Materials Science

Trade Science Inc.

An Indian Journal

Full Paper

Superposition model analysis of spin-hamiltonian parameters for Mn^{+2} doped in nickel maleate tetrahydrate single crystals

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PAC No. 76.30 -V

ABSTRACT

The Newman superposition model has been used to investigate the substitution of Mn^{2+} for Ni^{2+} site in Nickel maleate tetrahydrate single crystals. The calculated values of the spin-Hamiltonian parameters b^0_2, b^2_2 and b^0_4 at room temperature fit the experimental one taken from the literature for Mn^{2+} in NMTH, with average intrinsic parameters calculated as b^-_2 = -0.047 cm^{-1}, t_2 = 7 and b^-_4 = -0.0008 cm^{-1}, t_4=10, and satisfy the empirical equality $b^-_2 > 4b^-_4$. The satisfactory reproduction of experimental values of b^0_2, b^2_2, and b^0_4 indicates that Mn^{2+} substitutes in place of Ni^{2+} in the lattice and does not cause appreciable local distortion in the host crystals.
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INTRODUCTION

Electron paramagnetic resonance (EPR) investigations resulting that in most of the systems Mn^{2+} ions are coordinated by oxygens and usually the zero field splitting parameters are quite sensitive with respect to small structural changes. The empirical superposition model (SPM) suggested by Newman, has proved to be a very powerful method in probing the local structure of ion in a variety of crystals[1-5] and relating the fine structure constants to the actual arrangements of ligands around the impurity ion. In this paper we reports the SPM analysis of spin-Hamiltonian parameters of Mn^{2+} in Nickel maleate tetrahydrate (here after referred as NMTH) single crystals.

SUPERPOSITION MODEL

The SPM of the crystal field[2] based on the assumptions:

(i) The crystal field acting on the open-shell electrons of a paramagnetic ion is the resultant of a sum of contributions coming from nearest neighbors individual ligands in the crystal.

(ii) Each single-ligand contribution in the sum is axially symmetric about the line joining its centre to that of the paramagnetic ion and the nature of the ligand. The contribution of more distant neighbors as well as the interaction between ligands, are ignored. The ZFS parameters are given by

$$b^m n = \Sigma K^m_n (\Theta_i, \Phi_i) b^-_n (R_i) \qquad (1)$$

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where the summation is taken over all ligands R_i, Θ_i and Φ_i are the spherical coordinates of the ith ligand when the paramagnetic ion is at the origin. The b_n^- are called intrinsic parameters, which depend on the nature of the ligand and the covalency of the bonding, and obey a single potential law

$$b_n^- (R_i) = (R_o / R_i)^{t_n} \cdot b_n^- (R_o) \qquad (2)$$

where R_o is the normal metal ion-ligand distance and R_i is the distance of ith ligand from the origin. The power law exponent t_n depends on the particular system considered. Angular function $K_n^m (\Theta_i, \Phi_i)$ are tabulated by Rudowicz[6].

CRYSTAL STRUCTURE

The crystal structure of NMTH has been determined by K. Saroja et. al.[7] and Zhou Ping et al[8]. The crystal Ni $(COO-C_2H_2-COOH)_2.4H_2O$ belongs to triclinic system with the space group P $\bar{\Gamma}$ and Z = 1. The primitive cell constants are a = 5.1797(3) A°, b = 7.3097(4) A°, c = 9.1387(3) A°, α = 108.47(2)°, β = 104.63(1)°, γ = 92.84(2)° and cell volume is 314.373 A°³. The Ni^{2+} is at the origin of the crystal unit cell and coordinated by the oxygen atoms of four water molecules and two butane di-acid groups and the molecule is having central symmetry. The Ni^{+2} has quasi-equal bond distances to six oxygen atoms and the average

distance is 2.0597 A°. The bond angle of O-Ni-O is quasi-equal and the average bond angle is 90°, formed an octahedral structure given in TABLE 1.

The average bond distances of Ni-O are smaller than Mn-O but average bond angles O-Ni-O are quasi equal and similar to O-Mn-O are 90º within ± 1º correction; formed an octahedral structure. The crystal structure of Manganese Maleate trihydrate $[Mn(C_4H_2O_4)].3H_2O$ and Manganese Hydrogen Maleate Tetrahydrate $[Mn(C_4H_3O_4)_2].4H_2O$ is determined by T. Lis[9]. Manganese Hydrogen Maleate Tetrahydrate here after referred as MMTH is triclinic, P$\bar{I}$, a = 3.373(3) A°, b = 9.755(4) A°, c = 5.325(4) A°, α = 106.65(4), β = 86.68(4) and γ = 115.44(4) with z = 1. In crystals of MMTH the Mn^{+2} ions are octahedrally coordinated by four water o-atoms and two o-atoms from two monodentate hydrogen maleate ligands. The distorted octahedral coordination of Mn atoms is similar to that found in most Mn^{+2} carboxylate salts. The Mn-O distances and O-Mn-O bond angles are given in TABLE 1 which is compared with NMTH crystals.

