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Zero field splitting parameters of mn^{2+} doped TMSeH single crystal-A theoretical study

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Abstract

Crystal field parameters and zero field splitting parameters of Mn^{2+} doped tellurium magnesium selenate hexahydrate single crystals are evaluated with the help of superposition model and perturbation theory. The zero field splitting parameters give good agreement with the experimental values suggesting manganese ion being substituted at magnesium site in the studied crystal. The crystal field energy levels of the manganese ion found by diagonalizing the complete Hamiltonian show a reasonable match with the experimental values. The present approach may be used for the modeling of other ion-host systems to explore the various technological applications of the crystals.

Keywords: A. Inorganic compounds, A. Single Crystal, C. Crystal structure and symmetry, D. Crystal and ligand fields, D. Optical properties, E. Electron paramagnetic resonance

Introduction

The superposition model (SPM) is used for semi-empirical modeling of the crystal field (CF) parameters and zero field splitting (ZFS) parameters in optical [1–3] and electron paramagnetic resonance (EPR) spectroscopy [4–6]. The physical Hamiltonians with their applications in different areas have been discussed [7-9].

The hydrated double sulfates and selenates having general formula $M'_2 M''(XO_4)_2 \cdot 6H_2O$, where M' is a monovalent cation and M'' is a divalent cation and X = S or Se, form an isomorphous series of monoclinic compounds [10]. Interestingly the EPR study of these salts with paramagnetic ion doping was done to test bonding models of transition metal complexes [11, 12] and spin quenching as well as host spin lattice relaxation narrowing effects [12-15]. The EPR study of Mn^{2+} in tellurium magnesium selenate hexahydrate, $Tl_2Mg(SeO_4)_2.6H_2O$ (TMSeH) single crystals at 298 K and 77 K has been reported and various spin Hamiltonian parameters have been determined [16].

In the present study, the ZFS parameters D and E for the Mn^{2+} ion at Mg^{2+} site in TMSeH are evaluated at 298 K using CF parameters and perturbation theory [17]. The evaluated D and E show good agreement with the experimental values [16].

Crystal structure

TMSeH crystals are isomorphous to $(NH_4)_2Mg(SO_4)_2.6H_2O$. The crystal stucture is monoclinic with space group P2$_1$/α (C_2h^5) [18]. The lattice parameters are a =9.316, b= 12.596, c = 6.198Å and Z = 2. The divalent metal ion is surrounded by six oxygens O7, O8, O9, O7', O8' and O9' of water molecules. The structure is shown in Fig. 1 together with symmetry adapted axes system (SAAS).

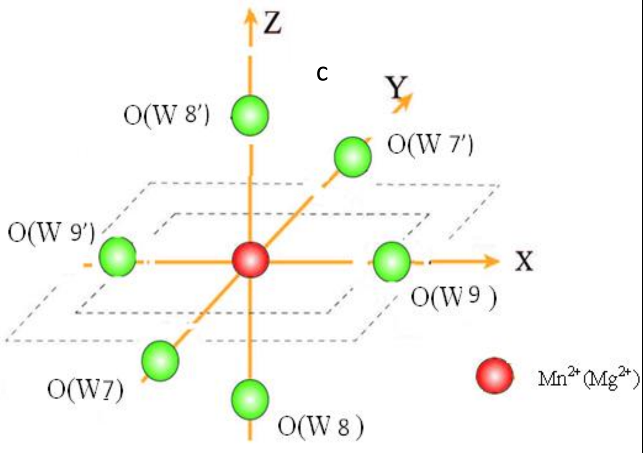

Fig 1: Coordination about Mn^{2+} in TMSeH single crystal.

The site symmetry about Mn^{2+}ions substituting for Mg^{2+} is orthorhombic, as indicated in EPR study [16].

