International Journal of Engineering Inventions
e-ISSN: 2278-7461, p-ISSN: 2319-6491
Volume 15, Issue 11 [November 2026] PP: 41-48

Study of Crystal Field Energy Levels and Zero Field Splitting Parameters of Mn^{2+}: $NiK_2 (SO_4)_2 \bullet 6H_2O$ Single Crystals

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Abstract
Using the superposition model (SPM), the crystal field (CF) and zero field splitting (ZFS) properties of Mn^{2+} doped Ni $K_2 (SO_4)_2.6H_2O$ (NKS) single crystals are analyzed.The ZFS parameter values thus found are in good agreement with the EPR experiment.CF energy levelsof Mn2+: NKS crystals are computed using the crystal field analysis (CFA) package.The majority of the computed and observed energy values correlate rather well. Thus, the theoretical finding verifies the experimental results.
Keywords: *Electron paramagnetic resonance, Superposition model,Zero field splitting, Crystal fields, Inorganic compounds, Single crystal.*

Date of Submission: 02-11-2026 Date of acceptance: 12-11-2026

I. Introduction

The nature of bondingand site symmetry are determined with impurity iondoping in crystals employing EPR, electron paramagnetic resonance.In crystals,doped Mn^{2+} impurity ion producescomplicated EPR spectra due to itshyperfine structure splitting.Since a small deviation from higher symmetryprovides appreciable change in its zero-field splitting, EPR investigations of Mn^{2+} ion doped in various crystals have been carried out extensively [1-7].

Superposition model (SPM) isanimportant tool forfindingthe local structure of the impurity ion in various crystals [8, 9]. SPMis applied forinvestigating the crystal field (CF) and zero field splitting (ZFS) parameters for several otherapplications [10–14]. SPM and the point-charge model [15, 16, 17] are oftenused to obtain the crystal field (CF) parameters.SPM is proposed for CF with certain assumptions as provided in[18].Using host crystal structural data, the (R_L, θ_L, Φ_L) spherical polar coordinates of each ligand areimportant for SPM CF analysis. When transition metal ions are added, local distortion is possibly caused by mismatches in ionic bonding, ionic size, and ionic charge. The spin-Hamiltonian parameters for Mn^{2+} and Fe^{3+} in CaO and MgO crystals have been determined [19]providing the SPM parameters which suggest the CF for 3d ions to satisfy the superposition principle. SPM intrinsic parameters based on reliable ligand distances have beenevaluated for the alkali earth oxides[20].

Theformula $A_2^+ B^{2+} (XO_4)_2. 6H_2$ Otypecrystals arein generalknown asTutton salt single crystals where Aisa monovalent cation, B standsfor a divalent cation (usually a transition metal ion) and Xrepresentssulfur or selenium [21–22]. Tutton salt crystals areinterestingisostructural crystal family with the same monoclinic symmetryandtwo formula units per unit cell (Z=2) [23]. Thesecrystals are of interestasthey are widely used inUVfilters [24].

Nickelpotassium sulphate hexahydrate (NKS),$NiK_2 (SO_4)_2.6H_2O$crystalsbelong to the Tutton salt crystal family and crystallize in the monoclinic crystal system. Withhigh purity,suitable crystal sizes and small transparency in the UV region,theyareusefulin optoelectronic devices [25].

NKS is often utilized in UV light filters [26].Nickel sulphate is used in electroplating baths and for the production of other nickel compounds [27].Potassium sulphate is a high-quality potassium fertilizer and industrial chemical widely used in agriculture and specialty applications. It provides potassium and sulphur without chloride, making it ideal for chloride-sensitive crops and processes [27].The specific applications of its components are probably connected to NKS.

EPR study of Mn^{2+}doped NKS has been doneat 300 K and the spin-Hamiltonian parameters areestimated [28]. The EPR spectrum displays a single set of five sextets when the magnetic field is altered in the a*c plane. This is because the a*c plane, a mirror plane normal to the b axis, is the plane where two divalent sites become equivalent. The divalent Ni^{2+} sites are occupied by the Mn^{2+} ions in the Tutton salt lattice, is therefore verified.$[Mn(H_2O)_6]^{2+}$magnetic complexes are formed when the divalent sites of the lattice of Tutton salt are replaced by Mn^{2+} ions, as indicated by angular variation studies. The orientations are discussed with the a*bc axis system, in whicha* is normal to b andc.

