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Modelingof Cr^{3+} doped KZnCSTSingle Crystals

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Abstract
The superposition model is utilized to evaluate the crystal field and zero field splitting parameters of single crystals of Cr^{3+} doped KZnCST ($KZnClSO_4.3H_2O$).Differentsitesfor Cr^{3+} ions in KZnCSTwithdistortion are employed for calculation. The zero field splitting parameters that are obtained theoretically with local distortion agree quite well with the experimental values.The optical energy levelsfor Cr^{3+} inKZnCSTare established with the Crystal Field Analysis Program and crystal fieldparameters.The findings indicate that in KZnCST single crystals, one Zn^{2+} ion is substituted by a Cr^{3+} ion.
Keywords:*Cr^{3+} ions in KZnCST; Crystal field;Optical spectroscopy;Superposition model;Zero-field splitting.*

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I. Introduction

One useful method for determining the local site symmetry of transition ions in crystals is electron paramagnetic resonance, or EPR.Additionally, it is employed in the identification and characterization of the defects in doped crystals that cause charge compensation [1].The Cr^{3+} ion doped into several crystalsprovidessufficient information regarding the crystal field (CF) and zero field splitting (ZFS) parameters[2-6].Doped impurities resulting small structural change influence the crystal's optical qualities.ZFS and CF parameters are primarily determined theoretically using the Superposition Model (SPM)[7-9].

The Zn analogue of $KMgClSO_4 \cdot 3H_2O$ single crystals used in the fertilizer industry is called KZnCST [10].It also falls under the group of mineral salts that are utilized as catalysts in a variety of chemical reactions, such as zeolites and antigorite [11, 12].

Studies of optical absorption and EPR have been conducted on Cr^{3+} ion doped KZnCST single crystals to determine the characteristics of the crystal field surrounding the Cr^{3+} ionand spin Hamiltonian parameters [10].The ionic radius of Zn^{2+}ion (0.074 nm) is slightly larger than that of the Cr^{3+}ion (0.0615 nm). Therefore Cr^{3+}ion substitutes for one of the Zn^{2+} ions as reported in[10].

The modified crystallographic axes (a, b, and c*) and the laboratory axes (x, y, and z) are chosen in parallel.The labels (X, Y, Z) represent the symmetry adopted axes (magnetic axes). The crystallographic *a* axis is found to correspond with the principal Z axis of the **g** and **D** tensors of Cr^{3+} ions.

The superposition model (SPM) analysis of the ZFS and CF parameters for Cr^{3+} ions in KZnCST single crystal is presented in this work.The objective is to knowthe ZFS parameters, the lattice distortion and the CF parametersfor the Cr^{3+} ions inKZnCSTat octahedral sites. The optical energy levelsfor Cr^{3+}ions in KZnCSTare computed using CF parameters and Crystal Field Analysis (CFA)computer program. The determined ZFS and CF parameters could be helpful in upcoming research for crystal searches related to a range of scientific and commercial applications.

II. Crystal structure

KZnCST, which is the Zn equivalent of KMgCST ($KMgClSO_4.3H_2O$), crystallizes in a monoclinic system with Z = 16 and space group C2/m.The parameters of the unit cell are as follows: β = 94◦ 55', b = 16.23 Å, c = 9.53 Å, and a = 19.72 Å [13].Along the b-axis, a lattice is made up of four chains: $(SO_4)_2$-$Zn(H_2O)_2$-$(H_2O)_2$-$Zn(H_2O)_2$-$(SO_4)_2$—the mirror plane containing the SO_4tetrahedra. The chains are present on the cell's (0 1 0) cross-section. The chains are held vertically together by K^+ and Cl^- ions.The asymmetric portion of the unit cell contains two Zn atoms.Figure 1 depicts the KZnCST crystal structure along with the symmetry-adopted axis system (SAAS).

