Theoretical study on the zero field splitting and dopant position of Mn^{2+} in $KH_3(SeO_3)_2$ single crystal

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ABSTRACT

In the present paper theoretical methods have been employed to investigate the zero field splitting (ZFS) parameter. The superposition model (SPM) with the microscopic spin-Hamiltonian theory and the coefficient of fractional parentage has been employed to investigate the dopant (manganese II) substitution in the potassium trihydrogen selenite (PTS) single crystal. The ZFS parameter by using the computational method of ORCA program package developed by Neese et al. has also been determined. The contribution of SOC (spin–orbit coupling) has been taken into consideration. The approach of CP (Coupled-Perturbed) method is found to be more appropriate than PK (Pederson–Khanna) method in the evaluation of ZFS for Mn(II) ion. The theoretical predictions of the zero field splitting (ZFS) parameter D on the basis of the above methodology has been compared with the experimental results. The theoretical results are appropriate with the experimental ones and indicate the interstitial occupancy of Mn^{2+} ion in the host matrix.

1. Introduction

The Electron paramagnetic resonance (EPR) study provides an insight into the microscopic properties related to the crystal structure, phase transition, pressure and temperature variation in the original system. The subjugated transition electrons play a vital role in transforming the dynamics of the base compounds [1–3]. Trihydrogen selenite crystal of the type $MeH_3(SeO_3)_2$ (Me = Li, Na, K, Rb, Cs and NH_4) belong to the class of ferroelectrics with hydrogen bonds [4–6]. The potassium trihydrogen selenite single crystal has been studied earlier due to their immense applications in dielectric and phase transition [7]. Empirical studies on potassium trihydrogen selenite (PTS) single crystal have been studied previously by imposition of Electron Spin Resonance (ESR) technique [8]. Zero field splitting (ZFS) of doped transition metal ions in single crystals has become the subject of immense research interest due to their potential applications in reflecting the symmetries, structural changes and optical transitions in the host lattices [9–13]. The chemical complexes which shows the property of uniaxial ZFS parameters have attracted considerable interest owing to their potential applications in high density information storage, quantum computing and magnetic refrigeration [14–16].

In EPR study, the zero field splitting factor corresponds to high spin paramagnetism arised from the magnetic dipolar interaction between the unpaired electrons in the doped system [17]. There are three possible positions of Mn^{2+} in the single crystal under consideration i.e. substitution of K^+, Se^{4+} or some interstitial position. The characterization techniques being employed reflect the geometrical information about the dpoant in the host compound whereas the superposition model highlights the information about the physico-chemical interaction of the doped magnetic ion with the coordinated ions and the geometrical site. The practicality of this model lies in the nearest neighbour interaction. In the primitive days, this technique was used in comparing the experimental results with ab initio calculations. The superposition model also takes overlapping and covalency parameters into account. Its application to the spin Hamiltonian parameter of d^5 ion ground states have been devised [18]. Though the superposition model of nearest neighbor interaction is primitive but it can be applied to those systems where covalency dominates for the dopant in the base compound. The spin Hamiltonian can be conceptually described by using the state operators acting on effective state functions. The operation of this quantum mechanical treatment will modify the energy levels and hence can be applied to relate the observed spectrum peaks to their physical origin [19,20]. The ligand field analysis at higher symmetry sites for full Hamiltonian including the electrostatic terms, trees correction, the spin–orbit interaction and the ligand field interaction within $3d^N$ (for N = 2 to 8) have been

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performed using a computer program developed by Yeung et al. [21]. The study of crystal field analysis of the $3d^N$ ions at low symmetry sites including the imaginary crystal field terms has been reported by Chang et al. [22]. The crystal filed package developed by them was found to be useful in analyzing the electron paramagnetic resonance spectra of $3d^N$ ions and in correlating the ligand field parameters with the spin Hamiltonian parameters. The zero field splitting may be due to admixture of the ground state with the higher excited states of the doped ion in the base compound [23,24].

The evaluation of ZFS parameters using theoretical computational program package of ORCA by Neese et al. has been reported [25–28]. This computer program can be used for Density Functional Theory (DFT) or wave-functional methods based on SCF techniques with different modules. The application of these computational tools to study ZFS parameters for doped transition metal ions in the host has been previously studied [29–32].

Superposition model (SPM) is a widely used technique to determine the zero field splitting parameters [33–35]. In the present theoretical study, Newman's Superposition technique has been imposed on considering the substitutional occupancy of Mn^{2+} in place of K^+ and Se^{4+} by evaluating the crystal field parameters using Wybourne's notation. The concept of coefficient of fractional parentage to analyse the dopant position in the base compound has been used for the first time to the best of our knowledge. The concomitancy of non-substitutional with that of interstitial occupancy has been analysed. The interstitial positions on the basis of experimental observations and the possible coordinates are evaluated using direction cosines for manganese in the base compound. In the present paper we describe the methods of Superposition principle, co-efficient of fractional parentage and the computational study with ORCA program package to evaluate the ZFS *D*-tensor.

