

Zero Field Splitting Parameter of Mn^{2+} -Doped $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ Single Crystals at Axial Symmetry Site

R. KRIPAL*

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

Received: 23.08.22 & Accepted: 07.11.22

Doi: [10.12693/APhysPolA.143.217](https://doi.org/10.12693/APhysPolA.143.217)

*e-mail: headphysics@allduniv.ac.in

Theoretical study of the crystal field parameters and the zero-field splitting parameter of Mn^{2+} -doped langbeinite $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystals is done using the superposition model and perturbation theory. The zero-field splitting parameter found here matches well with the experimental value. The theoretical study supports the conclusion of experimental study that Mn^{2+} substitutes for Cd^{2+} in $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystal.

topics: inorganic compounds, single crystal, crystal fields, optical properties

1. Introduction

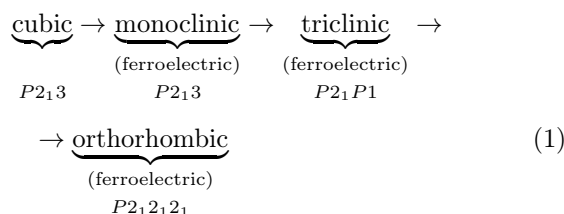
Electron paramagnetic resonance (EPR) investigations give structural distortions and local site symmetry of transition ions doped in different host systems [1–3]. Employing microscopic spin-Hamiltonian (MSH) theory, the spin Hamiltonian (SH) parameters determined from EPR are correlated with optical and structural parameters. Both experimental and theoretical studies indicate that the spin Hamiltonian parameters of transition ions (d^5) in crystals are quite sensitive to local distortion. Hence, the SH theory is largely used in crystals.

The crystal-field (CF) parameters of the d^5 ion can be obtained using the superposition model (SPM) [4, 5]. The zero-field splitting (ZFS) parameters are then evaluated employing the CF parameters [6]. The Mn^{2+} ion of the iron group is interesting due to its ground state being ${}^6S_{5/2}$ [7–10]. Electron spins interact through high-order interaction with the crystalline electric field, and in an external magnetic field they orient freely [11]. Since the S state ions have a large spin-lattice relaxation time, the Mn^{2+} ion gives well-resolved EPR lines [10–12] in most systems at room temperature (RT).

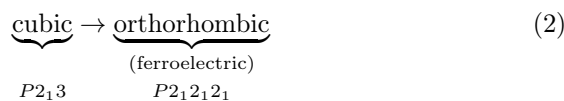
Langbeinite is a family of compounds having the formula $\text{A}_2\text{B}_2(\text{SO}_4)_3$, where A may be K^+ , NH_4^+ , Rb^+ , Tl^+ , or Cs^+ , and B may be Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} , Cd^{2+} , or Ca^{2+} . However, not all combinations of these cations have been obtained experimentally. The above crystals are isomorphous with the natural mineral langbeinite $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$ and have a high-temperature cubic structure with the space group $P2_13$ [13, 14]. Various langbeinite

compounds transform from a high-temperature cubic structure to either ferroelectric or ferroelastic low-temperature phases. It is established that one of two types of phase transitions, i.e.,

• Type I



• Type II



takes place as the temperature is lowered [15–18].

Ferroelectric langbeinite $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ shows a successive appearance of three phase transitions in the temperature range from 90 to 130 K [17].

EPR investigation of Mn^{2+} -doped $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystals were done at room temperature (RT) and the spin Hamiltonian parameters have been determined [19]. Substitutional and interstitial sites could be considered for the Mn^{2+} ion in $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ crystal. From EPR [19] it was concluded that Mn^{2+} ion enters the lattice of $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ substitutionally at Cd^{2+} site. In the present study, the CF parameters are obtained employing SPM, and then these parameters, together with MSH theory, provide the ZFS parameters for the Mn^{2+} ions at the substitutional Cd^{2+} site

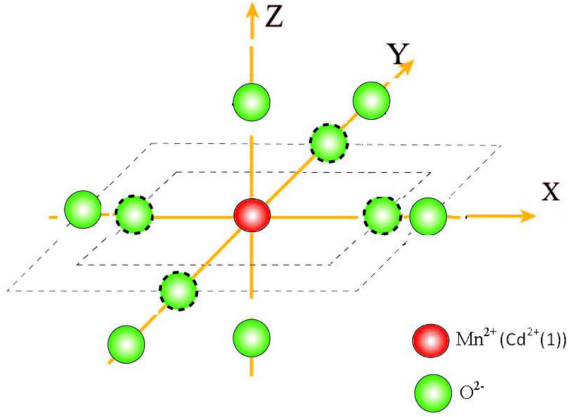


Fig. 1. Coordination around Mn^{2+} in $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystal.

in $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystal at RT. The zero-field splitting parameter D obtained using SPM gives a reasonable matching with the experimental value [19].