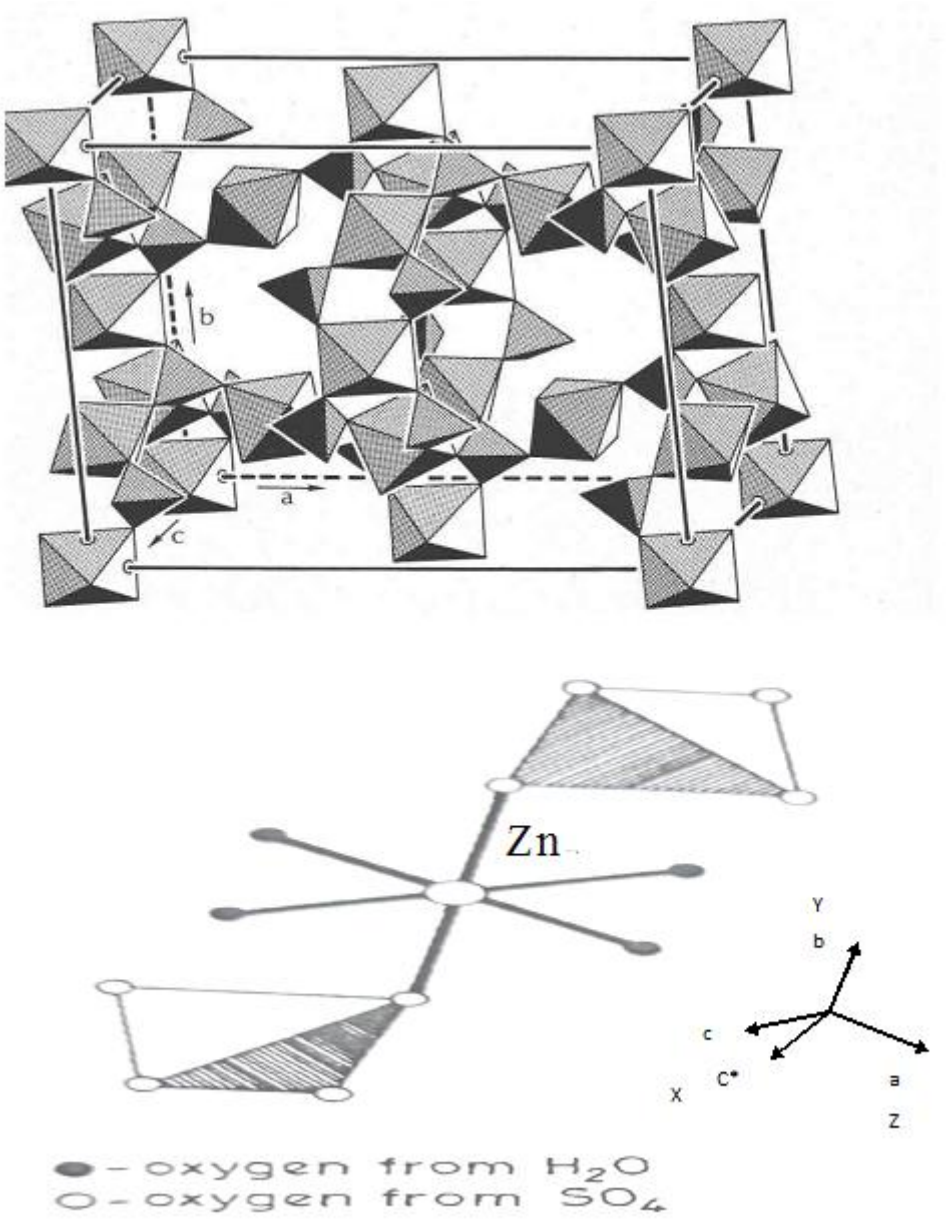

Fig.1. KZnCSTcrystal structure with the symmetry adopted axis system (SAAS).

The directions of metal-ligand bonds that are mutually perpendicular are the symmetry adopted axes (SAA) or local site symmetry axes.The two other axes (X, Y) are perpendicular to the Z axis for centers I, and the Z axis of SAAS is along the metal-ligand bond Zn-O (crystal *a*-axis) (Fig. 1).This implies that Cr^{3+} with roughly orthorhombic symmetry replaces Zn^{2+} in the KZnCST crystal. The ionic radius Cr^{3+} ion (0.0615 nm) is marginally smaller than Zn^{2+} ionic radius (0.074 nm), indicating that Cr^{3+} ioncan substitute$Zn^{2+}$with certain distortion.

