

Theoretical Study of Zero Field Splitting Parameters of Fe³⁺ doped TlInS₂ Single Crystal

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Crystal field parameters and zero field splitting parameters of Fe³⁺ doped TlInS₂ crystals are studied theoretically at room temperature using the superposition model and the perturbation theory. The zero field splitting parameters are determined without and with local distortion. These parameters give reasonable agreement with the experimental values when local distortion is taken into consideration. The theoretical study supports the experimental result that Fe³⁺ substitutes for In³⁺ in the TlInS₂ crystal.

topics: inorganic compounds, single crystal, crystal fields, electron paramagnetic resonance

1. Introduction

Electron paramagnetic resonance (EPR) yields information about local site symmetry and zero field splitting (ZFS) parameters of transition ions doped in crystals [1, 2]. For an orbital singlet ground state, the spin angular momentum contributes to the magnetic properties of transition-metal ions. Fe³⁺ ion in the iron group has half filled 3*d* shell and the ground state ⁶*S* (spin |*S*| = $\frac{5}{2}$). The Hamiltonian of a 3*d*⁵ ion can be expressed as the sum of the free-ion Hamiltonian, crystal field, spin-orbit, and spin-spin couplings, respectively.

Since the crystal fields play an important role in the spin-orbit mechanism, the superposition model (SPM) is used to calculate the crystal field (CF) parameters [3, 4]. As the positions of different ligands in the crystal are needed in this model, the relation between the model and the theories of local distortion in crystals would be of importance for predicting ZFS parameters for the 3*d*⁵ system [5].

Theoretical investigations on the spin Hamiltonian parameters of 3*d*⁵ ions have been carried out by several workers using perturbation procedures [6–11]. In general, the cubic field and the diagonal part of the free-ion Hamiltonian are considered the unperturbed terms, and the rest — the perturbation terms [12].

EPR study of Fe³⁺ doped tellurium indium sulfide TlInS₂ (TIS) single crystals was done earlier [13]. It is interesting to find the site of the impurity in the TIS crystal out of two possibilities, substitutional and interstitial. It was concluded from

the EPR study [13] that Fe³⁺ ion substitutes at the In³⁺ site in the crystal lattice. In the present investigation, the ZFS parameters *D* and *E* are computed for the Fe³⁺ ion at the substitutional In³⁺ site as well as at the interstitial site in the TIS crystal using CF parameters evaluated from SPM and perturbation expressions [14]. The object is to confirm whether the Fe³⁺ ion enters the crystal lattice substitutionally or interstitially and about the distortion introduced in the lattice. The results obtained for the Fe³⁺ ion at the substitutional site are in reasonable agreement with the experimental ones when local distortion is taken into consideration.

2. Crystal structure

The TIS crystal is isomorphic with TlGaSe₂ (TGS) [13]. The atomic positions for TIS crystal have not been determined so far. Therefore respective atomic positions in TGS are taken for TIS. Single crystals of TIS are monoclinic (as TGS) with *a* = 1.0772 nm, *b* = 1.0771 nm, *c* = 1.5636 nm, β = 100.6°, *Z* = 16, and space group *Cc* [15]. The crystal structure of TlInS₂ consists of alternating two-dimensional metal-chalcogen layers. The layers are formed of In₄S₁₀ tetrahedron complexes representing a combination of four elementary InS₄ tetrahedra and are connected together by common chalcogen atoms at the corners (Fig. 1). The elementary unit cell contains two partially disordered layers, having successive rows of the tetrahedron complexes turned away from each other by 90°. Monovalent Tl atoms are in trigonal prismatic cavities formed