2. Crystal structure

The crystal structure of $KH_3(SeO_3)_2$ is orthorhombic with space group P*bcn*. The cell contains four formula units with dimensions $a = 16.152$ Å, $b = 6.249$ Å and $c = 6.307$ Å [8]. Table 1 provides an insight into the lattice positions in the single crystal [36].

Fig. 1 shows the interatomic bond lengths and bond angles as observed from the X-ray study of potassium trihydrogen selenite (PTS) single crystal. Table 1 represents the respective values of interatomic bond lengths and bond angles in PTS single crystal. In a trigonal pyramid the Se—O bonds (1.707 Å) is shorter than a pure Se—O sigma bond (1.83 Å). Due to this fact there may be pi-bonding in the d-orbitals. This is confirmed by the fact that the angles at Se are significantly smaller (101°) than the tetrahedral angle [36].

3. Theoretical interpretation

The empirical results for the resonance field of Mn^{2+} in potassium trihydrogen selenite (PTS) single crystal is endowed through the usual spin Hamiltonian expression [37],

$$H = g\mu_B B.S + D\left[S_z^2 - \frac{1}{3}S(S+1)\right]$$
$$+ \frac{a}{6}\left[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2+3S-1)\right] + \frac{F}{180}$$
$$\times \left[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2\right]$$
$$+ AS_z I_z + K(S_x I_x + S_y I_y)$$

(1)

In the above expression 'g' signifies the spectroscopic splitting factor, μ_B is the Bohr magneton, *B* is the external applied magnetic field and *S* the electron spin operator. The parameters

Table 1
Interatomic distances and angles of PTS.

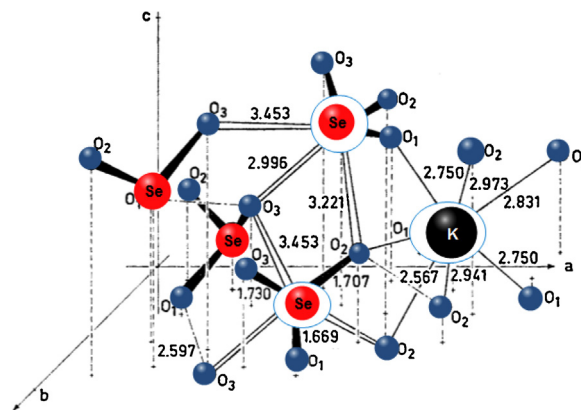| Interatomic Bond	Å	Interatomic Bond	Å	Angles	Degrees
$Se - O_1$	1.669	$K - O_2$	2.973	$O_1 - Se - O_2$	100.61
$Se - O_2$	1.707	$K - O_1$	2.831	$O_1 - Se - O_3$	102.41
$Se - O_3$	1.730	$K - O_1$	2.750	$O_2 - Se - O_3$	99.82

Fig. 1. The clinographic projection of the part of the structure realized from X-ray analysis at room temperature. The possible occupancy of the dopant (manganese II) in the host compound is encircled. The figure taken by permission from Ref. [36], copyright 1969, Danish Chemical Society.

a and *D* are the cubic and axial zero field splitting (ZFS) parameters respectively. The first term represents the electronic Zeeman interaction, the second term represents the axial component of the zero field splitting parameter, the third term represents the fourth-rank cubic ZFS term, the fourth term represents the axial fourth-rank ZFS term, the fifth and sixth terms are the hyperfine interaction terms (for the present case $I = 5/2$). The fourth, fifth and sixth terms have been omitted due to their negligible effect [2,20]. The third term has no significance because in the present case only the axial ZFS has been taken into account.

The zero field splitting originates from the magnetic interactions of the electrons. The Hamiltonian in the host system is generated from the coupling of the magnetic ion with the crystalline environment. In the present case for Mn^{2+} the efficacy of ground state splitting is due to induced breakdown of spin–orbit coupling with higher excited states [30]. The ZFS splitting depends upon orbit–orbit interaction too. The orbit–orbit interaction has not been considered by the researchers for the evaluation of ZFS for d^5 ions [38–41]. Nicholson and Burns have calculated and compared the axial ZFS factor *D* by using the Mossbauer absorption experiments and ESR study [42]. They found a disagreement between the theoretical and experimental results. By using the ESR measurements for Mn^{2+} doped $CdGa_2S_4$ and $CdGa_2Se_4$, the covalency in Mn—Se bond is found to be more responsible for the large value of axial ZFS factor in selenide [43].

Theoretical studies to determine the ZFS parameters have been studied earlier on manganese(II) doped single crystals using SPM considering the local site symmetry to be distorted octahedron [44–48]. From the X-ray diffraction (XRD) study of the PTS crystal structure the selenium and potassium have distorted octahedral symmetry [36]. When doped with manganese(II) ion, the crystal exhibits the axial ZFS and rhombic ZFS was absent [8]. The main idea for the determination of phenomenological crystal field parameters in consonance with the SPM is that *z*-axis should be coincident with the highest axis of symmetry in the chosen common coordinate system [33]. In view of the Newman's superposition principle of nearest neighbor interaction, we propose tetragonal symmetry for the dopant manganese(II) ion around oxygen atoms at the