Table 1 lists the spherical polar coordinates of ligands and Cr^{3+} ion position for center I in KZnCST[13].These data are used in KZnCST to compute ZFS and CF for Cr^{3+} ions.

III. Calculations of Splitting Parameters for Zero Field

The following spin Hamiltonian is utilized to ascertain the energy states of Cr^{3+} ions within crystals [14, 15, 16]:

$$\mathcal{H} = \mathcal{H}_{Ze} + \mathcal{H}_{ZFS} = \mu_B B.g.S + \sum B_k^q O_k^q = \mu_B B.g.S + \sum f_k b_k^q O_k^q , \quad (1)$$

where the constant magnetic field, Bohr magneton, and spectroscopic splitting factor are represented by the letters B, μ_B, and g, respectively. *S* presents the effective spin operator and $O_k^q(S_x, S_y, S_z)$ are the extended Stevens operators (ESO) [17, 18]; B_k^q and b_k^q are the parameters of ZFS, f_k = 1/3 and 1/60 the scaling factors for k = 2 and 4, respectively. For the Cr^{3+} ion (S = 3/2) at orthorhombic symmetry sites, the ZFS terms in (1) are determined as [19, 20]:

Table 1. The spherical polar co-ordinates (R, θ, ϕ) of ligands and the Cr^{3+} ion's fractional coordinates (center I) in single crystal of KZnCST.

Position of Cr^{3+}	Ligands	Spherical polar coordinates of ligands		
		R(Å)	θ^0	ϕ^0
ND: Substitutional	O1	9.4911	23.23	20.40
(0.0000, 0.0000, 0.0000)	O2	5.9749	48.65	72.31
	Ow1	2.1728	15.50	1.18
	Ow2	10.6079	49.75	87.31
	Ow3	7.7182	59.74	33.67
	Ow4	6.0005	76.52	84.99
WD: substitutional Centre I	O1	9.1378	8.27	56.07
(0.0979, 0.2803, -0.0337)	O2	4.3509	11.18	18.25
	Ow1	5.3067	62.93	75.84
	Ow2	8.2766	29.89	-66.51
	Ow3	6.9472	20.08	-37.50
	Ow4	2.6488	49.50	-41.90

ND = No distortion, WD = With distortion.

$$\mathcal{H}_{\mathrm{ZFS}} = B_2^0 O_2^0 + B_2^2 O_2^2 = \frac{1}{3} b_2^0 O_2^0 + \frac{1}{3} b_2^2 O_2^2 = D(S_z^2 - \frac{1}{3} S(S+1)) + E(S_x^2 - S_y^2)\,, \qquad (2)$$

The traditional orthorhombic ZFS parameters*D, E*and B_k^q , b_k^q have the following relations:

$$b_2^0 = D = 3\,B_2^0\,,\; b_2^2 = 3E = 3\,B_2^2\,. \qquad (3)$$

For ZFS, the parameters (in ESO notation) inany symmetryutilizing SPM [19-20] arefoundas:

$$b_k^q = \sum_i \bar{b}_k\,(R_0)\left(\frac{R_0}{R_i}\right)^{t_k} K_k^q\,(\theta_i, \varphi_i)\,, \qquad (4)$$

where (R_i, θ_i, φ_i) presentthe i-th ligand's spherical polar coordinates.The intrinsic parameters $\bar{b}_k$ representthe magnitude of a ligand's k-th rank ZFS contribution at a distance$R_i$and the coordination factors K_k^q givethe geometrical data. K_k^q for$k$ = 1 to 6 in ESO notation [21] are given in Appendix A1 of [22].