Theoretical investigation

The resonance magnetic fields can be obtained by the following spin-Hamiltonian [7, 19]

$$\mathcal{H} = g\mu_B \mathbf{B}.\mathbf{S} + D\{S_z^2 - \frac{1}{3}S(S+1)\} + E(S_x^2 - S_y^2) + \left(\frac{a}{6}\right)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2+3S-1)] + \mathcal{A}S_zI_z + \mathcal{B}(S_xI_x + S_yI_y) \qquad (1)$$

where g, μ_B, $\mathbf{B}$ are the isotropic spectroscopic splitting factor [3, 19-22], Bohr magneton, external magnetic field; D, E, a are the second-rank axial and rhombic, the fourth-rank cubic ZFS parameters and A and B are the hyperfine (I = 5/2) interaction constants. For an arbitrary orientation of the crystal, a complex spectum corresponding to two identical but differently oriented Mn^{2+} complexes is obtained in TMSeH crystal. When the magnetic field is in the ac plane, the EPR spectrum gives only one set of five sextets (ΔM = ±1, Δm = 0 transitions). Thus the ac plane is a mirror plane perpendicular to the b axis, where two Mn^{2+} sites become equivalent. The Mn^{2+} ions substitute at Mg^{2+}

sites and consequently $[\mathrm{Mn\ H2O})_6]^{2+}$ complexes are formed [16]. The principal axes of the Mn^{2+} complexes are obtained by finding maxima in the fine structure spread. The spectra yield orthorhombic symmetry. The direction of maximum overall splitting of EPR spectrum is taken as the z axis and the minimum as the x axis [23]. The laboratory axes (x, y, z) obtained from EPR spectra coincide with the

modified crystallographic axes (CAS*), a, b*, c. The z-axis of the local site symmetry axes (the symmetry adapted axes axes (x, y) are normal to the z-axis.

Magnesium ion in TMSeH is in a distorted octahedron of oxygen ions [16, 18] and the local symmetry is considered as orthorhombic of first kind (OR-I) [24]. In an OR-I symmetry, the ZFS parameters D and E of $3d^5$ ions are obtained [17, 25] as:

$$D = (3\xi^2/70P^2D)\,(-B^{2}_{20} - 21\,\xi\,B_{20} + 2B^{2}_{22}) + (\xi^2/63P^2G)\,(-5B^{2}_{40} - 4B^{2}_{42} + 14B^{2}_{44}) \qquad (2)$$

$$E = (\sqrt{6}\,\xi^2 / 70P^2D)\,(2B_{20} - 21\,\xi)\,B_{22} + (\xi^2 / 63P^2G)\,(3\sqrt{10}\,B_{40} + 2\sqrt{7}\,B_{44})\,B_{42} \qquad (3)$$

where P = 7B+7C, G = 10B+5C, and D = 17B+5C; B and C are the Racah parameters.

The parameters B, C and ξ, in terms of the average covalency parameter N, are given as [26-27]:

$$B = N^4B_0,\ C = N^4C_0;\ \xi_d = N^2\,\xi^{0}_{d} \qquad (4)$$

where B_0, C_0, and ξ^{0}_{d} are the free ion Racah and spin-orbit coupling parameters, respectively [21-22]. $B_0 = 960\ cm^{-1}$, $C_0 = 3325\ cm^{-1}$ and $\xi^{0}_{d} = 336\ cm^{-1}$ for free Mn^{2+} ion [19].

The optical study of the present system could not be obtained in literature survey, hence using optical absorption of Mn^{2+} doped crystal with oxygen ligands [28]: B = 917cm^{-1} and C = 2254 cm^{-1}were determined. The average value

[27] of $N = (\sqrt{B/B_0} + \sqrt{C/C_0})/2 = 0.911$ is used to find D and E from Eqs. (2) and (3).