Ni^{+2} is surrounded by three sets of oxygen ligands $Ni-O_1$, $Ni-O_5$ and $Ni-O_6$ each as nearest neighbors. Using the atomic positions and lattice constants, the values of the polar angle Θ_i that Ni-O bond makes with the c-axis and azimuthal angle Φi are calculated and are given in TABLE 2.

TABLE 1

NMTH Ref.[8]				MMTH Ref.[9]			
M-O Bond	Bond Length (A°)	Name of Bond	Bond Angle (°)	M-O Bond	Bond Length (A°)	Name of Bond	Bond Angle (°)
Ni-O₁	2.077 (0)	O(1)-Ni-O(5)	90	Mn-O₁	2.214(2)	O(1)-Mn-O(5)	92.5 (1)
Ni-O₅	2.021 (0)	O(1)-Ni-O(6)	90	Mn-O₅	2.205(0)	O(1)-Mn-O(6)	90.0 (0)
Ni-O₆	2.081 (0)	O(5)-Ni-O(6)	89.2	Mn-O₆	2.128(3)	O(5)-Mn-O(6)	87.3 (1)

TABLE 2

Ni-O Bond	Θ_i in degree	Φi in degree
Ni-O₁	36.19	-8.22
Ni-O₅	71.96	57.16
Ni-O₆	67.10	-41.21

RESULTS AND DISCUSSION

EPR study of Mn^{2+} in NMTH single crystals at room temperature and liquid nitrogen temperature has been published[10,11] and the results discussed the appropri-

ate concept for the observance of EPR of Mn^{2+} in paramagnetic host lattice. It was found that Mn^{2+} substitute for Ni^{2+} ions. The observed spectrum shows that the metal-water octahedral has orthorhombic distortion. The experimental values of spin– Hamiltonian parameters D, E and a have been determined by N.O. Gopal et. al[11] as D = (223 ± 6)10⁻⁴ cm⁻¹, E = (62 ± 2)10⁻⁴ cm⁻¹ and a = (6.5 ± 0.5) 10⁻⁴ cm⁻¹.

We have performed superposition model calculations and the spin-Hamiltonian parameters b_2^0, b_2^2 and b_4^0 for Mn^{2+} in NMTH is determined by using the rela-

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tions

$$b^0_2 = \sum_i 1/2(3\cos^2\Theta_i - 1) \, [R_o/R_i]^t_2 \, b^-_2 \qquad (1)$$

$$b^2_2 = \sum_i 3/2 \, (\sin^2\Theta \, \cos 2\varnothing) \, [R_o/R_i]^t_2 \, b^-_2 \qquad \textbf{and} \qquad (2)$$

$$b^0_4 = \sum_i 1/8 \, (35 \cos^4\Theta - 30 \cos^2\Theta + 3) \, [R_o/R_i]^t_4 \, b^-_4 \qquad (3)$$

Using equations (3) and (4) along with R_i, Θ_i, $\varnothing_i$ given in TABLE 2, $t_2 = 7$ for Mn^{2+}, R_o the reference distance for Mn^{2+} surrounded by pair of oxygens O_1, O_5 and O_6 respectively [TABLE 1], and taking experimental values of zero field splitting parameters b^0_2 and b^2_2 reported in publication[11], the values of respective intrinsic parameter b^-_2 are evaluated as -0.048 cm^{-1} and -0.044 cm^{-1}, which lie in the range -0.0267 to -0.1000 cm^{-1}[12-14]. By using average value of $b^-_2 = -0.47$ cm^{-1} and $t_2 = 7 \pm 1$, the calculated values of b^0_2 and b^2_2 fairly matched with experimental ones within error limits. Using eq. (5) along with values of R_i, Θ_i, $\varnothing_i$ and $t_4 = 10$, and experimental value of b^0_4, the intrinsic parameter b^-_4 is evaluated -0.00085 cm^{-1} which satisfy the empirical inequality $b^-_2 > 4 \, b^-_4$ [15].

CONCLUSION

The ionic radii of Mn^{2+} and Ni^{2+} are comparable, so the manganese ion on substituting the nickel cation site in NMTH, causes minimum change in bond lengths and bond angles from the values obtained for pure compound, hence local distortion should be minimum for the host lattice. By using $b^-_2 = -0.047$ cm^{-1} for the reproduction of experimental values b^0_2 and b^2_2 indicates that Mn^{2+} substitutes in place of Ni^{2+} in the lattice and does not cause appreciable local distortion in NMTH single crystals.

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