Eq. (4) establishes traditional ZFS parameters, D and E in terms of the intrinsic parameters $\bar{b}_k$, the power-law exponentst_k and the reference distance R_0,asgiven below [22,23-25]:

$$b_2^0 = D = \frac{\bar{b}_2(R_0)}{2}\left[\left(\frac{R_0}{R_i}\right)^{t_2} \sum_i (3\cos^2\theta_i - 1)\right]$$

$$b_2^2 = 3E = \frac{b_2^2}{3} = \frac{\bar{b}_2(R_0)}{2}\left[\left(\frac{R_0}{R_i}\right)^{t_2} \sum_i \sin^2\theta_i \cos 2\varphi_i\right] \qquad (5)$$

It is believed that the Cr^{3+} ion in KZnCST is substituted at the Zn^{2+} ion site and the interstitial site with a ligand environment that is similar.In KZnCST, the local symmetry of the Cr^{3+} ion is orthorhombic.In $LiNbO_3$having octahedral coordination of Cr^{3+} ion and Cr^{3+}-O^{2-} bond, $\bar{b}_2(R_0)$ = 2.34 cm^{-1} and t_2 = -0.12 [26] weretaken to compute b_2^0 and b_2^2. Given that the Cr^{3+} ion in KZnCST has distorted octahedral coordination (Fig. 1), oxygens functioning as ligands, the b_K^q for center I in the present study are estimatedusing $\bar{b}_2(R_0)$ = 2.34 cm^{-1} and t_2 = -0.96.

The spherical polar coordinates of ligands and the Cr^{3+} ion's location as listed in Table 1 are employed in the computation.In KZnCST single crystal, the conventional ZFS parameters, D and E of the Cr^{3+} ion, are determined using Eq. (5). The reference distance R_0 = 0.200 nm is used [27] to yield the ZFS parameters, and the values are: |D| = $930.9\times10^{-4}$$cm^{-1}$and |E| = $797.3\times10^{-4}$$cm^{-1}$ for center I. For symmetry that is orthorhombic, the ratio b_2^2 / b_2^0 should fall between 0 and 1 [28]. In the presentcalculation, the ratio $|b_2^2| / |b_2^0|$ = 2.569and |E| / |D| = 0.856for center I. It is discovered that the calculated values of |D| and |E| donotmatch with the experimental ones and $|b_2^2| / |b_2^0|$ also does notfall in the specified range [28].Hence, with above t_2 and reference distance R_0, the ZFS parameters |D| and |E| are calculated for Cr^{3+} at the Zn^{2+}site with distortion having position Zn^{2+}(0.0979, 0.2803, -0.0337)for center I. The local environment about Cr^{3+}ion is displayed in Fig. 2. The traditional ZFS parametersestimated now are $|D| = 1719.1\times10^{-4}$ cm^{-1}, $|E| = 261.0\times10^{-4}$ $cm^{-1}$for center I, which match well withthe values of the experiment. The ratio $|b_2^2| / |b_2^0|$ = 0.455 and |E| / |D| = 0.152 for center Ifallin the specified range[29]. Further,with above t_2 and reference distance R_0, the ZFS parameters|D| and |E| are computed for Cr^{3+} at the interstitial site but the valuesdetermined arelargely different fromthe experimental ones andfor this reason, they are not presented here.

