International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 10 Issue 10 ǁ October 2022 ǁ PP. 51-56

Modeling of Cr^{3+} doped $TlZnF_3$ Single Crystal

Ram Kripal
EPR Laboratory, Department of Physics, University of Allahabad, Allahabad-211002, India

Abstract
The zero field splitting parameter D of Cr^{3+} doped $TlZnF_3$ (TZF) single crystal is evaluated by perturbation formula using microscopic spin Hamiltonian theory and crystal field parameters obtained from superposition model. The theoretical ZFS parameter for Cr^{3+} in TZF single crystal is compared with the experimental value given by electron paramagnetic resonance (EPR). The local distortion is taken into account to obtain the crystal field parameters and good fit to the experimental ZFS parameter. The theoretical study gives the ZFS parameter D matching with the experimental one for the centers A, B, C and D.

Keywords: *A. Inorganic compounds; D. Crystal fields; D. Optical properties; D. Electron paramagnetic resonance.*

Date of Submission: 20-09-2022 Date of acceptance: 04-10-2022

I. Introduction

Electron paramagnetic resonance (EPR) gives information about the local site symmetry and zero field splitting (ZFS) parameters of transition ions incorporated in crystals [1, 2]. It also helps to identify and characterize the defects which provide the charge compensation in the doped crystals. Cr^{3+} is one of the most studied ions with $3d^3$ electronic configurations and $^4F_{3/2}$ ground state. The ground state responsible for the electron paramagnetic resonance acts like a $^4A_2$ state [3].

The major mechanism for the zero field splitting of the ground state of $^4A_2$ ($3d^3$) ions is the spin-orbit interaction from an admixture of higher multiplets of $3d^3$ configuration because of the combined effect of crystal field and the spin-orbit coupling [4]. The superposition model (SPM) has been satisfactorily used for several $3d^n$ ions [5, 6] to calculate the crystal field parameters and spin Hamiltonian parameters. EPR of Cr^{3+} ion has been largely studied in several types of single crystals, since the zero field splitting of this ion is very sensitive to small distortion in the crystal. EPR study of Cr^{3+} ion in $TlZnF_3$ (TZF) crystal has been done earlier [7]. There are two possibilities of Cr^{3+} ion entering the crystal of TZF, substitutional and interstitial. It is interesting to find the site of this paramagnetic impurity. Experimental study [7] suggested that Cr^{3+} ion substitutes the Zn^{2+} ion with charge compensation.

In the present study, the ZFS parameter D for Cr^{3+} ion is computed using perturbation equation employing crystal field parameters from super position model. The result obtained is in good match with the experimental one.

II. Crystal Structure

TZF crystal is hexagonal with space group $P6_3/mmc$ as $CsMnF_3$ [8]. The unit cell parameters are a = 0.6213 (nm), c = 1.5074 (nm) and Z = 6 [8]. The structure is the same as for $BaTiO_3$ and with very similar values of the atomic coordinates. Each Tl atom has 12 fluorine neighbors at an average distance of 0.313 nm. One third of the Zn atoms occupy the centers of fluorine octahedra that share their corners with other octahedra as in the perovskite structure. The remaining two thirds of the Zn atoms are in distorted fluorine octahedra that each shares one face and three corners with other octahedra; these Zn atoms are in pairs 0.300 nm apart. The structure is shown in Fig.1. The site symmetry at Cr^{3+} ion is axial or tetragonal.

As the crystallographic axis system (CAS), (a, b, c), is not Cartesian, the modified crystallographic axis system CAS* (a, b*, c) is taken as shown in Fig. 1 (the axis a is perpendicular to c and b*). A common axis system (a||x, b*||y, c||z) is considered to simplify the calculations.