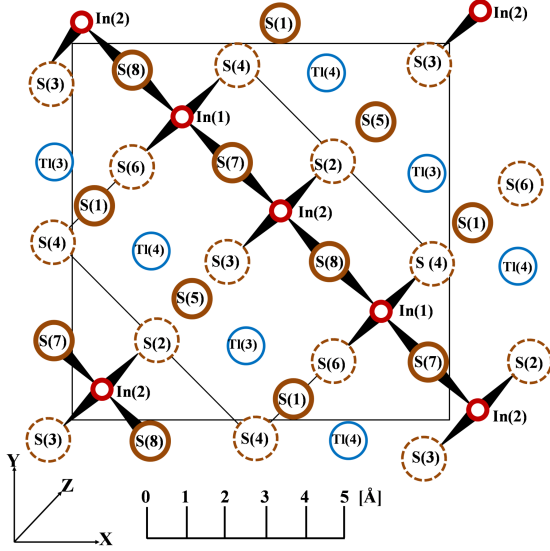


Fig. 1. Crystal structure of TIS with symmetry adopted axis system (SAAS).

from the combination of the In_4S_{10} tetrahedra into a layer. In Fig. 1, each successively lower layer is shifted along the $[010]$ direction by the length of the edge of the small InS_4 tetrahedron with respect to the upper layer.

Consequently, a deviation from the tetragonal symmetry occurs. The angle between the monoclinic c -axis and the layer plane is about 100° . For the perfect InS_4 tetrahedron, the crystal field has the cubic symmetry at the In site due to the effect of nearest ligands (sulfur ions). The orthorhombic symmetry of the crystal field is caused by the influence of Tl atoms located in the trigonal cavities between the tetrahedral complexes.

3. Calculations of CF and ZFS parameters

The experimental EPR spectrum can be analyzed using the spin Hamiltonian [16, 17]

$$\begin{aligned} \mathcal{H} = & \mu_B g \mathbf{B} \mathbf{S} + A S_z I_z + B (S_x I_x + S_y I_y) \\ & + D \left(S_z^2 - \frac{S(S+1)}{3} \right) + E (S_x^2 - S_y^2) \\ & + \frac{a}{6} \left[S_x^4 + S_y^4 + S_z^4 - \frac{S(S+1)(3S^2 + 3S + 1)}{5} \right], \end{aligned} \quad (1)$$

where g is the spectroscopic splitting factor, μ_B is the Bohr magneton and \mathbf{B} is the external magnetic field. Next, A and B represent hyperfine terms [18–20], D and E are the second rank axial and rhombic ZFS parameters, respectively, while a is the fourth rank cubic one. The laboratory axes (x, y, z) are parallel to the modified crystallographic axes ($\mathbf{a}, \mathbf{b}, \mathbf{c}^*$). The local site symmetry axes, i.e., the symmetry adopted axes (SAA) are the mutually perpendicular directions of metal–ligand bonds.

The Z -axis of of SAAS in four equivalent sites is along the crystal \mathbf{c}^* -axis, and the other two axes (X, Y) lie in the ab plane.

The Z -axis of SAAS is along the metal–ligand bond In–S (4) (for sites I and III) and In–S (2) (for sites II and IV). The two other axes (X, Y) are normal to the Z axes for all the four sites (see Fig. 1). This shows that Fe^{3+} substitutes for In^{3+} in the crystal lattice of TIS. The ionic radius of Fe^{3+} ion 0.064 nm [21] is slightly less than the ionic radius of In^{3+} (0.080 nm), implying thereby that Fe^{3+} ion can go at the location of In^{3+} with some distortion.

The ZFS parameters of Fe^{3+} ion located at four equivalent sites in Fig. 1 are determined with the help of perturbation theory [22, 23] and are then compared with the experimental values.

As discussed in the introduction, the spin Hamiltonian of a d^5 ($6S$ state) ion can be given as a sum of free ion (\mathcal{H}_0), spin–orbit coupling (\mathcal{H}_{so}), spin–spin coupling (\mathcal{H}_{ss}), and crystal field (\mathcal{H}_c) Hamiltonians,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{ss}} + \mathcal{H}_c, \quad (2)$$

with

$$\mathcal{H}_c = \sum_{k,q} B_{kq} C_q^{(k)}, \quad (3)$$

where B_{kq} are the CF parameters and $C_q^{(k)}$ are the Wybourne spherical tensor operators. For the orthorhombic symmetry crystal field, $B_{kq} \neq 0$ only with $k = 2, 4$ and $q = 0, 2, 4$. The crystal field theory has been widely employed to study the spin Hamiltonian parameters of transition ions doped in crystals [24–27]. In this study, the CF parameters B_{kq} are computed using SPM [22].