In thiswork, the ZFS parameters D and E are computed for the Mn^{2+} ion inNKSat 300K (room temperature, RT)using CF parameters from SPM and perturbation equations [29]. The aim is to find the Mn^{2+} ion position in the NKS crystal as well as the distortion taking place in the lattice. The EPR experimental values match well with the Mn^{2+} ion parameters at the Ni^{2+}substitutional site in the NKS crystal with local distortion.The crystal field analysis (CFA) program and the CF parameters are used to calculate the CF energy levels in single crystals of Mn^{2+} doped NKS.The computed and observed CF energy levels correspond reasonably well.Understanding how the CF theory and SPM procedureare applicable to Mn^{2+}:NKSto get SPM parameters database is the study's further goal. Computer simulation of magnetic and spectroscopic characteristics of molecular nanomagnet (MNM) and their design will get benefit from this. The transition ion-based MNM have single-molecule magnets (SMM) [30], single-chain magnets (SCM) [31], and single ion magnets (SIM) [32].Due toMNM's interesting properties, such as magnetization's macroscopic quantum tunneling and possible applications in high-density information storage and quantum computing, the above systems have attracted manyresearchers [30, 31].DifferentSMM or SCMsystems with Mn^{2+}andCr^{3+} ions have beenprepared[33].Since simpler crystal model calculationscan become a foundation for complicated ones, ZFS parameter estimations for Mn^{2+}: MNMs may be performed using the model parameters discovered here. A number of crystals can be produced using this modeling technique for a range of commercial and scientific applications.

II. Crystal Structure

Crystal structure of NKS Tutton salt is monoclinic with space group P 2_1/ a [34].β = 105.04°, Z = 2, b = 12.1904, c = 6.1368 and a = 9.0049 Ågive the unit cell parameters.S is in the fourfold coordination (SO_4), K is in the eightfold coordination (KO_8) and Ni^{2+} is in the sixfold coordination (NiO_6) surrounded by six water oxygen ligands (OW1, OW2, OW3, OW1', OW2', OW3'). The room-temperature crystal structure of NKS and the symmetry-adapted axis system (SAAS) are shown in Fig. 1. The point group symmetry of Ni^{2+}/Mn^{2+} ions in NKS is D_{2h}.

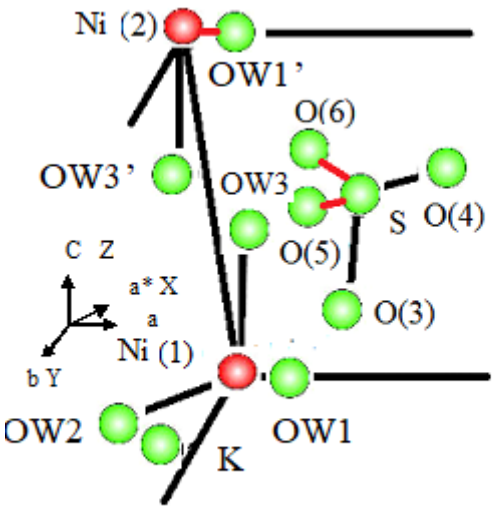


Fig. 1. The room-temperature crystal structure of NKS and the symmetry-adapted axis system (SAAS).

III. Crystal Field and Zero Field Splitting Parameter Calculations

In general, paramagnetic impurities are introduced into diamagnetic hosts to perform EPR studies. As it is normally expected that the impurity resonance lines may be broadened by the dipolar and exchange interaction of the paramagnetic host and paramagnetic impurity, the use of paramagnetic hosts is not encouraged. However, in spite of above expectation, reasonably sharp spectra have been observed in many

paramagnetic hosts [35, 36].In the present system of Mn^{2+}: NKS also, a good EPR spectrum of impurity ion is observed[28]and so spin Hamiltonian for impurity Mn^{2+} ion only in NKS crystal is considered for analysis.