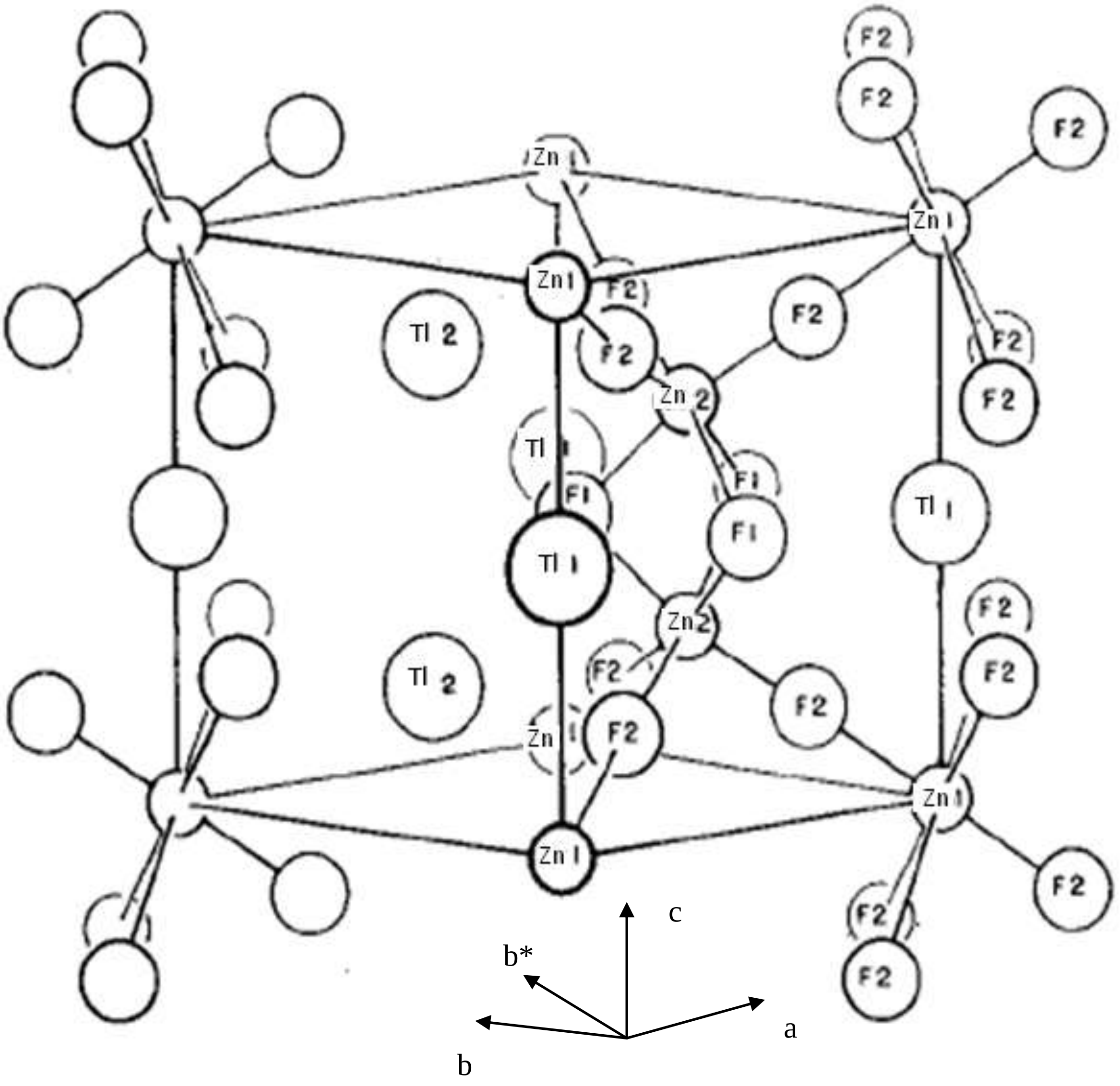

Fig. 1. Ligands around Cr^{3+} in TZF where symmetry adopted axis system (SAAS) is shown.