The SPM is employed to obtain the CF parameters, B^{kq} for Mn^{2+} ion in TMSeH single crystal and ZFS parameters are The crystal-field splitting of rare-earth ions [29] as well as of transition ions [30-32] have been interpreted by SPM. This model gives the CF parameters as [17, 29]

$$B_{kq} = \sum \bar{A}_k\,(R_j)\,K_{kq}\,(\theta^j, \phi^j) \qquad (5)$$

where R_j are the distances between the Mn^{2+} ion and the ligand ion j, R^0 is the reference distance. θ^j are the bond angles in a chosen axis system (SAAS) [33, 34]. The summation is taken over all the nearest neighbour ligands

and the coordination factor K_{kq} (θ^j, ϕ^j) are the explicit functions of angular position of ligand [17, 33, 35-36]. The intrinsic parameter $\bar{A}_k\,(R_j)$ is obtained by the power law [24] as:

$$\bar{A}_k\,(R_j) = \bar{A}_k\,(R^0)\,(R^0/R^j)^{t_k} \qquad (6)$$

where $\bar{A}_k\,(R^0)$ is intrinsic parameter for a given ion host system. The symbol t_k is called power law exponent. The CF parameters, B_{kq} are evaluated from Eq. (5) [37].

For $3d^5$ ions, the ratio $\bar{A}_2\,(R^0)\,/\,\bar{A}_4\,(R^0)$ lies in the range 8 - 12 [31]. In the present study, the ratio $\bar{A}_2\,(R^0)\,/\,\bar{A}_4\,(R^0) = 12$ is taken. For $3d^5$ ions in the 6-fold cubic coordination $\bar{A}_4\,(R^0)$ has the relation: $\bar{A}_4\,(R^0) = (3/4)\ Dq$ [22]. Because (SAA)) is along the Mn-O (W8) bond and the other two

$\bar{A}_4\,(R^0)$ is independent of the coordination [38], the above relation is used to get $\bar{A}_4\,(R^0)$ using Dq = 756 cm^{-1} [28].

Result and discussion

The ionic radius of the Mn^{2+} ion (0.080 nm) is slightly larger than the Mg^{2+} (0.066 nm) ion, some distortion will take place [39] when Mn^{2+} substitutes at Mg^{2+} site. The bond distances of different ligands, R_j along with the angles θ_j and ϕ^j are calculated from the crystal structure data of TMSeH crystal and are given in Table 1.

Table 1: Coordinates of ligands, Mn-ligand bond distances R_j and coordination angles θ^j and ϕ^j for Mn^{2+} ion doped TMSeH single crystals.

Position of Mn^{2+}	**Ligands**				**Spherical coordinates of ligands**					
		x	y (Å)	z	R(nm)		θ ^{0}		ϕ°	
Site I: Substitutional Without distortion										
Mg (0, 0, 0)	O7	0.1694	0.1694	0.1669	0.2082	R_1	85.40	θ_1	85.32	φ_1
	O8	-0.1607	0.1096	0.0303	0.2085	R_2	89.16	θ_2	94.42	φ_2
	O9	-0.0020	-0.0691	0.2982	0.2048	R_3	81.63	θ_3	90.05	φ_3

	O7’	-0.1694	-0.1045	-0.1669	0.2082	R_4	94.60	θ_4	94.68	φ_4
	O8’	0.1607	-0.1096	-0.0303	0.2085	R_5	90.83	θ_5	85.58	φ_5
	O9’	0.0020	0.0691	-0.2982	0.2048	R_6	98.37	θ_6	89.94	φ_6
With Distortion										
O7		0.3382				$R_1+\Delta R_1$				
O8		0.3385				$R_2+\Delta R_2$				
O9		0.3448				$R_3+\Delta R_3$				
O7’		0.3482				$R_4+\Delta R_4$				
O8’		0.3685				$R_5+\Delta R_5$				
O9’		0.3548				$R_6+\Delta R_6$				