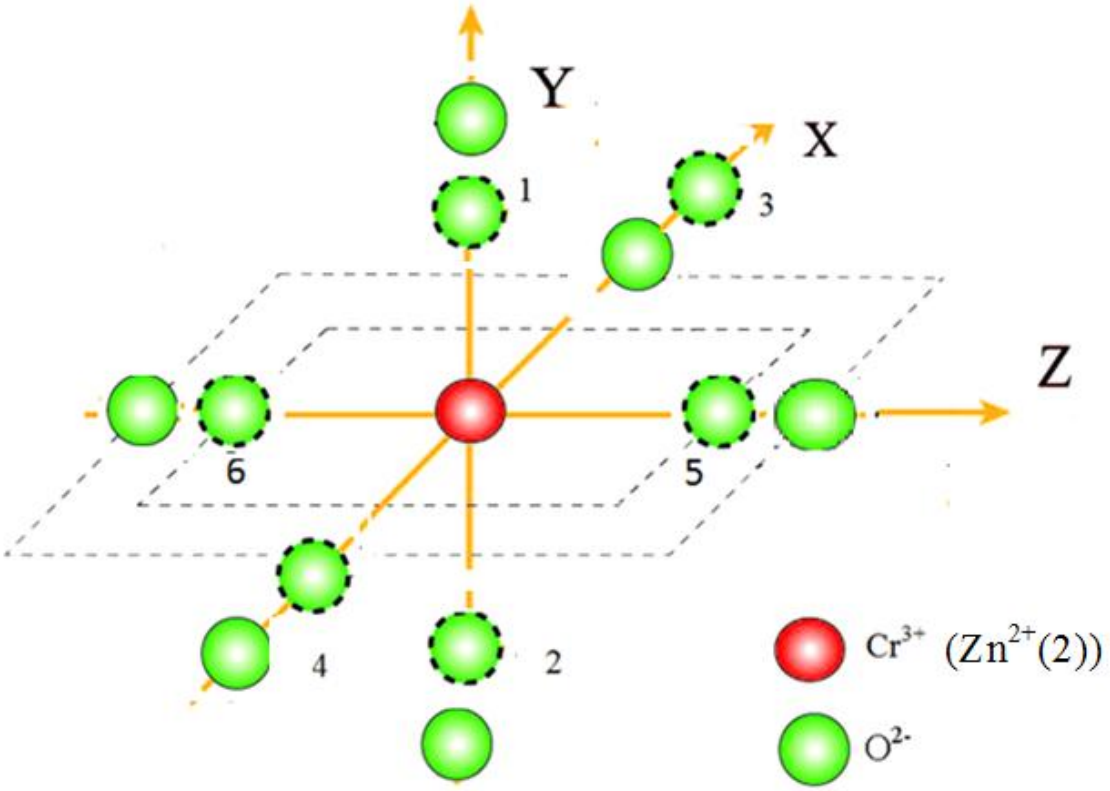

Fig. 2. Graphical presentation of local environment (dotted circles show positions after distortion).

Table 2 shows the experimental and calculated ZFS parameters of the Cr^{3+} ion in KZnCST. Itis noted from Table 2 that theZFS parameters|D| and |E|are in goodagreement withthe values of the experiment [10] when the distortion is included into calculation.

Table 2.ZFS parameters of Cr^{3+} in KZnCST single crystal for center I, both experimentally determined and calculated, along with the reference distance.

		Calculated ZFS parameters (cm^{-1})			Conventional ZFS parameters ($10^{-4}cm^{-1}$)		
Site	R_0Å	$\|b_2^0\|$	$\|b_2^2\|$	$\|b_2^2\|/\|b_2^0\|$	$\|D\|$	$\|E\|$	$\|E\|/\|D\|$
ND	2.00	0.09309	0.23919	2.569	930.9	797.3	0.856
Center I							
WD	2.00	0.17191	0.07831	0.455	1719.1	261.0	0.152
					1719.0[e]	261.0[e]	0.152

WD = With distortion, ND = No distortion, [e] = experimental.

IV. Calculations of the Crystal Field Parameters

The transition ion CF energy states in crystals [29–32] can be determined using Wybourne operators as [14, 33, 34]:

$$\mathcal{H}_{CF} = \sum_{kq} B_{kq} C_q^{(k)} \quad (6)$$

where $\mathcal{H}_{CF}$ is CF Hamiltonian. The metal-ligand complex's CF parameters in equation (6) areestablishedusing SPM [19-20] asgiven below:

$$B_{kq} = \sum_i \bar{A}_k \left(\frac{R_0}{R_i} \right)^{t_k} K_{kq}(\theta_i, \varphi_i). \quad (7)$$

R_0 represents the reference distance,R_i, θ_i, $\varphi_i$givethe i^{th} ligandspherical polar coordinates and K_{kq} are the coordination factors [29]. To obtain B_{kq} (k = 2, 4; q = 0, 2, 4) the following values are taken: $\bar{A}_2$ = 40, 400 cm^{-1}, t_2 = 1.3, $\bar{A}_4$ =11, 700 cm^{-1} and t_4 = 3.4 [29]. The B_{kq} parameters evaluated are given in Table 3.For center I, the ratio $|B_{22}|/|B_{20}|$ = 0.353 demonstrates that the established B_{kq} parameters are standardized [28]. By diagonalizing the total Hamiltonian and using the B_{kq}parameters in Table 3 and the CFA computer program [30, 31], the CF energy levels of the Cr^{3+} ion in KZnCST single crystals are determined.The calculated energy values are shown in Table 4.For Cr^{3+}: KZnCST, the calculated and experimental energy values are contrasted [10].The experimental and theoretical energy values appear to be in a fair amount of agreement, as Table 4 shows.Hence, the experimental results are supported by the examination of Cr^{3+} ions at Zn^{2+} sites theoretically in KZnCST[10].