III. Theoretical aspect

In this section, the ZFS parameter of Cr^{3+} ion is determined using the microscopic spin Hamiltonian (MSH) theory [9]. The computed value is then compared with the experimental one. For Cr^{3+} ions at axial symmetry the effective spin Hamiltonian considering the ZFS and Zeeman terms can be given as [5].

$$\mathcal{H} = D\left\{S_Z^2 - \frac{1}{3}S(S+1)\right\} + \mu_B g_x B_Z S_Z + \mu_B g_\perp (B_x S_x + B_y S_y) \quad \text{........ (1)}$$

where $g_{||}$ and $g_\perp$ are the spectroscopic splitting factors, μ_B is the Bohr magnetron and B is the external magnetic field. The parameter D is the second rank axial ZFS parameter.

For a transition ion in the crystal, the crystal field is written as

$$\mathcal{H}_c = \sum B_{kq} C_q^{(k)} \quad \text{......... (2)}$$

where B_{kq} are the crystal-field parameters and $C_q^{(k)}$ are the Wybourne spherical tensor operators.

In TZF single crystal, the local symmetry around Cr^{3+} ions is axial or tetragonal. In tetragonal symmetry, the ZFS parameter D is written as [5]

$$D = \tfrac{1}{2}\left[\varepsilon\left(\left| E'({}^4F \downarrow {}^4A_{2g} \downarrow {}^4B_1) >\right) - \varepsilon\left(\left| E''({}^4F \downarrow {}^4A_{2g} \downarrow {}^4B_1) >\right)\right] \quad (3)$$

Diagonalization of the full Hamiltonian matrices gives the energy levels and eigen- vectors as functions of B_{kq}, B, C and ξ ; where B_{kq} are defined above, B and C are Racah parameters describing electron-electron repulsion and ξ is the spin-orbit coupling parameter. The values of B and C for transition ion in a crystal are less than those of the free ion. The average covalency parameter N takes into consideration the covalency, where N can have value between zero to one and for pure ionic bond N=1. The parameter N depends on the property of the metal-ligand bond. In terms of average covalency parameter N, we can write the Racah parameters [10-12] and spin-orbit coupling parameter as

$$B = N^4 B_0, \qquad C = N^4 C_0, \qquad \xi = N^2 \xi_0 \qquad \text{…………. (4)}$$

where B_0 and C_0 are Racah parameters for free ion and ξ_0 is free ion spin orbit coupling parameter. For Cr^{3+} ion $B_0 = 830\ cm^{-1}$, $C_0 = 3430\ cm^{-1}$, $\xi_0 = 276\ cm^{-1}$ are used [11].

Using the values of Racah parameters ($B = 695\ cm^{-1}$, $C = 3180\ cm^{-1}$) evaluated from optical study of Cr^{3+} doped crystal having fluorine ligands [13], the average covalency parameter N = 0.968 is obtained using

$$N = \left[\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}}\right] / 2. \qquad \text{…… (5)}$$

IV. Results and discussion

The SPM gives the crystal field parameters [14, 15] as

$$B_{kq} = \sum_j \overline{A_k}(R_j) K_{kq}(\theta_j, \phi_j) \qquad \text{…….. (6)}$$

where the co-ordination factor $K_{kq}(\theta_j, \varphi_j)$ is an explicit function of the angular position of the ligand. The intrinsic parameter $\overline{A_k}(R_j)$ is given as

$$\overline{A_k}(R_j) = \overline{A_k}(R_0)\left(\frac{R_0}{R_j}\right)^{t_k} \qquad \text{…….. (7)}$$

where R_j is the distance between the d^n ion and the ligand, $\overline{A_k}(R_0)$ is the intrinsic parameter of the reference crystal, t_k is the power law exponent and R_0 is reference distance between metal and ligand. According to superposition model the relation between the local structure parameters and crystal field parameters are expressed as [5]

$$B_{20} = -2\bar{A}_2\left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_2} - 4\bar{A}_2\left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_2} \qquad \text{…… (8)}$$

$$B_{40} = 16\bar{A}_4\left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_4} + 12\bar{A}_4\left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4} \qquad \text{…… (9)}$$

$$B_{44} = 2\sqrt{70}\,\bar{A}_4\left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4} \qquad \text{……. (10)}$$