In TIS crystal the local field symmetry around Fe^{3+} ions is considered to be orthorhombic (OR-I) [13, 21]. In OR-I symmetry, the ZFS parameters D and E are found as [27]

$$\begin{aligned} D = & \frac{3\zeta^2}{70P^2D} \left(-B_{20}^2 - 21\zeta B_{20} + 2B_{22}^2 \right) \\ & + \frac{\zeta^2}{63P^2G} \left(-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2 \right), \end{aligned} \quad (4)$$

and

$$\begin{aligned} E = & \frac{\sqrt{6}\zeta^2}{70P^2D} \left(2B_{20} - 21\zeta \right) B_{22} \\ & + \frac{\zeta^2}{63P^2G} \left(3\sqrt{10}B_{40} + 2\sqrt{7}B_{44} \right) B_{42}, \end{aligned} \quad (5)$$

respectively, where $P = 7B + 7C$, $G = 10B + 5C$, and $D = 17B + 5C$. Here, B and C are the Racah parameters, describing electron–electron repulsion, and ζ is the spin–orbit coupling parameter. It is noted that the values of B and C for transition metal ion in a crystal are lower than those of the free ion. By considering the average covalency parameter N , we write the Racah parameters [22, 28] as $B = N^4 B_0$ and $C = N^4 C_0$ (where B_0 and C_0 are Racah parameters for free ion), and spin–orbit coupling parameter as $\zeta = N^2 \zeta_0$ (where ζ_0 is free ion spin–orbit coupling parameter).

TABLE I

Atomic coordinates in TIS crystal along with bond length R (without and with distortion) and angles θ and φ . The position of Fe^{3+} is substitutional (one site): In(1) (0.4249, 0.1907, 0.9584).

Ligands	x [Å]	y [Å]	z [Å]	Spherical coordinates of ligands		
				R [nm]	θ [°]	φ [°]
without distortion						
S4	0.0278	0.4468	0.3776	$R_1 = 0.2352$	$\theta_1 = 80.76$	$\varphi_1 = 89.31$
S6	0.2697	0.3112	0.8767	$R_2 = 0.2322$	$\theta_2 = 67.81$	$\varphi_2 = 82.79$
S7	0.0731	0.1864	0.5592	$R'_1 = 0.2432$	$\theta'_1 = 76.70$	$\varphi'_1 = 88.23$
S8	0.3261	0.0607	0.0526	$R'_2 = 0.2412$	$\theta'_2 = 88.75$	$\varphi'_2 = 82.22$
with distortion						
S4			0.25017	$R_1 + \Delta R_1$		
S6			0.30200	$R_2 + \Delta R_2$		
S7				$R'_1 + \Delta R'_1 = 0.31300$		
S8				$R'_2 + \Delta R'_2 = 0.31100$		

TABLE II

Crystal field parameters and zero field splitting parameters of Fe^{3+} doped TIS single crystal for site I with $\frac{A_2}{A_4} = 10$.

	R_0 [nm]	Crystal field parameters [cm^{-1}]					Zero field splitting ($\times 10^{-4}$) [cm^{-1}]		
		B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	$ D $	$ E $	$\frac{ E }{ D }$
without distortion	0.212	-28518.4	-39071.2	4022.414	1555.506	11554.99	36894	16145	0.437
with distortion	0.212	19129.13	-13372.9	1875.114	699.4775	7637.822	6728	2208	0.328
							6727*	1588*	0.236*

*experimental

For free Fe^{3+} ion, $B_0 = 1130$, $C_0 = 4111$, and $\zeta_0 = 589 \text{ cm}^{-1}$ are taken [22].