2. Crystal structure

$\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystal (langbeinite type I) has a cubic structure at 295 K with lattice parameter $a = 1.0421$ nm, space group $P2_13$ [20]. Metal cations occupy special positions along the threefold axes. Each Tl atom is surrounded by nine O atoms that form a complicated polyhedron. Every Cd1 and Cd2 atom is coordinated by six O atoms, forming distorted octahedra, which are generated by the application of threefold axes on the symmetry-independent atoms O3, O4, O1 and O2. The atoms Cd1 and Cd2 are not at the midpoints of the octahedra, but are shifted by 0.003 nm towards the O4 triplet for Cd1 and 0.013 nm towards the O2 triplet for Cd2. The oxygen coordination around Cd^{2+} (1) is shown in Fig. 1. The site symmetry around Mn^{2+} ions can be considered approximately axial, as indicated by the EPR investigation of Mn^{2+} -doped $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ [19].

3. Theoretical investigation

The Mn^{2+} ion in $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystal substitutes at Cd^{2+} site [19]. The SH of $3d^5$ ion in crystal field of axial symmetry is written as [21–23]

$$\begin{aligned} \mathcal{H} = & g\mu_B \mathbf{B} \cdot \mathbf{S} + D(S_z^2 - S(S+1)) \\ & + \frac{a}{6} \left[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1) \right] \\ & + \frac{F}{180} \left[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 \right. \\ & \left. - 6S(S+1) + 3S^2(S+1)^2 \right] + A\mathbf{I} \cdot \mathbf{S}, \end{aligned} \quad (3)$$

where the first term gives electronic Zeeman interaction; \mathbf{B} is the external magnetic field, g is the spectroscopic splitting factor and μ_B is Bohr magneton. The second, third, and fourth terms represent the second-order axial, fourth-rank cubic and fourth-rank axial ZFS terms [9]. The fifth term is the hyperfine interaction term. In (1), S , D , a , F are the effective spin vector, the second-order axial, fourth-rank cubic and fourth-rank axial ZFS parameters, respectively. The isotropic approximation for the electronic Zeeman interaction is used for Mn^{2+} ions [9, 24, 25].

The Hamiltonian for a d^5 ion is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{cf} + \mathcal{H}_{so}, \quad (4)$$

where

$$\mathcal{H}_{cf} = \sum_{kq} B_{kq} C_q^k \quad (5)$$

represents the crystal field Hamiltonian, whereas \mathcal{H}_0 and \mathcal{H}_{so} represent the free ion Hamiltonian and the spin-orbit (SO) coupling, respectively. In (5), B_{kq} denotes CFP in Wybourne notation and C_q^k is the orbital angular momentum operator. Since the spin-spin coupling is very small [26–28], its contribution to (5) has been neglected. The crystal field of SO interaction is taken as a perturbation term [29–31]. The strong-field scheme calculation in the F -state ions was done by Macfarlane [32, 33]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is given as [30]

$$\begin{aligned} D^{(4)}(\text{SO}) = & \frac{\xi^2}{63P^2G} (14B_{44}^2 - 5B_{40}^2) \\ & - \frac{3\xi^2}{70P^2D} B_{20}(B_{20} - 14\xi), \end{aligned} \quad (6)$$

where $P = 7(B + C)$, $G = 10B + 5C$ and $D = 17B + 5C$. Here, P , G , and D are the energy separations between the excited quartets and the ground sextet; the Racah parameters B and C give the electron-electron repulsion, and ξ is the spin-orbit coupling parameter. Only the fourth order term is considered in (6), because the other perturbation terms are negligible [30, 32, 33]. In terms of the average covalency parameter N , the parameters B , C and ξ are given as $B = N^4 B_0$, $C = N^4 C_0$ and $\xi = N^2 \xi_0$, where B_0 , C_0 and ξ_0 are the Racah parameters and the spin-orbit coupling parameter for free ion [34, 35], respectively. For Mn^{2+} ion, $B_0 = 960 \text{ cm}^{-1}$, $C_0 = 3325 \text{ cm}^{-1}$, $\xi_0 = 336 \text{ cm}^{-1}$ [9] are used in this calculation. Using the equation

$$N = \frac{1}{2} \left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}} \right), \quad (7)$$

one can evaluate N .

By employing SPM, the CF parameters for Mn^{2+} in the $\text{Tl}_2\text{Cd}_2(\text{SO}_4)_3$ single crystal are obtained, and then with (6) the ZFS parameter D is determined. The similar method has been used for finding ZFS parameters by many previous workers [36].