Table 3.B_{kq} parameters of Cr^{3+} for center I with distortion in a single crystal of KZnCST.

		Calculated B_{kq} (cm^{-1}) Parameters used for CFA program					
Site	R_0(Å)	B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	$\|B22\|/\|B20\|$
Center I							
WD	2.00	24311.49	-8594.43	-14664.1	1198.291	-7246.45	0.353

WD = With distortion.

The spectra of optical absorptionof Cr^{3+}-activatedphosphors are currentlyexplained usingFranck-Condon analysis withconfigurational-coordinate (CC)model[35]. The various excited state-ground state transitions in $Cr^{3+}$are a result of strong coupling (CC model)of the lattice vibrations [35]. The CCmodelis not beingconsidered and hence there is difference between excited-state peak energies found here and energies of the zero-phonon line (ZPL)described in [35, 36]. Two groups of oxide-phosphors doped with Cr^{3+} are taken up: (i) O-Cr-A type, (ii) O-Cr-B type. The luminescence properties of type (i) phosphors are obtained from the ^2E_g-related luminescence transitions as their crystal-field strength falls in the region of Dq/B > 2.1while type (ii) phosphors have a crystal-field strength lying within the range of Dq/B < 2.1, hence, the optical transitions associated with $^4T_{2g}$ are utilized to find their luminescence properties. KZnCST: Cr^{3+} falls under (i) type phosphors (Dq/B =2.38 which is >2.1) [36].

V. Summary and Conclusions

For Cr^{3+} ions in KZnCST single crystals, the zero-field splitting (ZFS) and crystal field (CF) parameters are computed using the superposition model (SPM).Calculations are performed using Cr^{3+} ions in KZnCST crystal at the Zn^{2+} ion sites, interstitial site, and distortion models.When distortion is taken into account, the calculated conventional ZFS values for the Cr^{3+} ion at Zn^{2+} sites in KZnCST single crystal show

good agreement with the experimental values.The Cr^{3+} ions are established to be substituted atZn^{2+}ion sites in KZnCST. The CF energy values for Cr^{3+} ions at Zn^{2+}sites evaluatedwith CFA program and CF parameters present a reasonable agreement withthe experimental ones. So, the theoretical inferences validate the experimental conclusion.

Table 4. Energy valuesfound through experimentation and computation(center I) of Cr^{3+}in KZnCSTsingle crystal.

Transition from $^4A_{2g}(F)$ state	Observed band (cm^{-1})	Calculated band from CFA (cm^{-1}) Center I
$^2E_g(G)$	11975	10388, 11521
$^2T_{1g}(G)$		12161, 12418, 12485
$^4T_{2g}(F)$	17235	15396, 16932, 16978, 17354, 17925, 18716
$^4T_1g(F)$	24385	19759, 20876, 21866, 23380, 23834, 24744
$^4T_{1g}(P)$		26175, 26544, 26625, 27045, 27590, 28162
$^2T_{1g}(aD)$		31866, 33603, 34554
$^2E_g(bD)$		34780, 35559

(The spin-orbit coupling constant, Racah parameters A, B, and C, and the Trees correction are 276, 0, 724, 2484, and 70 cm^{-1}, respectively)

The modeling procedure used in the current investigationcan be helpful in correlating EPR and optical data for many other ion-host systems to obtain crystals ofseveral commercial and scientific applications.

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Declarations:

Ethical Approval:

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Competing interests:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Authors' contributions:

MarojBharati and Vikram Singh- performed calculations, wrote the manuscript and prepared the figure.
Ram Kripal- idea and supervision.
All authors have reviewed the manuscript.

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