cdot}6H_2O{:}Mn^{2+}$ respectively,

TABLE 1: The EPR Zero-Field Splitting Parameters D and $(a - F)$ in the Temperature Range 19−297 K for the Mn^{2+} Ion in the $ZnSiF_6 \cdot 6H_2O:Mn^{2+}$ System as a Function of the Two Parameters ΔR and $\Delta\theta$[a]

T (K)	ΔR (Å)	$\Delta\theta$ (deg)	ΔE_1	ΔE_2	D	$(a - F)$	D_{expt}[b]	$(a - F)_{expt}$[b]
19	0.126	−1.253	−780.5	−244.6	−130.6	10.06	−130.6	10.0
29	0.129	−1.272	−783.2	−245.9	−131.0	9.81	−131.0	9.8
43	0.131	−1.290	−788.4	−247.8	−131.9	9.70	−131.9	9.7
60	0.130	−1.302	−798.8	−251.1	−133.6	9.80	−133.5	9.8
88	0.134	−1.351	−816.4	−257.4	−136.5	9.53	−136.0	9.5
134	0.135	−1.435	−864.6	−273.6	−144.5	9.43	−144.5	9.4
190	0.149	−1.627	−932.7	−297.4	−155.9	8.71	−155.9	8.8
255	0.164	−1.807	−984.0	−315.1	−164.4	8.35	−164.3	8.4
297	0.178	−1.960	−1018.5	−327.4	−170.1	7.80	−170.2	7.8

[a] ΔE_1, ΔE_2, D, and $(\alpha - F)$ are in units of 10^{-4} cm^{-1}. [b] The estimated uncertainties of experimental findings D and $(a - F)$ are $\pm 0.5 \times 10^{-4}$ cm^{-1} and $\pm 0.3 \times 10^{-4}$ cm^{-1}, respectively.[19]

TABLE 2: The EPR Zero-Field Splitting Parameters D and $(a - F)$ in the Temperature Range 50−300 K for the Mn^{2+} Ion in the $ZnSiF_6 \cdot 6D_2O:Mn^{2+}$ System as a Function of the Two Parameters ΔR and $\Delta\theta$[a]

T (K)	ΔR (Å)	$\Delta\theta$ (deg)	ΔE_1	ΔE_2	D	$(a - F)$	D_{expt}[b]	$(a - F)_{expt}$[b]
50	0.137	−1.324	−790.8	−249.2	−132.2	9.31	−132.2	9.3
100	0.154	−1.520	−854.1	−271.4	−142.8	8.58	−142.5	8.6
150	0.155	−1.616	−905.7	−288.5	−151.4	8.66	−151.5	8.7
200	0.161	−1.734	−953.0	−304.7	−159.2	8.37	−159.0	8.4
250	0.175	−1.894	−993.4	−318.9	−166.0	7.89	−165.9	7.9
300	0.177	−1.956	−1020.1	−327.8	−170.4	7.90	−170.4	7.9

[a] ΔE_1, ΔE_2, D, and $(a - F)$ are in units of 10^{-4} cm^{-1}. [b] The estimated uncertainties of experimental findings D and $(a - F)$ are $\pm 0.3 \times 10^{-4}$ to $\pm 1.0 \times 10^{-4}$ cm^{-1} and $\pm 0.2 \times 10^{-4}$ to $\pm 0.5 \times 10^{-4}$ cm^{-1}, respectively.[23]

TABLE 3: The Local Thermal Expansion Coefficients α for the Mn^{2+} Ion in the $ZnSiF_6 \cdot 6H_2O:Mn^{2+}$ System in the Temperature Range 19−297 K

T (K)	19−29	29−43	43−60	43−60	88−134	134−190	190−255	255−297
α (K^{-1})	1.44×10^{-4}	6.87×10^{-5}	-2.83×10^{-5}	6.69×10^{-5}	1.05×10^{-5}	1.12×10^{-4}	1.11×10^{-4}	1.60×10^{-4}

TABLE 4: The Local Thermal Expansion Coefficients α for the Mn^{2+} Ion in the $ZnSiF_6 \cdot 6D_2O:Mn^{2+}$ System in the Temperature Range 50−300 K

T (K)	50−100	100−150	150−200	200−250	250−300
α (K^{-1})	1.63×10^{-4}	9.62×10^{-6}	5.77×10^{-5}	1.34×10^{-4}	1.92×10^{-5}

and to vary from 0.137 Å to 0.177 Å and from −1.324° to −1.956°, for $ZnSiF_6 \cdot 6D_2O:Mn^{2+}$ respectively. The $\Delta R > 0$ means that the local lattice structure around an octahedral Mn^{2+} center has an expansion distortion, and this may be ascribed to the fact that the radius of $Mn^{2+}(r_i = 0.80$ Å$)$ is larger than that of the host ion $Zn^{2+}(r_h = 0.74$ Å$)$,[34] and the Mn^{2+} ion will push the water molecule (H_2O or D_2O) ligands outward, and we also find that the total tendency of the local lattice expansion distortion will be more and more obvious with the temperature rising, whether the Mn^{2+} ion is doped in the $ZnSiF_6 \cdot 6H_2O$ or $ZnSiF_6 \cdot 6D_2O$ complex. Furthermore it is noted that there exist some slight variations at $T = 60$ K for Mn^{2+} in $ZnSiF_6 \cdot 6H_2O$, whereas this phenomenon does not exist for Mn^{2+} in $ZnSiF_6 \cdot 6D_2O$. In order to explain the above phenomenon further, in the following we will study the dependence of the local thermal expansion coefficients on the temperature for Mn^{2+} in $ZnSiF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6D_2O$ complex molecules.