In order to interpret crystal-field splitting, SPM is effectively applied. This model has also been used for the $3d^n$ ions [32, 33, 37]. The crystal field parameters, using this model, are obtained from the equations [38]

$$B_{20} = -\frac{2\bar{A}_2 R_0^{t_2}}{(R_{10} + \Delta R_1)^{t_2}} - \frac{4\bar{A}_2 R_0^{t_2}}{(R_{20} + \Delta R_2)^{t_2}}, \quad (8)$$

$$B_{40} = \frac{16\bar{A}_4 R_0^{t_4}}{(R_{10} + \Delta R_1)^{t_4}} + \frac{12\bar{A}_4 R_0^{t_4}}{(R_{20} + \Delta R_2)^{t_4}}, \quad (9)$$

$$B_{44} = \frac{2\sqrt{70}\bar{A}_4 R_0^{t_4}}{(R_{20} + \Delta R_2)^{t_4}}, \quad (10)$$

in which R_0 is the reference distance, usually taken as the average value of all four bond lengths (for axial symmetry); \bar{A}_2 , \bar{A}_4 and t_k are the intrinsic parameter and the power law exponent, respectively.

4. Results and discussion

The average of two out of the four $Mn^{2+}-O^{2-}$ bond lengths is $R_{10} = 0.4275$ nm and the average value of the other two bond lengths is found to be $R_{20} = 0.3414$ nm. Note that ΔR_1 and ΔR_2 give the distortion parameters. In octahedral coordination, $\bar{A}_4(R_0) = \frac{3}{4}Dq$ [6, 25]. For the $3d^5$ ions, the ratio $\frac{\bar{A}_2}{\bar{A}_4}$ lies in the range 8–12 [32, 33, 37]. The power law exponents for the Mn^{2+} ion are taken as $t_2 = 3$, $t_4 = 7$. Semi-*ab initio* calculations are carried out for other transition metal ions to find the intrinsic parameter values in SPM, a similar calculation is used here.

From the optical absorption study [39], the values of B , C and Dq are found as 917, 2254 and 756 cm^{-1} , respectively. First, no local distortion is considered and the value of D is determined. For this, taking $\frac{\bar{A}_2}{\bar{A}_4} = 10$ and $R_0 = 0.220$ nm, which is the sum of the ionic radii of $Mn^{2+} = 0.080$ nm and $O^{2-} = 0.140$ nm, the B_{kq} parameters are $B_{20} = -7610.21$ cm^{-1} , $B_{40} = 400.1558$ cm^{-1} , $B_{44} = 437.0726$ cm^{-1} and the value of D is obtained as $D = 265.6 \times 10^{-4}$ cm^{-1} . The EPR study gives the experimental value $D = 151.63 \times 10^{-4}$ cm^{-1} [19]. From the above, it is seen that the theoretical value is larger than the experimental one.

Now, taking the local distortions as $\Delta R_1 = -0.0437$ nm and $\Delta R_2 = -0.0450$ nm, and also $R_0 = 0.220$ nm and the ratio $\frac{\bar{A}_2}{\bar{A}_4} = 10$, the B_{kq} parameters are obtained as $B_{20} = -5337.51$ cm^{-1} , $B_{40} = 175.6468$ cm^{-1} , $B_{44} = 183.748$ cm^{-1} . Then, the value of D given as $D = 151.63 \times 10^{-4}$ cm^{-1} is in good agreement with the experimental value of $D = 151.63 \times 10^{-4}$ cm^{-1} . The interstitial site was also studied, but the D value was inconsistent with the experimental value, so data is not reported here.

5. Conclusions

The axial symmetry zero-field splitting parameter D for Mn^{2+} in $Tl_2Cd_2(SO_4)_3$ single crystal has been determined using the superposition model and perturbation theory. The theoretical D value matches well with the experimental value when distortion is taken into consideration. This study shows that the Mn^{2+} ion occupies the substitutional Cd^{2+} site which supports the conclusion of the experimental EPR study.

Acknowledgments

The author is thankful to the head of the Department of Physics, University of Allahabad, for providing the facilities of the department.