where R_0 is the reference distance. Here, the reference distance is taken as 0.255 nm, which is slightly larger than the sum of ionic radii of Cr^{3+} ion (0.0615 nm) and F^- ion (0.133 nm) [12]. Because of the difference between the impurity ion and host ion, the local environment of the paramagnetic ion may be different to that of the replaced host ion. It is assumed that the bond lengths will be changed. The bond lengths may be described in terms of the distortion parameters ΔR_1 and ΔR_2, i.e. $R_1 = R_{10} + \Delta R_1$, $R_2 = R_{20} + \Delta R_2$. For octahedral coordination $\overline{A_4}$ is given as [16]

$$\overline{A_4}(R_0) = \frac{3}{4} Dq \qquad \text{……. (11)}$$

From optical study [13], Dq = 1535 cm^{-1}. Thus the relation gives the value of $\overline{A_4}(R_0)$= 1151.25 cm^{-1}. It is seen that the ratio of $\overline{A_2}(R_0)$ and $\overline{A_4}(R_0)$ lies between 8 to 12, [11, 17, 18]. In the present study, $\frac{\overline{A_2}}{\overline{A_4}}$ =10 is taken, which gives $\overline{A_2}$ = 11512.5 cm^{-1}. In SPM, the non-zero crystal field parameters B_{kq} of Cr^{3+} ion in TZF are computed by considering the parameters $\overline{A_2}$ and $\overline{A_4}$ as well as arrangement of fluorine atoms around Cr^{3+} ion, for the matched experimental ZFS parameter. For Cr^{3+} ion in TZF, the parameters $t_2 = 2$ and $t_4 = 4$ have been used. When Cr^{3+} ion substitutes the Zn^{2+} ion, the position of transition metal ion Cr^{3+} and spherical coordinates of ligands are given in Table 1. The ZFS parameter D of Cr^{3+} ion in TZF crystal is computed from the expression (3) [5] using parameters B, C, ξ and B_{kq}. The distortion parameters are taken as ΔR_1 = -0.5861 nm and ΔR_2 =- 0.5680 nm with R_{10} = 0.9062 nm and R_{20} = 0.9062 nm for center A. The distance R_{10} is the average of the Cr^{3+}-$F2^-$(1) and Cr^{3+}-$F2^-$(2') bond lengths and R_{20} is the average of the Cr^{3+}-$F2^-$(1') and Cr^{3+} -G$F2^-$(2) bond lengths. The distortion parameters for B, C and D centers are ΔR_1 = -0.6460 nm, ΔR_2 =- 0.6432 nm; ΔR_1 = -0.0851 nm, ΔR_2 =- 0.0720 nm; ΔR_1 = -0.5460 nm, ΔR_2 =- 0.6350 nm, respectively with R_{10} = 0.9263 nm and R_{20} = 0.9640 nm. The calculated crystal field parameters and ZFS parameter together with reference distance with distortion are given in Table 2. The above parameters without distortion with the same reference distance are also shown in Table 2. The ZFS parameter calculated using crystal field parameters from superposition model for all the centers A, B, C and D without distortion is smaller than the experimental value [7]. The

Table 1. Fractional position of Cr^{3+} ion together with spherical co-ordinates (R, θ, ϕ) of ligands in TZF single crystal.

Position of Cr^{3+} (Fractional)	Ligands	Spherical co-ordinates of ligands		
		R(nm)	θ^0	ϕ^0
			(degree)	
Site : Substitutional	F2 (1)	0.9062	82.5	68.4
Zn1 (0, 0, 0)	F2 (1')	0.9062	97.4	68.4
Centre A	F2 (2)	0.9062	97.4	26.5
	F2 (2')	0.9062	82.5	26.5
Site : Substitutional	F1 (1)	0.6764	123.8	63.4
Zn2 (0, 0, 0.5)	F1 (2)	0.6764	56.1	26.5
Centres B, C, D	F2 (1')	1.2516	134.1	63.4
	F2 (2')	1.1009	125.3	26.5

Table 2. Crystal field (CF) parameters and zero field splitting (ZFS) parameter D of Cr^{3+} doped TZF single crystal with and without distortion.