Using the values of the Racah parameters ($B = 720$ and $C = 2500 \text{ cm}^{-1}$) evaluated from the optical study of the Fe^{3+} ion with S ligand [29], the average parameter N is obtained with the expression

$$N = \frac{1}{2} \left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}} \right). \quad (6)$$

The CF parameters in SPM are given [27, 30] by

$$B_{kq} = \sum_j \overline{A}_k(R_j) K_{kq}(\theta_j, \varphi_j). \quad (7)$$

Here, 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

$$\overline{A}_k(R_j) = \overline{A}_k(R_0) \left(\frac{R_0}{R_j} \right)^{t_k}, \quad (8)$$

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, R_0 is the reference distance between metal and ligand and t_k is the power law exponent. For Fe^{3+} doped crystals, $t_2 = 3$ and $t_4 = 5$ are

used [26]. The same values were used in our calculation here. As the co-ordination around Fe^{3+} ion is tetrahedral, \overline{A}_4 is determined as [31]

$$\overline{A}_4(R_0) = -\frac{27}{16} Dq. \quad (9)$$

Using optical study [29], the value of $Dq = 720 \text{ cm}^{-1}$. Hence, the value of $\overline{A}_4(R_0) = 1215 \text{ cm}^{-1}$. For $3d^5$ ions the ratio $\overline{A}_2/\overline{A}_4$ lies between 8–12 [22, 32, 33]. In our study, this ratio is taken as 10, which gives $\overline{A}_2 = 12150 \text{ cm}^{-1}$.

4. Results and discussion

The CF parameters B_{kq} of Fe^{3+} ion at four equivalent sites are calculated using SPM with the help of parameters \overline{A}_2 and \overline{A}_4 , as well as the arrangement of S ions around Fe^{3+} ion (Fig. 1). Atomic coordinates in TIS crystal together with bond length R (without and with distortion) and angles θ and φ (one site) are shown in Table I. The calculated CF parameters, using (7) and transformation S5 for standardization [20], and ZFS parameters, along with reference distance R_0 , are given in Table II. The value of $R_0 = 0.212 \text{ nm}$ is slightly lower than the average of four ligand distances from the central metal

TABLE III
Experimental and calculated (CFA package) energy band positions of Fe³⁺ doped TIS single crystal.

Transition from ⁶ A _{1g} (S)	Observed wave number [cm ⁻¹]	Calculated wave number [cm ⁻¹]
⁴ T _{1g} (G)	14489 16389	13816, 14884, 15005, 15398, 15532, 16528
⁴ T _{2g} (G)	19300	18891, 18930, 20271, 20384, 20497, 20687
⁴ E _g (G)		21380, 21528
⁴ A _{1g} (G)		22605
⁴ T _{2g} (D)	23803	22713, 23129, 23330, 23397, 23691, 24529
⁴ E _g (D)		25901, 26786
⁴ T _{1g} (P)		30947, 31558, 31922, 32497, 32855, 33175
⁴ A _{2g} (F)		35837
⁴ T _{1g} (F)		37574, 37986, 38783, 38893, 38905, 39155
⁴ T _{2g} (F)		40934, 42222, 42276, 42403, 42827, 43279

ion (0.2379 nm) and, together with local distortion, provides ZFS parameters for all the four equivalent sites in reasonable agreement with the experimental values [13]. The ZFS parameters found using $R_0 = 0.212$ nm and without local distortion are larger than the experimental values. For comparison, the interstitial sites for Fe³⁺ ions also were studied. The calculated values of ZFS parameters come out to be inconsistent with the experimental ones and so are not being given here to save space.

Using the mentioned CF parameters and CFA program [34, 35], considering the OR-I symmetry of the crystal field, the optical spectra of Fe³⁺ doped TIS crystals are calculated. The energy levels of the doped ion are obtained by diagonalization of the complete Hamiltonian within the $3d^N$ basis of states in the intermediate crystal field coupling scheme. The calculated energy values are given in Table III together with the experimental values for comparison. There is a reasonable agreement between these two. Thus, the conclusion drawn on the basis of SPM supports the experimental result that Fe³⁺ ions substitute at In³⁺ site in the crystal [13].

5. Summary and conclusions

CF parameters and ZFS parameters for Fe³⁺ ion doped TIS have been determined using the superposition model and perturbation theory, respectively. The calculated ZFS parameters are in reasonable agreement with the experimental ones. The calculated optical spectra are in reasonable agreement with the experimental result. The conclusion drawn

on the basis of the superposition model supports the experimental result that Fe³⁺ ions substitute at In³⁺ site in the TIS crystal.

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