The EPR spectraof Mn^{2+}: NKS areanalyzedwith the spin Hamiltonian [11]:

$$E(S_x^2 - S_y^2) + D\left\{S_Z^2 - \frac{1}{3}S(S+1)\right\} + \mu_B B.g.S = \mathcal{H}(1)$$

where B, μ_B,g, DandE representtheir usual meaning as given in [37–38]. For NKS, the crystallographic axis system (CAS) (a, b, c) does not form a Cartesian coordinate system. Hence, for the calculations, a modified crystallographic axis system (CAS*) (a*, b, c) must be selected [39, 40].Modified crystallographic axes a*, b, c (a* is normal to b and c axes)and x, y, z laboratory axes are given in Fig. 1. The mutually perpendiculardirections of metal-ligand bonds are taken as the local symmetry axes of the site or the symmetry adapted axes (SAA).As displayed in Fig.1, the SAAS axis-Z, which travels along the crystal c axis, i- perpendicular to (X, Y).When Mn^{2+} ions are doped in NKS crystal, theyreplaceNi^{2+}(1) siteswith certainloca distortionin the lattice [41].

The spin Hamiltonian for Mn^{2+} ionistaken as [41],

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

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

where,$B_{kq}$and $C_q^{(k)}$ stand fortheCF parameters (in Wybourne notation)and spherical tensor operators. In the orthorhombic symmetry crystal field,$B_{kq} \neq 0$ only for k = 2, 4; q = 0, 2, 4. The CF parameters, B_{kq} in NKSare obtainedusing SPM [42].

For SPM calculations of ZFS parameters of Mn^{2+} ions in NKS, we go to the microscopic spin Hamiltonian (MSH) expressions derived by perturbation theory [10] for the 2nd-rank ZFS parameters (D, E). The effect of the spin–orbit interaction (ς) is taken as a perturbation to the free-ion and CF Hamiltonian, while the spin–spin interaction is neglected due to its small contribution in comparison to the spin–orbit interaction[29, 43]. The MSH approach [29, 43] gives the fourth-order perturbation contributions to the orthorhombic ZFS parameters D and E.

The site symmetry of Mn^{2+} ions in NKS crystal is orthorhombic (OR-type I) [11],for which the ZFS parameters D and E are determined as follows [43, 44]:

$$D = \left(\frac{3\varsigma^2}{70P^2D'}\right)[-B_{20}^2 - 21\varsigma B_{20} + 2B_{22}^2] + \left(\frac{\varsigma^2}{63P^2G}\right)[-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2] \quad (4)$$

$$E = \left(\frac{\sqrt{6}\varsigma^2}{70P^2D'}\right)[2B_{20} - 21\varsigma]B_{22} + \left(\frac{\varsigma^2}{63P^2G}\right)[3\sqrt{10}B_{40} + 2\sqrt{7}B_{44}]B_{42} \quad (5)$$

In above, the spin-orbit coupling parameter is provided by ς , while the Racah parameters are shown by C and B andG = 10B+5C, P = 7B+7C, D' = 17B+5C.TakingN, the average covalency parameter, $\varsigma = N^2\varsigma_0$, $B = N^4B_0$, $C = N^4 C_0$, where ς_0 is free ion spin-orbit coupling parameterand B_0 and C_0arefree ion Racah parameters[42, 45]. $\varsigma_0 = 336$ cm^{-1},$B_0 = 960$ cm^{-1} and $C_0 = 3325$ $cm^{-1}$for free Mn^{2+} ion[11].

In terms of Racah parameters, N is obtainedfrom ($\sqrt{B/B_0} + \sqrt{C/C_0}$)/2 = N.The Racah parameters (B = 850 cm^{-1}, C = 2970 cm^{-1}) are found from optical study of Mn^{2+} ionin zinc cesium sulphate hexahydrate where ligands are oxygens [46], since no optical absorption study of Mn^{2+}dopedNKSisgiven in literature. $[Mn(H_2O)_6]^{2+}$ complexes are formed when the Mn^{2+} ion replaces the divalent sites of Zn^{2+} in zinc cesium sulphate hexahydrate and the optical absorption spectra are because of $[Mn(H_2O)_6]^{2+}$complexes [41]. As the same complex forms in Mn^{2+}doped NKS, its optical absorption spectra will conform to those of Mn^{2+}: zinc caesium sulphate hexahydrate.For SPM analysis ofMn^{2+} in $BiVO_4$ [43] Yoem et al. have used optical spectra of Mn^{2+}: MgO due to similar ligands in the crystal. Therefore, for Mn^{2+}doped NKScrystal, it seems appropriate to use the Mn^{2+} optical absorption data in zinc cesium sulphate hexahydrate.