				Crystal- field parameters (cm^{-1})			Zero-field splitting parameter ($10^{-4}cm^{-1}$)
	ΔR_1 (nm)	ΔR_2 (nm)	R_0(nm)	B_{20}	B_{40}	B_{44}	D
A	-0.5861	-0.5680	0.255	-40786.0	7416.252	6224.413	-2387.38
	0.0000	0.0000	0.255	-5469.3	202.0918	120.7729	-70.23
B	-0.6460	-0.6432	0.255	-48140.6	12607.03	7688.459	3496.92
	0.0000	0.0000	0.255	-4966.78	173.3974	94.30986	-60.27
C	-0.0851	-0.0720	0.255	-5878.75	155.5028	128.6478	-78.82
	0.0000	0.0000	0.255	-4966.78	173.3974	94.30986	-60.27
D	-0.5460	-0.6350	0.255	-38011.8	3723.223	6950.186	1849.31
	0.0000	0.0000	0.255	-4966.78	173.3974	94.30986	-60.27

ZFS parameter calculated using crystal field parameters from superposition model for all the center with distortions into consideration is in good agreement with the experimental value [7] as seen from Table 2. Using B_{kq} parameters and CFA program [19-20], the optical spectra of Cr^{3+} doped TZF crystal are calculated. The energy levels of the impurity ion are determined by diagonalizing the complete Hamiltonian within the $3d^N$ basis of states in the intermediate crystal field coupling scheme. The Hamiltonian contains the Coulomb interaction (in terms of B and C parameters), Trees correction, the spin-orbit interaction, the crystal field Hamiltonian, the spin-spin interaction and the spin-other orbit interaction. The calculated energy values are given in Table 3 (input parameters are given below the Table) together with the experimental values [7] for comparison. It is seen from Table 3 that there is a reasonable agreement between the calculated and experimental energy values. The energy values obtained without distortion were inconsistent from the experimental ones, therefore are not being given here.

Table 3. Calculated energy band positions of Cr^{3+} doped TZF single crystal together with the experimental values for comparison.

Transition from $^4A_2(F)$	Observed energy bands (cm^{-1})	Calculated energy bands (cm^{-1}) With distortion			
		A	B	C	D
$^2Eg(G)$	14144	13238, 13287	14018, 14123	13901, 14185	13926, 14114
$^2T_1g(G)$	15152	13970, 14170, 15849	14401, 14476, 14499	14414, 14770, 15242	14456, 14474, 14485
$^4T_2g(F)$	15350	15982, 16143, 16199, 16247, 16271, 16790	14581, 17095, 17299, 19215, 20087, 20143	15417, 16160, 16391, 16421, 16774, 16827	14526, 15965, 15994, 16408, 16441, 17942
$^4T_1g(F)$	22100	18348, 23134, 24961, 25017, 26067, 26351	21129, 21159, 21175, 21196, 27878, 28678	19227, 19446, 19507, 20697, 20900, 27269	19804, 22761, 22801, 24025, 24329, 24513
$^4T_1g(P)$	34483	32890, 33571, 33591, 33793, 33877, 35575	30295, 30476, 30628, 34760, 35020, 36428	27420, 27455, 27684, 27695, 28451, 28600	30261, 31015, 31999, 32009, 32422, 34579

Input parameters: Numbers of free ion parameters = 5, number of d shell electrons = 3, number of fold for rotational site symmetry = 1; Racah parameters in A, B and C, spin-orbit coupling constant and Trees correction are 0, 695, 3180, 240 and 70 cm^{-1}, respectively; number of crystal field parameters = 3; B_{20}, B_{40}, B_{44} are taken from Table 2, spin-spin interaction parameter, M0 = 0.0000; spin-spin interaction parameter, M2 = 0.0000; spin-other-orbit interaction parameter, M00 = 0.0000; spin-other-orbit interaction parameter, M22 = 0.0000; magnetic field, B = 0.0 Gauss; angle between magnetic field B and z-axis =0.00 degree.