Taking R_0 to be slightly smaller than the sum of ionic radii of Mn^{2+} (0.080 nm) and O^{2-} (0.140 nm) [40] i.e. $R_0 = 0.1866$ nm, $\bar{A}_2(R^0)/\bar{A}_4(R^0) = 12$, $t_2= 4$, $t_4= 5$; no distortion, we find B_{kq} and then |D| and |E| being different than the experimental values as shown in Table 2. Taking other parameters as above and $t_2= 3$ $t_4= 7$ [33], the values of |D| and |E| are different than the experimental ones and also the ratio |E|/|D| comes out to be larger than 0.33 and therefore $t_2= 4$, $t_4= 5$ were taken for calculation. Since |D| and |E| estimated with no distortion were different than the experimental values, the distortion was introduced into calculation. The bond distances of different ligands R_j and the angles θ_j and ϕ_j for this case are also given in Table 1. The calculated CF parameters, B_{kq} from Eq. (5) and transformation S5 for standardization [23] as well as ZFS parameters |D| and |E| using other parameters as above are shown in Table 2. From Table 2, |D| and |E| give reasonable match with the experimental values when distortion is introduced into calculation. Such model calculations have been done in case of Mn^{2+} and Fe^{3+} doped anatase TiO_2 crystal [41]. The interstitial sites for Mn^{2+} ions in TMSeH crystal were also considered but ZFS parameters found were quite inconsistent with the experimental values and hence have not been given here.

Table 2. CF parameters and ZFS parameters calculated by the SPM for Mn^{2+} ion doped TMSeH single crystal along with experimental values.

Crystal -field parameters (cm^{-1})							**Zero-field splitting parameters ($\times 10^{-4} cm^{-1}$)**		
Site	**R_0(nm)**	**B_{20}**	**B_{22}**	**B_{40}**	**B_{42}**	**B_{44}**	**|D|**	**|E |**	**|E|/|D|**
Without distortion									
Site I	0.1866	-26120.7	-32351.7	5486.266	5850.294	8925.979	8414.8	4216.3	0.50
With distortion									
Site I	0.1866	-3667.18	-2888.8	411.7105	438.5171	2716.331	255.4	86.3	0.33
						Exp.	256.0	71.0	0.28

Using calculated CF parameters and CFA program [42] the optical absorption spectra of Mn^{2+} doped TMSeH single crystals are determined. The CF energy levels of the Mn^{2+} ion are obtained by diagonalizing the complete Hamiltonian in the intermediate crystal field coupling scheme. The calculated energy values are presented in Table 3 together with the experimental ones for comparison. It is seen from Table 3 that there is a reasonable match between the two. Hence, the result obtained using SPM with distortion supports the experimental observation that Mn^{2+} ions substitute at Mg^{2+} sites in TMSeH single crystal [16].

Table 3

Transition from $^6A_{1g}$(S)	**Observed wave number (cm^{-1})**	**Calculated wave number (cm^{-1})**
$^4T_{1g}$(G)	16044	
$^4T_{2g}$(G)	20433	19993, 19997, 20879, 20900, 21136, 21167
^4E_g(G)	24108	22523, 22547, 22581, 22625
$^4A_{1g}$(G)	24242	23671, 23687
$^4T_{2g}$(D)	26724	26448, 26521, 26601, 26679, 27315, 27326
^4E_g(D)	30451	30264, 30525, 30725, 30822
$^4T_{1g}$(P)	33956	32769, 32855, 33098, 33399, 33595, 34185
$^4A_{2g}$(F)	36846	36836, 36867
$^4T_{1g}$(F)	38521	38049, 38125, 38193, 38254, 39552, 39562

Conclusions

The zero-field splitting (ZFS) parameters have been determined using the superposition model and perturbation theory. The calculated ZFS parameters for Mn^{2+} ions substituting at the Mg^{2+} site in TMSeH single crystal are in reasonable agreement with the experimental values. The CF energy levels of the Mn^{2+} ion obtained using CF parameters and CFA program show reasonable match with the experimental ones. It is concluded that the Mn^{2+} ion substitutes at Mg^{2+} site in TMSeH single crystal. Thus the theoretical results support the experimental observation. The process used in the present study may be applied for the modeling of other ion-host systems to explore the crystals for various technological and industrial applications.

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