The CF parameters are estimated using SPM [18, 43],with co-ordination factor $K_{kq}(\theta_j, \varphi_j)$ and intrinsic parameter $\overline{A_k}(R_j)$, given by

$$\sum_j K_{kq}(\theta_j, \phi_j)\, \bar{A}_k(R_j) = B_{kq} \qquad (6)$$

$\overline{A_k}(R_j)$ is obtainedfrom the relation

$$\overline{A_k}(R_0)\left(\frac{R_0}{R_j}\right)^{t_k} = \bar{A}_k\left(R_j\right) \qquad (7)$$

where the parameters $\overline{A_k}(R_0)$, R_0,t_k and R_j are discussed in [43]. For Mn^{2+}doped crystals, $t_2 = 3$ and $t_4 = 7$have been used by earlierworkers[43], the same values aretaken herefor Mn^{2+}: NKS crystal.Since the co-ordination about Mn^{2+} ion is octahedral, $\overline{A_4}$ is evaluatedfrom the relation [43]

$$\overline{A_4}(R_0) = \frac{3}{4} Dq \qquad (8)$$

The optical study [46]yields Dq = 790 cm^{-1}, which gives $\overline{A_4}(R_0)$ = 592.5 cm^{-1}. For $3d^5$ ions the ratio $\frac{\overline{A_2}}{A_4}$ lies in the range 8 - 12 [42, 43-49]. With $\overline{A_2}$ =10 $\overline{A_4}$,5925 cm^{-1} = $\overline{A_2}$ .is obtained.

IV. Results and Discussion

From the arrangementof ligands about Mn^{2+} ion (Fig. 1) and SPM, the Mn^{2+} ion's CF characteristics at the Ni^{2+} sites in NKS are computed.For site I in the single crystal of NKS, Table 1 shows the coordinates of atoms, bond length R (with and without distortion) and angles θ, φ.The CF and ZFS parameters as well as R_0 areshown in Table 2. Table 2 gives that R_0 = 0.200 nm beingslightly less than the sum of radii of ions(0.223 nm) of Mn^{2+} = 0.083 nm and O^{2-} = 0.140 nm with no distortion and $\frac{\overline{A_2}}{A_4}$ = 8, 10, 12 yield ZFS parameter values at octahedralsubstitutional site I to be largelydifferent from the EPR experimentalones[28].Experimental ZFS parameters |D| and |E| (10^{-4} cm^{-1}) obtained from EPR measurement are 422.5, 38.7, respectively.|E|/|D| isfound as 0.091which issmallerthan the standard value 0.33 [38]. With no distortion considered, |D| and |E| obtained aregreater than the EPR measurement values. |E|/|D| is also larger than thestandard value 0.33 [38]. Local distortion is, therefore,introduced inthe calculation. For local distortion an iterative processas in [44] has been used by changing R, θ and φ to minimize the difference between calculated and experimental D and E and E/D reaching to standard value 0.33[38] with lattice strainbeing minimum.Using local distortion and above R_0, the substitutional octahedral sites' ZFS parameters are computed for $\frac{\overline{A_2}}{A_4}$ =8, 10, 12 and are listed in Table 2. The ZFS parameter |D|is smaller than the experimental value (error 22.8 %),|E| is greater than the experimental one (error 149.6%) for $\frac{\overline{A_2}}{A_4}$ =8 while both |D| and |E| aregreater for $\frac{\overline{A_2}}{A_4}$ =12 (error 26.6% for D and 397.4 % for E). |E|/|D| is smaller than 0.33 (the standard value)for $\frac{\overline{A_2}}{A_4}$ =8 andgreater for $\frac{\overline{A_2}}{A_4}$ =12, while |D| is in good agreementwith the EPR experimental value and |E| is greater than the experimental value for $\frac{\overline{A_2}}{A_4}$ =10 [28] but |E|/|D| comes out to be equal to the standard value 0.33 [38].Hence $\frac{\overline{A_2}}{A_4}$ =10 seemsto be quiteappropriate.The

power law exponent parameters $t_2 = 3$ and $t_4 = 7$ with transformation S2 for standardization [38]have beenused to obtain|E|/|D| ratio equal to 0.33 and calculated ZFS parameters very near to experimental valuesestimated from EPR. Similar value of $\frac{\overline{A_2}}{A_4}$ has beenused for Mn^{2+}doped diglycine calcium chloride tetrahydrate [50], Fe^{3+} doped $BiVO_4$ [42]and Mn^{2+} doped ZKS single crystals[44].