The local thermal expansion coefficient can be expressed as the following:[35]

$$\alpha = \frac{1}{R}\frac{\Delta R}{\Delta T} \tag{15}$$

By using the local lattice distortion structure parameters of Table 1 and Table 2 and eq 16, we may determine the local thermal expansion coefficients in the temperature range 19−297 K for the Mn^{2+} ion in $ZnSiF_6 \cdot 6H_2O$ and in the temperature range 50−300 K for the Mn^{2+} ion in $ZnSiF_6 \cdot 6D_2O$; the values are listed in Table 3 and Table 4, and the functions of α vs T are shown in Figure 2 and Figure 3, respectively. From Figure 2 and Figure 3 we can see that there exist two anomalistic peak values in the thermal expansion coefficients of the lattice of the $ZnSiF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6D_2O$ complexes in their own temperature range. From our calculations we find that the change of α for Mn^{2+} in $ZnSiF_6 \cdot 6H_2O$ is slower than that of Mn^{2+} in $ZnSiF_6 \cdot 6D_2O$. Of course, careful experimental investigations especially ENDOR experiment are required in order to clarify the local lattice distortion structure and the local expansion coefficient of Mn^{2+} ion in $ZnSiF_6 \cdot 6H_2O:Mn^{2+}$ ($ZnSiF_6 \cdot 6D_2O:Mn^{2+}$) systems in detail.

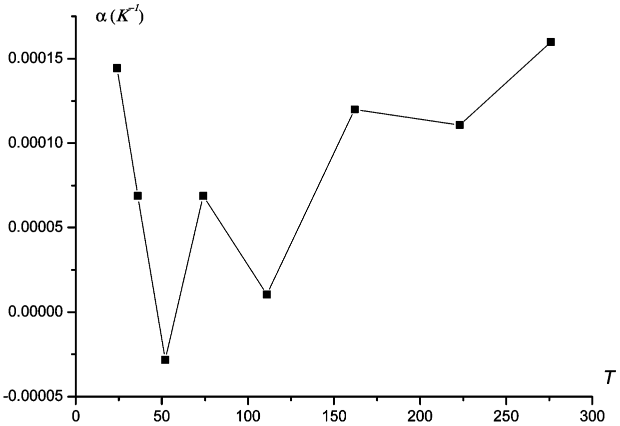

Figure 2. The theoretical values of α for the Mn^{2+} ion in $ZnSiF_6 \cdot 6H_2O$ are plotted against temperature.

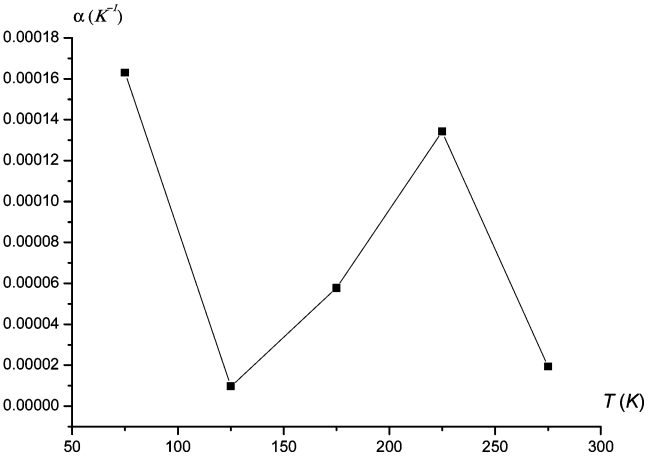

Figure 3. The theoretical values of α for the Mn^{2+} ion in $ZnSiF_6 \cdot 6D_2O$ are plotted against temperature.

IV. Conclusion

A theoretical method for the study of the inter-relation between electronic and molecular structure has been proposed. By analyzing the temperature-dependent EPR spectra of Mn^{2+} ions in $ZnSiF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6D_2O$, the local lattice distortions and local thermal expansion coefficients for the Mn^{2+} ion in $ZnSiF_6 \cdot 6H_2O$ in the temperature range 19−297 K and Mn^{2+} ion in $ZnSiF_6 \cdot 6D_2O$ in the temperature range 50−300 K have been determined by means of the complete energy matrices for a d^5 configuration ion in a trigonal crystal field. We derived the range of bond length $R = 2.204-2.256$ Å and angle $\theta = 53.417-52.710°$ for $ZnSiF_6 \cdot 6H_2O:Mn^{2+}$ in the temperature range 19−297 K and $R = 2.215-2.255$ Å, $\theta = 53.346-52.714°$ for $ZnSiF_6 \cdot 6D_2O:Mn^{2+}$ in the temperature range 50−300 K. We note that the local lattice structure around an octahedral Mn^{2+} center has an expansion distortion, whether the Mn^{2+} ion is doped in $ZnSiF_6 \cdot 6H_2O$ or $ZnSiF_6 \cdot 6D_2O$ complex. This may be ascribed to the fact that the radius of Mn^{2+} is larger than that of the host ion Zn^{2+}, and the Mn^{2+} ion will push the water molecule (H_2O or D_2O) ligands outward. The theoretical values of the local thermal expansion coefficients are reported first. The two anomalistic peak values are found in their own temperature range, and the change tendency of the local thermal expansion coefficients is different between Mn^{2+} in $ZnSiF_6 \cdot 6H_2O$ and Mn^{2+} in $ZnSiF_6 \cdot 6D_2O$ complex molecules.

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