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# Crystal field parameters and low-liyng energy levels for $Mn^{2+}$ doped in $Zn_2Sio_4$

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Using the superposition model (SPM) of the crystal fields (CF), we modeled the crystal field parameters (CFPs) acting on $Mn^{2+}$ ions, doped in the triclinic sites symmetry of $Zn_2SiO_4$. The modeling of the CFPs of the system has been done using the ascent in symmetry method by approximating the triclinic site symmetry by a higher symmetry, like the orthorhombic or the cubic symmetries. In both cases, orthorhombic and cubic symmetry, the crystal field parameters were calculated. The CFPs calculated, in the case of tetrahedral symmetry, were used for the diagonalization of the $Mn^{2+}$ Hamiltonian of the system. The obtained results are compared with the experimental data.

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*Keywords*: $Mn^{2+}$, Energy levels, Crystal field parameters

## 1. Introduction

The $Mn^{2+}$ (manganese) ion belongs to the $3d^5$ electronic configuration which doped in the luminescent compounds as zinc sulphate, willemite, germanates, fluorides, etc., it actions like an activator.

For the free $Mn^{2+}$ ion, the electrostatic interactions between electrons, gives rises to 16 LS terms: one spin-sextet $^6S$, four spin-quartets $^4PDFG$, and eleven spin-doublets $^2SPD_{1,2,3}F_{1,2}G_{1,2}HI$. The fundamental energy level is $^6S$, with the spin of the five electrons being parallel. The next excited energy levels are: $^4G$, $^4P$, $^4D$, $^4F$, etc. In the free ion all the transitions between the fundamental level and the quartet type excited levels are forbidden, but in the crystal, these are allowed and those can be described as a retour of one of the electrons spin. Also, are forbidden the transitions between the fundamental level and the doublet type levels [1].

The matrix of the crystal field Hamiltonian in the basis spanned by the wave functions of the above-given terms will be either 100 by 100 (if the spin-orbit (SO) interaction is neglected) or 252 by 252 (if the SO interaction is considered).

The Tanabe-Sugano diagram [2] for the $d^5$ electron configurations in high symmetry of crystal field is shown in Fig. 1. The number of the energy levels is large and many levels overlap. The ground term is the orbital singlet $^6S$ with high spin complexes; it can not be split by a crystal field of any symmetry. The absence of any other spin sextet terms implies that all ground state absorption transitions in the high spin $d^5$ complexes are spin forbidden and are very weak in the experimental spectra [3].

$Mn^{2+}$ in octahedral compounds is known as both high-spin (five unpaired electrons) and low-spin (one unpaired electrons) species. Tetrahedral $Mn^{2+}$ complex was reported in the high-spin form only [4].

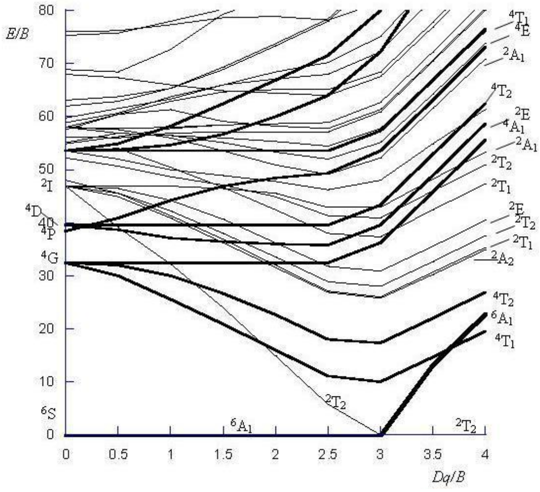

*Fig. 1. Tanabe-Sugano diagram for the $d^5$ configuration in an octahedral or tetrahedral crystal field. C/B=4.5 [2].*

$Zn_2SiO_4$ is known as an emitting green phosphor, like a transparent material in UV and Visible, and in practice is used for electroluminescent devices, lamps and plasma display panels because of its high saturated color, very strong luminescence, long lifespan, lack of moisture sensitivity and chemical stability, for medical imaging detectors for low voltage radiography and fluoroscopy [5-11].