Table 1. Coordinates of atoms, bond length Randθ, φangles in NKS (site I).

Position of Mn^{2+}Ligands	Spherical polar coordinates of ligands								
		x	y	z	R(nm)θ^0		φ^o		
			(Å)						
	Without distortion								
Site : Substitutional Zn(1) (0.0000, 0.0000, 0.0000)	OW1	0.16694	0.11095	0.1630	0.20759	R_1	85.49	θ_1 85.37	φ_1
	OW2	- 0.16659	0.11244	0.0356	0.20849	R_2	89.02	θ_2 94.58	φ_2
	OW3	0.00028	- 0.06662	0.3016	0.20206	R_3	81.41	θ_3 89.99	φ_3
	OW1’	-0.16694	-0.11095	-0.1630	0.20759	R_4	94.50	θ_4 94.62	φ_4
	OW2’	-0 .16694	0.38905	0.6630	0.66693	R_5	84.29	θ_5 91.44	φ_5
	OW3’	0.16694	0.61095	0.3370	0.77712	R_6	87.51	θ_6 88.76	φ_6
	With distortion								
I	OW1				0.24759		65.49	81.37	
	OW2				0.25371		69.02	98.58	
	OW3				0.26206		61.41	91.99	
	OW1’				0.27759		74.50	96.12	
	OW2’				0.75193		74.29	93.44	
	OW3’				0.86212		83.51	86.76	

Table 2. Mn^{2+}doped NKScrystal:ZFS and CF parameters.

Parametersof	Parametersof CF (cm^{-1})				ZFS ($10^{-4}cm^{-1}$)					
Site	R_0(nm)	B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	|D|	|E |	|E|/|D|
Without distortion									
Site I									
$\frac{\overline{A_2}}{A_4}$ = 8	0.200	-16995.0	-20998.8	5192.393	5528.984	8017.853	3270.6	1665.8	0.509
$\frac{\overline{A_2}}{A_4}$ =10	0.200	-21243.8	-26248.5	5192.393	5528.984	8017.853	4689.9	2402.2	0.512
$\frac{\overline{A_2}}{A_4}$ =12	0.200	-25492.5	-31498.2	5192.393	5528.984	8017.853	6411.5	3289.2	0.513
			With distortion						
Site I									
$\frac{\overline{A_2}}{A_4}$ = 8	0.200	-6868.11	2772.827	-298.715	-81.8618	2763.488	326.1	96.6	0.296
$\frac{\overline{A_2}}{A_4}$ =10	0.200	-8585.14	3466.034	-298.715	-81.8618	2763.488	422.5	140.5	0.333
							Exp. 422.5	38.7	0.091
$\frac{\overline{A_2}}{A_4}$ =12	0.200	-10302.2	4159.241	-298.715	-81.8618	2763.488	535.0	192.5	0.359

The CFA package [51] and CF parameters B_{kq} (with distortion) are used to calculate the optical spectra of Mn^{2+}doped NKS single crystals.The total Hamiltonian is diagonalized in order to find the CF energy levels of the Mn^{2+} ion,

