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Study of optical absorption and EPR spectra of Mn^{2+} ion in cadmium maleate dihydrate

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Abstract. The optical absorption and EPR spectra of Mn^{2+} ion doped in cadmium maleate dihydrate have been theoretically investigated by diagonalizing the complete energy matrices for a d^5 configuration ion in a trigonal ligand-field. According to the suggestion of the optical absorption studies, we assume that the Mn^{2+} ion enters the host lattice interstitially and the distorted octahedral symmetry for the impurity ion is trigonal. Moreover, the local lattice structure parameters of the system are determined. The results show that the six oxygen ions around the Mn^{2+} ion are at the same distance $R = 2.115$ Å, and there are three Mn-O bonds forming an angle θ_1 of 66.26° with the C_3-axis and three others forming an angle θ_2 of 43.40°.

PACS. 71.70.Ch Crystal and ligand fields – 71.70.Gm Exchange interactions – 75.30.Et Exchange and superexchange interactions

1 Introduction

EPR and optical absorption are two powerful tools to study the local environment around the transition-metal ion doped into various crystals, because both of them are very sensitive to distortion of the local lattice structure of the impurity ion. During the last decades, there has been a growing interest in the carboxylic acids doped with transition-metal ions, partly because of their excellent physical and chemical properties, and partly because of their extensive application in chemical and industrial fields [1–8]. In particular, EPR and optical spectra investigations of the systems have shown many important and interesting conclusions [1–7]. The single crystal of cadmium maleate dihydrate ($C_4H_6CdO_6$) is a typical carboxylic acid. Its crystal structure is monoclinic with space group $P2_1/c$. It contains two crystallographically and chemically distinct cadmium atoms [9]. EPR analyses indicate that when the Mn^{2+} ion is doped into the crystal $C_4H_6CdO_6$, it will substitute for neither of the two Cd atoms but enter the lattice interstitially [1,2]. Furthermore, the optical spectra of Mn^{2+} ion in $C_4H_6CdO_6$ have also been examined [2]. It is found that the impurity Mn^{2+} ion occupies a distorted octahedral site and the site symmetry exhibits trigonal.

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. It is well known that for a d^5 configuration ion in a weak ligand-field, the high-spin ground state is the $^6A_1$ state. To describe the $^6A_1$ state ground-state splitting, the spin-Hamiltonian should include three EPR parameters a, D and $(a - F)$. Parameter a corresponds to a fourth-order spin operator and represents a cubic component of the crystalline electric field. Parameters D and $(a - F)$ are, respectively, the second-order and fourth-order spin operators, and represent a component of the crystalline electric field that is axially symmetric about the C_3-axis. In the present paper, by considering the local lattice structure distortion, the EPR parameters and optical absorption of Mn^{2+} ion in the $C_4H_6CdO_6$ crystal will be simultaneously studied by diagonalizing the complete energy matrices for a d^5 configuration ion in a trigonal ligand-field. Moreover, the investigation of optical spectra is based on the actually trigonal symmetry instead of a cubic approximation. This is different from any previous study of the optical spectra [2].

2 Theoretical analysis

2.1 EPR parameter

The EPR spectra of d^5 configuration Mn^{2+} ion in a trigonal ligand-field may be analyzed by employing the spin

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Hamiltonian [10]:

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

From equation (1) the explicit expressions of the energies in the ground state ${}^6\mathrm{A}_1$ for a zero-magnetic field can be written as:

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

Then the zero-field splitting energies $\varDelta E_1$, $\varDelta E_2$ in the ground state ${}^6\mathrm{A}_1$ may be obtained as functions of EPR parameters a, D and $(a-F)$ [11]:

$$\varDelta E_1 = E\left(\pm\frac{5}{2}\right) - E\left(\pm\frac{1}{2}\right) = \pm\frac{1}{3}\left[(18D+a-F)^2 + 80a^2\right]^{\frac{1}{2}},$$
$$\varDelta E_2 = E\left(\pm\frac{3}{2}\right) - E\left(\pm\frac{1}{2}\right) = \frac{3}{2}(a-F) - D \pm \frac{1}{6}\left[(18D+a-F)^2 + 80a^2\right]^{\frac{1}{2}}, \quad (3)$$

where the positive and negative signs correspond to $D \geq 0$ and $D < 0$, respectively. Kuang has demonstrated that the low-symmetry EPR parameters D and $(a-F)$ are almost independent of the cubic EPR parameter a for $\mathrm{Al_2O_3{:}Fe^{3+}}$ system [12]. Yu had given the explicit expressions of D, F, a by using high order perturbation method [13]:

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

where $W(M_S, M_S')$ denotes perturbation matrix elements. From equation (4) we note that parameters D and $(a-F)$ are not related to cubic parameter a. Therefore, we can take the experimental value of EPR parameter a and calculate the EPR parameters D, $(a-F)$ from equation (3), when the values of $\varDelta E_1$, $\varDelta E_2$ are obtained by diagonalizing the complete energy matrices of the electron-electron repulsion, the ligand-field and the spin-orbit coupling for a d^5 configuration ion in a trigonal ligand-field.