It is seen from Table 2 that taking into account a small lattice distortion provides good agreement between theoretical and experimental results. This indicates that the distortion model used here is quite reasonable. The parameters ΔR_1 and ΔR_2 are negative, which shows that the bond length of Cr-F is smaller than Zn-F. Since the charge of Cr^{3+} is larger as compared to Zn^{2+}, the Coulomb interaction between Cr^{3+} and F^- should be larger than that between Zn^{2+} and F^-. This is consistent with the smaller bond length discussed above. When distortion in the lattice is neglected, a smaller value of D is obtained. Taking a small distortion, the calculated ZFS parameter D is close to the experimental value. This suggests that local distortion plays an important role in the contributions to ZFS parameter and hence must be taken into consideration.

V. Conclusions:

Cr^{3+} ions substitute at Zn^{2+} sites in TZF crystal. The charge and ionic radii differences between Cr^{3+} and Zn^{2+} produce local distortion around Cr^{3+} ion. The theoretical study of ZFS parameter has been performed using perturbation formula and crystal field parameters determined from superposition model. Considering local distortion, the ZFS parameter for Cr^{3+} ion in TZF crystal for all the centers A, B, C and D matches with the experimental value. Thus our result supports the conclusion drawn from the experimental study.

Acknowledgement

The author is thankful to the Head, Department of Physics for providing the departmental facilities and to Prof. C. Rudowicz, Faculty of Chemistry, Adam Mickiewicz. University, Poznan, Poland for CFA program.

References:

[1]. J. A. Weil, J. R. Bolton, J. E. Wertz, Electron Paramagnetic Resonance: Elementary Theory and Practical Applications, Wiley, New York, 1994.
[2]. Z. Wen-Chen, W. Shao-Yi, D. Hui-Ning, Z. Jian, Spectrochim. Acta A 58(2002)537-541.
[3]. Y. Y. Yeung, D. J. Newman, Phys. Rev. B 34(1986)2258-2265.
[4]. R. R. Sharma, T. P. Das, R. Orbach, Phys. Rev. 149(1966)257-269.
[5]. Q. Wei, Acta Phys. Polon. A 118(2010)670-672.
[6]. M. G. Brik, N. M. Avram (Eds.), Optical Properties of 3d-Ions in Crystals: Spectroscopy and Crystal Field Analysis, Chapter 3, Springer, 2013, pp. 95-121.
[7]. H. Ebisu, M. Arakawa, H. Takeuchi, J. Phys.: Condens. Matter 17(2005)4653-4663.
[8]. A. Zalkin, K. Lee, D. H. Templeton, J. Chem. Phys. 37(1962)697-699.
[9]. C. Rudowicz, Magn. Reson. Rev. 13 (1987) 1-89.
[10]. W. L. Yu, M. G. Zhao, J. Phys. C: Solid State Phys., 18(1984) L525-L527.
[11]. A. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970.
[12]. C. K. Jorgensen, Modern Aspects of Ligand Field Theory, North-Holland, Amsterdam, 1971, p.305.
[13]. R. J. M. da Fonseca, A. D. Tavares Jr, P. S. Silva, T. Abritta, N. M. Khaidukov, Solid State Commun. 110(1999)519-524.
[14]. W. L. Yu, M. G. Zhao, Phys. Rev. B 37 (1988) 9254-9267.
[15]. D. J. Newman, B. Ng, Rep. Prog. Phys. 52(1989)699-763.
[16]. D.J. Newman, B. Ng (Eds.), Crystal Field Handbook, Cambridge University Press, Cambridge, 2000.
[17]. D. J. Newman, D. C. Pryce, W.A. Runciman, Am. Miner. 63 (1978) 1278-1281.
[18]. T. H. Yeom, S. H. Choh, M. L. Du, J. Phys.: Condens. Matter 5 (1993) 2017-2024.
[19]. Y. Y. Yeung, C. Rudowicz, J. Comput. Phys. 109(1993) 150-152.
[20]. Y. Y. Yeung, C. Rudowicz, Comput. Chem.16 (1992) 207-216.