$Zn_2SiO_4$ under ordinary conditions crystallizes in the phenacite structural type and belongs to the rhombohedral space group R-3 (No. 148) [12]. The unit cell parameters are: a = b =13.948 Å, c = 9.32 Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ [12] (see Fig. 2).

All the structure's ions occupy the 18*f* position in the crystal; the $Zn^{2+}$ is occupying two non-equivalent Zn1 and Zn2 positions in the structure. The local symmetry of the

$Zn^{2+}$ ions is triclinic ($C_1$) [12, 13]. The $Mn^{2+}$ ions will isovalent substitute the Zn1 positions, due to the close ionic radii of the host and substitution atoms.

The symmetry of the new created complex will be a tetrahedral one, the new complex formed being $[MnO_4]^{6-}$ [1, 6-10].

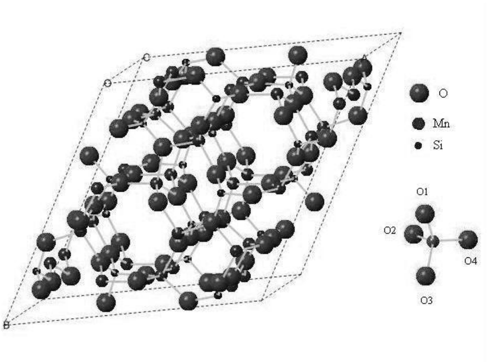

*Fig. 2. The crystal structure of $Zn_2SiO_4$. Drawn with VESTA developed by Momma and Izumi [14].*

The crystallographic axis system (CAS) for $Zn_2SiO_4$ (a, b, c), does not form a Cartesian system. For our SPM analysis we adopt the Cartesian axis system (x, y, z) coinciding with the CAS* defined as follows: x||a, y||b||C2, and z||c* with the c*-axis perpendicular to the plane (ab), and the $C_2$ axis - a symmetry element of the space group. In the present paper we model the CFPs and simulate the low-lying energy levels scheme for $Mn^{2+}$ doped $Zn_2SiO_4$ in tetrahedral Zn1 site, in the frame of SPM of CF.

## 2. Theoretical methods

For $Mn^{2+}$ ions, with the effective spin S=5/2, located at triclinic symmetry sites, for which no symmetry axes exist, the crystal field Hamiltonian, in terms of the extended Stevens operators, $O_k^q$, can be expressed as:

$$\begin{aligned} H_{CF} &= B_2^0 O_2^0 + B_2^1 O_2^1 + B_2^{-1} O_2^{-1} + B_2^2 O_2^2 + B_2^{-2} O_2^{-2} \\ &+ B_4^0 O_4^0 + B_4^1 O_4^1 + B_4^{-1} O_4^{-1} + B_4^2 O_4^2 + B_4^{-2} O_4^{-2} \\ &+ B_4^3 O_4^3 + B_4^{-3} O_4^{-3} + B_4^4 O_4^4 + B_4^{-4} O_4^{-4} \end{aligned} \tag{1}$$

where $B_k^q$ represent the crystal field parameters associated with the extended Stevens operators $O_k^q$ [15,16].

The number of the admissible non-zero CFPs in the equation above, for a given order *k*, is determined by the group theory for a given local site symmetry case and increases with lowering symmetry.

To calculate the CFPs, we used the SPM of the crystal field developed by D. J. Newman [17]. With the calculated CFPs, we have diagonalizated the crystal field Hamiltonian to get the energy levels scheme.

It has been established that the superposition model developed by Newman provides a useful method for analyzing crystal field parameters in terms of so called intrinsic parameters $\bar{A}_k(R_i)$ which represent the corresponding axially symmetric parameters for single ligand contributions. They are independent of the angular coordination of the ligands and their values are determined by the electronic processes of the interaction between the metal ion and a ligand. According to the superposition model, the contributions to the crystal field splitting are all of short range nature and are due to covalence, overlap, and configuration interaction which are scaled by power-laws.