2.2 Complete energy matrix

The perturbation Hamiltonian for a d^5 configuration ion in a trigonal ligand-field can be expressed as [14,15]:

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

where the first term is the electron-electron interactions, the second term is the spin-orbit coupling interactions, and the third term is the ligand-field potential energy that can be represented as:

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

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

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

where $Y_{l,m}$ are the spherical harmonic. In equation (6) γ_{l0}, γ_{lm}^c and γ_{lm}^s are associated to the local structure around d^5 configuration ion by the relations:

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

where θ_τ and φ_τ are the 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.

According to the perturbation Hamiltonian (5), three 84 × 84 matrices have been constructed on the basis of the irreducible representations $\varGamma_4(\varGamma_5)$ and $\varGamma_6$ of C_3^* double group [14]. The matrix elements are functions of the Racah parameters B, C, the spin-orbit coupling coefficient ζ and the crystal field parameters B_{20}, B_{40}, B_{43}^c, B_{43}^s which are generally defined as [16]:

$$\begin{aligned}
B_{20} &= (5/4\pi)^{\frac{1}{2}}\gamma_{20}\langle r^2\rangle,\\
B_{40} &= (9/4\pi)^{\frac{1}{2}}\gamma_{40}\langle r^4\rangle,\\
B_{43}^c &= (9/8\pi)^{\frac{1}{2}}\gamma_{43}^c\langle r^4\rangle,\\
B_{43}^s &= i(9/8\pi)^{\frac{1}{2}}\gamma_{43}^s\langle r^4\rangle. \qquad (9)
\end{aligned}$$

For the Mn^{2+} ion in cadmium maleate dihydrate, the local structure symmetry is suggested to be trigonal [2]. Based on the superposition model, the ligand-field parameter B_{43}^s will vanish and the other terms can be deduced as:

$$\begin{aligned}
B_{20} &= 3G_2(\tau)(3\cos^2\theta - 1),\\
B_{40} &= (3/4)G_4(\tau)(35\cos^4\theta - 30\cos^2\theta + 3),\\
B_{43}^c &= \left(3\sqrt{35}/2\right)G_4(\tau)\sin^3\theta\cos\theta, \qquad (10)
\end{aligned}$$

where

$$\begin{aligned}
G_2(\tau) &= -eq_\tau G^2(\tau),\\
G_4(\tau) &= -eq_\tau G^4(\tau),\\
G^k(\tau) &= \int_0^R R_{3d}^2(r)r^2\frac{r^k}{R^{k+1}}dr + \int_R^\infty R_{3d}^2(r)r^2\frac{R^k}{r^{k+1}}dr. \qquad (11)
\end{aligned}$$

In equations (10), (11), R and θ denote the Mn-O distance and the angle between Mn-O bond and C_3-axis respectively. According to the van Vleck approximation for $G^k(\tau)$ integral [17], we have the relationships:

$$\begin{aligned}
G_2(\tau) &= -eq_\tau\frac{\langle r^2\rangle}{R^3} = \frac{A_2}{R^3},\\
G_4(\tau) &= -eq_\tau\frac{\langle r^4\rangle}{R^5} = \frac{A_4}{R^5}, \qquad (12)
\end{aligned}$$

where

$$A_4 = -eq_\tau\langle r^4\rangle, \quad A_2 = -eq_\tau\langle r^2\rangle,$$

and

$$A_2/A_4 = \langle r^2\rangle/\langle r^4\rangle. \qquad (13)$$

If we can get A_4 from the corresponding optical spectra and the value of $\langle r^2\rangle/\langle r^4\rangle$ from the parametrized wave function, then A_2 can be determined too. Subsequently, with use of equations (10) and (12), the relationship between the local structure parameters and its optical spectrum as well as the EPR parameters can be studied by employing the complete energy matrices.