Table 3 lists the CF energy levels(observed and calculated) for substitutional site [46]. From the characteristicand the position of the bands observed, they have been attributed to a Mn^{2+} ion in octahedral symmetry [44, 46, 52]. The assignment of different bands has been done as in [44, 53]. CFA package [51] can perform diagonalization of the total Hamiltonian within the $3d^N$ basis of states in the intermediate crystal field coupling scheme yielding the CF energy levels and the state vectors. The spin–spin interaction (M_0), Trees correction (α), the spin–orbit interaction (ζ), and the spin-other orbit interaction (M_{00}, $M_{22;}$ two parameters),the Coulomb interaction (usingRacah B and C parameters), the Hamiltonian of the crystal field are all considered for the Hamiltonian of CFA package.The following free-ion parameter valuesare taken in the CFA computations: B = 850 and C = 2970, ζ_0 = 336, α = 76 cm^{-1}, M_{00} = 0.2917, M_{22} = 0.0229, M_0 = 0.2917 and M_2 = 0.0229. Thecomplete Mn^{2+}spectra consist of 120 degenerate states, only a few energy levels based on intensity are shown here [44, 53]. The transitions pertaining to$^4T_{2g}(G)$, $^4T_{1g}(G)$and $^4T_{1g}(P)$ exhibit greater deviation than those pertaining to $^4A_{1g}(G)$, $^4E_g(G)$, $^4T_{2g}(D)$, $^4E_g(D)$, $^4A_{2g}(F)$, and $^4T_{1g}(F)$. The causes for larger deviations of above transitions may be vibronic coupling, electron correlation effects or limitations of the CF model [41].The optical absorptionspectra of Cr^{3+}-activated phosphors have been understood using Franck-Condon analysis with the configurational-coordinate (CC) model [54]. The different excited state-ground state transitions in Cr^{3+} are a result of the lattice vibrations' strong coupling (CC model) [54]. The CC model has not been used here and so there is difference between excited-state peak energies obtained and energies of the zero-phonon line (ZPL) [54, 55].

Table 3. Energy levels (calculated andobserved)insingle crystal of Mn^{2+}: NKS.

Transition from state $^6A_{1g}(S)$	Observed (cm^{-1})	Calculated (cm^{-1})
		I
$^4T_{1g}(G)$	18436	23141, 23195, 23344, 23441, 23459, 23508
$^4T_{2g}(G)$	22815	23737, 23768, 24147, 24182, 24249, 24282
$^4E_g(G)$	24783	24832, 24850, 24858, 24876
$^4A_{1g}(G)$	24850	24877, 24881
$^4T_{2g}(D)$	28003	26895, 26949, 28326, 28341, 29344, 29434
$^4E_g(D)$	29870	29717, 29860, 30198 30283
$^4T_{1g}(P)$	32435	31928, 31942, 34786, 34978, 35037, 35192
$^4A_{2g}(F)$		36524, 36831
$^4T_{1g}(F)$	41460	41176, 41271, 41330, 41632, 41684, 42653

Table 3 demonstrates that the calculated and observed energy levels are in reasonableconformity. So, the theoretical studyvalidatesthe EPR experimental result [28, 46] that Mn^{2+} ions enter the NKScrystal at substitutional Ni^{2+}octahedral site.The obtained model parameters of this research can be applied to ZFS parameter evaluations of Mn^{2+} ions in molecular nanomagnets at similar sites. The modeling process employed here may be useful in exploring crystals having numerousapplications in science and industry.

V. Conclusions

The splitting parameters for zero field and crystal field for Mn^{2+} ion doped NKS single crystals are found utilizing perturbation expressions and superposition model.The zero field splitting parameters calculated for $\frac{\overline{A_2}}{\overline{A_4}}$ =10 validate the results of the EPR experiment.The computed CF energy levels and the values from the experiment are reasonably in agreement.Consequently, the result of EPR experimentthat Mn^{2+} ions replace Ni^{2+} sites in NKS crystal is theoretically confirmed.The parameters of ZFS for Mn^{2+} ions in molecular nanomagnets at similar locations canbe obtained using the model parameters ofthe current study.The present modeling methodmay be helpful inexploringseveralcrystals havingnumerous applications in science and industry.

Acknowledgement

The author is grateful to Prof. C. Rudowicz of Faculty of Chemistry, Adam Mickiewicz University in Poznan, Poland, for the CFA program, and the Head of the Physics Department,University of Allahabad in Prayagraj for making availabledepartmental amenities.

Declarations

Ethical Approval:

No animal or human subjects were used in this investigation, and it has not been performed in any private or protected places. Corresponding places did not need specific approvals.

Competing interests:

The author certifies that none of the work presented in this paper could have been influenced by competing personal relationships or financial interests.

Authors' contributions:

Ram Kripal: concept and oversight, wrote the manuscript, prepared the figure and carried out the computations.
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Funding:

There has been no funding.

Availability of data:

The data are available on request from the author.

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