The main assumption of the superposition model is that the parameters $B_k^q$ result from a linear superposition of single ligand contribution of the form [17]:

$$B_k^q = \sum \bar{A}_k(R_i) K_k^q(\theta_i, \phi_i) \tag{2}$$

where $K_k^q$ are the coordination factors determined by the angular coordination of the ligands and $\bar{A}_k(R_i)$ are the intrinsic parameters. The summation in eq. (2) goes over the nearest-neighbor ligands of the impurity ion.

$$\bar{A}_k(R_i) = \bar{A}_k(R_0)\left(\frac{R_0}{R_i}\right)^{t_k} \tag{3}$$

In (3), $R_i$ is the metal-ligand distance and $R_0$ is the reference distance, $t_k$ are the power law exponents and are adjustable parameters [17]. $R_i$ may be different from the cation-anion distance in the host structure $R_h$ due to the distortions arising from mismatch of the radius of the host atom $r_h$ and that of the substitution atom $r_i$. $R_i$ is often approximated as [18]:

$$R_i \approx R_h + \frac{1}{2}(r_i - r_h) \tag{4}$$

The atomic positions of ions in $Zn_2SiO_4$ referred in the CAS*, in the space group R-3 are given in the Table 1.

*Table 1. Ligand bond length and angular positions for the Zn1 (18f) site in $Zn_2SiO_4$.*

| $R_i$ (Å)(Calculated with (4)) | $R_{hi}$ (Å) [12] | $\theta_i$ (°) | $\phi_i$ (°) |
|---|---|---|---|
| 1.9749 | 1.9449 | 122.47 | 63.93 |
| 1.9784 | 1.9484 | 19.20 | 2.86 |
| 1.9811 | 1.9511 | 89.39 | -10.72 |
| 1.9823 | 1.9523 | 120.74 | -79.53 |

## 3. Results

Based on the equations (1-4), on the geometry of the crystal [12], and on the general formula for of CFPs [19], we calculated these parameters (see the Table 2).

*Table 2. CFPs (in cm$^{-1}$) for $Mn^{2+}$: $Zn_2SiO_4$ system.*

| Parameter | Value |
|---|---|
| $B_2^{-2}$ | 723 |
| $B_2^{-1}$ | 2131 |
| $B_2^{0}$ | -1562 |
| $B_2^{1}$ | 1294 |
| $B_2^{2}$ | 1292 |
| $B_4^{-4}$ | 2956 |
| $B_4^{-3}$ | -5802 |
| $B_4^{-2}$ | -1269 |
| $B_4^{-1}$ | -215 |
| $B_4^{0}$ | -196 |
| $B_4^{1}$ | 5517 |
| $B_4^{2}$ | 2872 |
| $B_4^{3}$ | 14989 |
| $B_4^{4}$ | -3713 |

This table, at the first glance, indicates large low symmetry components and the low symmetry character of these CFPs values may be *apparent* only. In order, to extract more structural information concerning the actual CFPs, we used the *ascent in symmetry* method [20]. This method consists in approximations of the triclinic site symmetry by a higher symmetry, like the orthorhombic or the cubic symmetries. First, we consider the approximation of the triclinic site symmetry by the orthorhombic symmetry, represented by adoption of the average of the spherical polar coordinates of all ligands obtained using the following relations [20]:

$$R_{av} = \frac{1}{4}\sum_i R_i \tag{5}$$

$$\theta_{av} = \frac{1}{4}\left(-\theta_1 + \theta_2 + \theta_3 - \theta_4 + 360\right) \tag{6}$$

$$\phi_{av} = \frac{1}{4}\left(\phi_1 - \phi_2 - \phi_3 + \phi_4 + 360\right) \tag{7}$$

The spherical polar coordinates of all tetrahedral ligands in orthorhombic site symmetry [20], are given in the Table 3.