3 Calculations

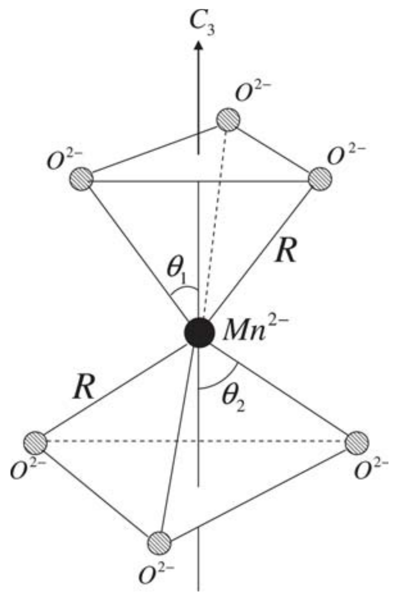

Fig. 1. Local structure of distorted octahedral Mn^{2+} ion in cadmium maleate dihydrate.

Cadmium maleate dihydrate (CMDH) belongs to monoclinic single crystal [9]. It contains two distinct cadmium atoms. One of them Cd(1) is surrounded by six oxygen atoms, four of which are from water molecules and two are from the carboxyl groups. The other atom Cd(2) is eight-coordinated with four chelated carboxyl groups from the two maleate ligands. By analyzing the EPR spectra, it is indicated that when the Mn^{2+} ion is doped into the crystal, it will substitute for neither of the two Cd atoms but enter the lattice interstitially [1,2]. The local lattice environment around the impurity ion is provided by the oxygen ligands O(12), O(12′) of Cd(1) and O(2), O(2′), O(4), O(4′) of Cd(2) (as shown in Fig. 1 of Ref. [1]). The optical spectra investigation of Mn^{2+} ion in CMDH shows that Mn^{2+} ion occupies a distorted octahedral site and the site symmetry exhibits trigonal [2]. The trigonal distortion may be described by two parameters $\Delta\theta_1$ and $\Delta\theta_2$ on the basis of the assumption that the six oxygen ions around Mn^{2+} ion are at the same distance R. If θ_1 and θ_2 are used to represent the angles between Mn-O bonds and C_3-axis in the up and down pyramids in the system CMDH:Mn^{2+} respectively, as shown in Figure 1, then the following relations are obtained:

$$\begin{aligned}
\theta_1 &= \theta_0 + \Delta\theta_1,\\
\theta_2 &= \theta_0 + \Delta\theta_2, \qquad (14)
\end{aligned}$$

where $\theta_0 = 54.73561°$. In the previous works, the optical spectra of $MnCO_3$ have been reported in detail [18,19] and the Mn^{2+} ion in $MnCO_3$ is surrounded by six oxygen ions, which is similar to the CMDH:Mn^{2+} system. Therefore, based on the optical spectra analysis, $A_4 = 26.7375$ a.u. is determined for the octahedral Mn^{2+} ion. Meanwhile, by using the radial wave function of Mn^{2+} ion in complexes [20,21], the values of $\langle r^2\rangle$ and $\langle r^4\rangle$ can be estimated

Table 1. The ground-state zero-field splitting ΔE_1, ΔE_2 and the EPR parameters a, D and $(a-F)$ for Mn^{2+} ion in the CMDH:Mn^{2+} system as a function of $\Delta\theta_1$ and $\Delta\theta_2$, while $R = 2.115$ Å.

$\Delta\theta_1$ (deg.)	$\Delta\theta_2$ (deg.)	$10^4\Delta E_1$ (cm^{-1})	$10^4\Delta E_2$ (cm^{-1})	$10^4 a$ (cm^{-1})	$10^4 D$ (cm^{-1})	$10^4(a-F)$ (cm^{-1})
11.00	–9.5	2010.1	686.2	15	334.4	10.34
11.00	–10.18	1921.5	656.4	15	319.6	10.12
11.00	–11.00	1808.3	618.9	15	301.0	10.31
11.52	–10.50	2034.8	694.2	15	338.5	10.19
11.52	**–11.33**	**1923.4**	**656.7**	**15**	**320.0**	**10.00**
11.52	–12.20	1797.5	614.7	15	298.9	9.92
12.00	–11.80	1998.8	681.9	15	332.5	10.00
12.00	–12.30	1927.4	658.0	15	320.6	9.93
12.00	–12.85	1844.6	630.4	15	306.8	9.93
Expt. [2]		**1923.9**	**656.9**	**15**	**320.0**	**10.00**

as follows:

$$\langle r^2\rangle = 2.7015,$$
$$\langle r^4\rangle = 19.41225, \tag{15}$$

so $A_2 = 3.72071$ a.u. is obtained with use of equation (13). In this case, the trigonal ligand-field parameters (B_{20}, B_{40}, B^c_{43}) are only the functions of $\Delta\theta_1$, $\Delta\theta_2$ and R.