References

- [1] C. Rudowicz, S.K. Misra, *Appl. Spectrosc. Rev.* **36**, 11 (2001).
- [2] P. Gnutek, Z.Y. Yang, C. Rudowicz, *J. Phys. Condens. Matter* **21**, 455 (2009).
- [3] Z.Y. Yang, Y. Hao, C. Rudowicz, Y.Y. Yeung, *J. Phys. Condens. Matter* **16**, 3481 (2004).
- [4] S.K. Misra, in: *Handbook of ESR*, Vol. 2, Eds. C.P. Poole Jr., H.A. Farach, Springer, New York 1999, Ch. IX, p. 291.
- [5] H. Anandlakshmi, K. Velavan, I. Sougandi, R. Venkatesan, P.S. Rao, *Pramana* **62**, 77 (2004).
- [6] I. Stefaniuk, *Opto-Electron. Rev.* **26**, 81 (2018).
- [7] S.K. Misra, *Physica B* **203**, 193 (1994).
- [8] S.K. Misra, S. Diehl, D. Tipikin, J.H. Freed, *J. Magn. Reson.* **205**, 14 (2010).
- [9] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford 1970.
- [10] C. Rudowicz, P. Gnutek, M. Açıkgöz, *Appl. Spectrosc. Rev.* **54**, 673 (2019).
- [11] V.S.X. Anthonisamy, M. Velayutham, R. Murugesan, *Physica B* **262**, 13 (1999).
- [12] T.H. Yeom, S.H. Choh, M.L. Du, *J. Phys. Condens. Matter* **5**, 2017 (1993).
- [13] A. Zemann, J. Zemann, *Acta Cryst.* **10**, 409 (1957).
- [14] H.F. McMurdie, M.C. Morris, J. deGroot, H. E. Swanson, *J. Res. Natl. Bur. Stand. A* **75A**, 435 (1971).
- [15] S.C. Abraham, F. Lissalde, J.L. Bernstein, *J. Chem. Phys.* **68**, 1926 (1978).
- [16] N. Yamada, T. Hikita, M. Maeda, T. Ikeda, *J. Phys. Soc. Jpn.* **49**, Suppl. B, 102 (1980).

- [17] B. Brezina, M. Glogarova, *Phys. Status Solidi A* **11**, K39 (1972).
- [18] T. Ikeda, G. Yasuda, *Jpn. J. Appl. Phys* **14**, 1287 (1975).
- [19] S.K. Misra, S.Z. Korczak, *J. Phys. C Solid State Phys.* **20**, 4485 (1987).
- [20] A. Guelylah, G. Madariaga, T. Brezczewski, *Acta Cryst. C* **52**, 2954 (1966).
- [21] M.G. Zhao, M.L. Du, G.Y. Sen, *J. Phys. C Solid State Phys.* **18**, 3241 (1985).
- [22] W.L. Yu, *Phys. Rev. B* **39**, 622 (1989).
- [23] Z.Y. Yang, *J. Phys. Condens. Matter* **12**, 4091 (2000).
- [24] D.J. Newman, B. Ng, *Rep. Prog. Phys.* **52**, 699 (1989).
- [25] W.L. Yu, M.G. Zhao, *Phys. Rev. B* **37**, 9254 (1988).
- [26] K.D. Singh, S.C. Jain, T.D. Sakore, A.B. Biswas, *Acta Cryst. B* **31**, 990 (1975).
- [27] C. Rudowicz, H.W.F. Sung, *Physica B* **300**, 1 (2001).
- [28] C.J. Radnell, J.R. Pilbrow, S. Subramanian, M.T. Rogers, *J. Chem. Phys.* **62**, 4948 (1975).
- [29] J.A. Weil, J.R. Bolton, *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*, 2nd ed., Wiley, New York 2007.
- [30] W.L. Yu, M.G. Zhao, *J. Phys. C Solid State Phys.* **18**, L525 (1984).
- [31] J.F. Clare, S.D. Devine, *J. Phys. C Solid State Phys.* **17**, L581 (1984).
- [32] R.M. Macfarlane, *J. Chem. Phys.* **47**, 2066 (1967).
- [33] R.M. Macfarlane, *Phys. Rev. B* **1**, 989 (1970).
- [34] S. Altshuler, B.M. Kozyrev, *Electron Paramagnetic Resonance in Compounds of Transition Elements*, Wiley, New York 1974.
- [35] R.R. Sharma, R. Orbach, T.P. Das, *Phys. Rev.* **149**, 257 (1966).
- [36] W.L. Yu, M.G. Zhao, *Phys. Stat. B* **140**, 203 (1987).
- [37] Y.Y. Yeung, in: *Optical Properties of 3d-Ions in Crystals, Spectroscopy and Crystal Field Analysis*, Eds. M.G. Brik, N.M. Avram, Springer, Heidelberg 2013, Ch. 3, p. 95.
- [38] Q. Wei, *Acta Phys. Pol. A* **118**, 670 (2010).
- [39] R. Kripal, H. Govind, S.K. Gupta, M. Arora, *Physica B* **392** 92 (2007).