*Table 3. The spherical polar coordinates of all tetrahedral ligands in the orthorhombic site symmetry.*

| i | $R_i$ (Å) | $\theta_i$ (°) | $\phi_i$ (°) |
|---|---|---|---|
| 1 | $R_{av}$=1.979 | 56.35 | -80.07 |
| 2 | $R_{av}$=1.979 | 56.35 | 91.93 |
| 3 | $R_{av}$=1.979 | 123.65 | 88.07 |
| 4 | $R_{av}$=1.979 | 123.65 | -91.93 |

Using the approximated coordinates from Table 3, CFPs calculations yield non-zero exclusively the orthorhombic CFPs, while lower symmetry CFPs acquire zero values (see Table 4).

*Table 4. CFPs (in cm$^{-1}$) for $Mn^{2+}$: $Zn_2SiO_4$ system.*

| Parameter | Value |
|---|---|
| $B_2^{0}$ | 1496 |
| $B_2^{2}$ | 39356 |
| $B_4^{0}$ | 1215 |
| $B_4^{2}$ | 6631 |
| $B_4^{4}$ | -6949 |

It can see that the ratio $B_2^2 / B_2^0$ is about 26, so the procedure of standardization [21] is needed.

Now we consider the approximation of the triclinic symmetry by cubic one. For this purpose, we used the program SYMMOL [22] and the data from Table 1 and the new coordinates for ligands are obtained. With these new coordinates and general formula (2) and (3), we calculated the CFPs of $Mn^{2+}$: $Zn_2SiO_4$ system. For this, we adopted the relations from [23, 24]

$$\bar{A}_4 = \frac{1}{8}\bar{B}_4 = -\frac{27Dq}{16} \tag{8}$$

with $\frac{\bar{A}_2}{\bar{A}_4} = 9 \div 12$ for the iron-group ions [23]. In our case, we take $\frac{\bar{A}_2}{\bar{A}_4} = 10.8$.

Using the above equations we obtained: $B_4^0 = 1304$ cm$^{-1}$ and $B_4^4 = 6521$ cm$^{-1}$.

With the CFPs calculated in last case, and Dq = 562 cm$^{-1}$, B = 622 cm$^{-1}$ and C = 3504 cm$^{-1}$ [7], $t_2$=3 and $t_4$=5, we diagonalized the Hamiltonian of the $Mn^{2+}$ ion in order to simulate the scheme of the energy levels. The results are shown in the second column of the Table 5.

*Table 5. Low-lying energy levels scheme of $Mn^{2+}$: $Zn_2SiO_4$ system calculated in SPM.*

| Energy levels ($O_h$ notations) | Energy ($cm^{-1}$) | |
|---|---|---|
| | Superposition model | Observed [7] |
| $^6A_1$ | 0 | 0 |
| $^4T_1$ ($^4G$) | 20 960 | 20 367 |
| $^4T_2$ ($^4G$) | 22 900 | 23 095 |
| $^4A_1$ + $^4E$($^4G$) | 23 740 | 23 736 |
| $^4T_2$ ($^4D$) | 27 104 | 26 316 |
| $^4E$ ($^4D$) | 28 094 | 28 050 |

As can see from this table the obtained results are in good agreement with the experimental data.

## 4. Conclusions

In this paper we have been investigated the $Mn^{2+}$ ion, doped in $Zn_2SiO_4$ in the low triclinic site symmetry. The modeling of the CFPs of the system have been done, in the SPM of the crystal field, using the ascent in symmetry method. This method consists in approximations of the triclinic site symmetry by a higher symmetry, like the orthorhombic or the cubic symmetries. In both cases, orthorhombic and cubic symmetry, we used the superposition model expressions and the crystal field parameters were calculated. In the case of the high tetrahedral symmetry the calculated crystal field parameters were used to diagonalized the $Mn^{2+}$ Hamiltonian and to simulate the scheme of the energy levels.

A comparison of these calculated energy levels with those experimentally obtained was made and a good agreement is observed.

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