In order to decrease the number of adjustable parameters and to reflect the effect of covalence, we may use the Curie's covalence theory to determine the optical parameters as following [22]:

$$B = N^4 B_0, \quad C = N^4 C_0, \quad \alpha = N^4\alpha_0,$$
$$\beta = N^4\beta_0, \quad \zeta = N^2\zeta_0, \tag{16}$$

where N is the average covalence parameter, the free-Mn^{2+} ion parameters $B_0 = 918$ cm^{-1}, $C_0 = 3273$ cm^{-1}, $\alpha_0 = 65$ cm^{-1}, $\beta_0 = -131$ cm^{-1} and $\zeta_0 = 347$ cm^{-1} have been obtained [23]. The covalence factor $N = 0.979237$ can be ascertained by using the energy level $^4E_g(G)$ of the optical spectra of CMDH:Mn^{2+} system [2]. Then by diagonalizing the complete energy matrices, the optical spectra and EPR parameters D and $(a-F)$ of the CMDH:Mn^{2+} system may be simulated with use of the Mn-O bond length R and the distortion parameters $\Delta\theta_1$ and $\Delta\theta_2$. $R = 2.115$ Å is estimated by use of the equation $6Dq = A_4/R^5$, and Dq is the ligand-field strength, which can be obtained from the energy level $^4T_{1g}(G)$ of the optical spectra of CMDH:Mn^{2+} system [2]. It is finally found that both the optical absorption and EPR spectra reported by Rao et al. are reasonably explained by adjusting the lattice structure parameters $\Delta\theta_1$, $\Delta\theta_2$. Meanwhile, the distortion parameters $\Delta\theta_1 = 11.52$, $\Delta\theta_2 = -11.33$ are determined. All the results are listed in Tables 1 and 2.

It can be seen from Tables 1 and 2 that the theoretical values agree well with the experimental values. However, from Table 2, the transitions from the ground-state $^6A_1$ to excited state $^4A_2{}^4T_{1g}(G)$, $^4A_1{}^4T_{2g}(G)$ and $^4E^4E_g(G)$, which are absent in the observed optical spectra, are obtained in the theoretical calculation. This needs the further experimental investigation. By diagonalizing the complete energy matrices, we also study the EPR parameters a, D and $(a-F)$ reported by Bansal et al. [1], but the optical spectra cannot be simulated simultaneously. This indicates that the EPR parameters from reference [2] are more reasonable.

Table 2. The observed and calculated optical spectra for Mn^{2+} in the CMDH:Mn^{2+} system.

Transition	Calculated[a] (cm^{-1})	Observed[b] (cm^{-1})
$^4A_2\ ^4T_{1g}(G)$	17914[c]	
$^4E\ ^4T_{1g}(G)$	18541	18686 ($^4T_{1g}(G)$)
$^4A_1\ ^4T_{2g}(G)$	22357[c]	
$^4E\ ^4T_{2g}(G)$	22854	22721 ($^4T_{2g}(G)$)
$^4E\ ^4E_g(G)$	24614[c]	
$^4A_1\ ^4A_{1g}(G)$	24684	24684 ($^4E_g(G)$)

[a] $B = 844$ cm^{-1}, $C = 3010$ cm^{-1}, $R = 2.115$ Å, $\Delta\theta_1 = 11.52$ and $\Delta\theta_2 = -11.33$. [b] Spectra data obtained from reference [2]. [c] Three transitions are absent in the observed optical spectra.

4 Conclusion

The EPR and optical-absorption spectra of Mn^{2+} ion in the CMDH:Mn^{2+} system have been studied by employing the complete energy matrices for a d^5 configuration ion in a trigonal ligand-field. On the assumption that Mn^{2+} ion enters the lattice interstitially and occupies a trigonaly-distorted site, the local structure parameters $R = 2.115$ Å, $\theta_1 = 66.26°$, $\theta_2 = 43.40°$ for the CMDH:Mn^{2+} system are determined by simulating successfully the experimental findings of optical absorption and EPR spectra.

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