

## Superposition model analysis of zero field splitting for $Mn^{2+}$ in $(Mg)_2SiO_4$ single crystals

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### ABSTRACT

The Newman superposition model has been used to investigate the substitution of  $Mn^{2+}$  for  $Mg^{2+}$  site in  $(Mg)_2SiO_4$  single crystals. The calculated values of zero field splitting parameter  $b_2^0$  at room temperature fit the experimental one taken from the literature with average intrinsic parameters  $b_2(O) = -0.0419$  c for oxygen taken  $t_2 = 7$  and  $t_4 = 10$  for  $Mn^{2+}$  doped in  $(Mg)_2SiO_4$  single crystal. The values of  $b_2$  determined for  $Mn^{2+}$  doped in  $(Mg)_2SiO_4$  single crystals is  $-0.073$  cm<sup>-2</sup>. The superposition model analysis shows that for large values of  $b_2^0$ ,  $b_2^2$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$  intrinsic parameters  $\bar{b}_{2,2}$  and  $\bar{b}_{2,4}$  can be estimated with suitable error but for small values of these spin – Hamiltonian parameters it is very difficult to predict the correct sign and magnitude. The present study about superposition model is very useful to get information about the zero field splitting of parameters ions in some host single crystals.

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### KEYWORDS

EPR;  
Superposition model;  
ZFS parameters.

### INTRODUCTION

Electron Paramagnetic Resonance (EPR) is regarded as an effective method to study the local geometry and local Properties in the vicinity of impurity ions doped in the single crystals. Many EPR investigations resulting in the determination of spin-Hamiltonian parameters of S-state ions in various single crystals have been reported in the literature<sup>[1-2]</sup>; few attempts have been made to relate these to the crystalline environment of the substituted ion, apart from using its point symmetry to restrict the number of parameters. In order to understand the various characteristics of transition-metal complex

molecules, it is important to establish the inter-relations between electronic and molecular structure. Newman proposed the empirical superposition model (SPM) relating the fine structure constants to the actual arrangements of ligands around the impurity ions<sup>[3-4]</sup> and usually the zero-field splitting (ZFS) parameters  $b_2^0$ ,  $b_2^2$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$  are quite sensitive with respect to small structural changes, where  $Mn^{2+}$  ions are coordinated by fluorine and chlorine in single crystals.

The objective of this paper is to study the local distortion produced by substitution  $Mn^{2+}$  in place of host ions  $Mg^{2+}$  in  $(Mg)_2SiO_4$  in single crystals which can lead to variation of magnetic properties.

## Full Paper

### SUPERPOSITION MODEL

#### The SPM of the crystal field is based on two assumptions

The total ZFS experienced at an ion in a crystal is due to its nearest neighboring ions. The electric field at an ion caused by another ion depends upon exactly what ions are present, and the distance between them, irrespective of the other surroundings. Therefore in calculations, the total electric field at central ion M is given by the axially symmetric contributions of the ligands and the contribution of the far distant neighbors as well as interaction between ligands are ignored. The ZFS parameters are given by

$$b_n^m = \sum K_n^m(\theta_i, \phi_i) \bar{b}_n(R_i) \quad (1)$$

where the summation is taken over all ligands.  $R_i$ ,  $\theta_i$  and  $\phi_i$  are the spherical coordinates of the  $i^{\text{th}}$  ligand when the paramagnetic ion is at the origin. The angular functions  $K_n^m(\theta_i, \phi_i)$  are tabulated by Newman et al<sup>[4]</sup> and Rudowicz<sup>[5]</sup>. The  $\bar{b}_n$  is the intrinsic parameter, which depends upon the nature of the ligand and the co-valency of the bonding, and obeys the single potential law

$$\bar{b}_n(R_i) = (R_o/R_i)^{t_n} \bar{b}_n(R_o) \quad (2)$$

where  $R_o$  is the normal distance of the metal ion-ligand and  $R_i$  of the  $i^{\text{th}}$  ligand from the origin. The power law exponent  $t_n$  depends on the particular system being brought into use.

According to the SPM, from equations (1) and (2), the ZFS parameters  $b_2^0$ ,  $b_2^2$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$  are given by

$$b_2^0 = \sum_i [(3\cos^2\theta_i - 1)/2][R_o/R_i]^{t_2} \bar{b}_2[M,O] \quad (3)$$

$$b_2^2 = \sum_i [(3\sin^2\theta_i \cos 2\phi_i)/2][R_o/R_i]^{t_2} \bar{b}_2[M,O] \quad (4)$$

$$b_4^0 = \sum_i [(35\cos^4\theta_i - 30\cos^2\theta_i + 3)/8][R_o/R_i]^{t_4} \bar{b}_4[M,O] \quad (5)$$

$$b_4^2 = \sum_i [5/2(7\cos^2\theta_i - 1) \sin 2\theta_i \cos 2\phi_i][R_o/R_i]^{t_4} \bar{b}_4[M,O] \quad (6)$$

$$b_4^4 = \sum_i [(35\sin^4\theta_i \cos 4\phi_i)/8][R_o/R_i]^{t_4} \bar{b}_4[M,O] \quad (7)$$

### RESULT & DISCUSSION

#### $Mn^{2+}$ doped in $(Mg)_2SiO_4$

Forsterite  $(Mg)_2SiO_4$  has a crystal structure belonging to the olivine group, the most recent and complete analysis of which has been done by Birle, Gibbs, Moore and Smith<sup>[5]</sup>. This structure consists of a slightly deformed hexagonal-closed-packed array of oxygen atoms, in which one half of the octahedral voids are occupied by M atoms and one-eighth of the available tetrahedral voids by Si atoms. The unit cell is orthorhombic with  $Z=4$  and the space group is Pbnm. The M atoms are in two kinds of sites indicated by M(1) and M(2). The M(1) octahedron lies on the inversion centre and approximates a trigonal anti-prism. The M(2) octahedron, with point symmetry  $C_v$ , can not be approximated by any symmetrical polyhedron.

It has been shown that some crystals which belonging to the olivine group and contain two different metallic atoms in the molecule are ordered. For example, in montocellite,  $CaMgSiO_4$ , Mg and Ca are ordered in M(1) and M(2) sites respectively<sup>[6,7]</sup>.  $CaMnSiO_4$  is isomorphous to monticellite<sup>[8]</sup>; in lithiophilite,  $LiMnPo_4$ , Li occupies the smaller M(1) and Mn the larger M(2) sites<sup>[9]</sup>. However there is disagreement about whether system in the olivine group, which contain various concentrations of different metallic ions, show ideal substitution. Eliseev concluded that the  $(Fe_xMg_{1-x})SiO_4$  system disobeys Vegard's law and he proposed  $Fe^{2+}Mg^{2+}$  ordering<sup>[10]</sup>. Ghose<sup>[11]</sup>, noting this suggestion, predicted from ionic size considerations that  $Fe^{2+}$  ions would be preferred in the M(2) sites, whereas the  $Mg^{2+}$  would go into the M(1) sites. Independent measurements by several authors contradict these conclusions for ordering. In general it is found that the olivine system shows ideal substitutions for Mg, Mn, Fe, and Ca ions and complete references are given in the paper published by Birle et al<sup>[5]</sup>. These authors, in particular, interpreted their results as indicating disorder

of Mg and Fe atoms. However they did not exclude the possibility for minor cations such as Ca and Mn to occupy one site preferentially.

crystal structure of  $(\text{Mg})_2\text{SiO}_4$  is isomorphous to  $\text{LiMnPO}_4$  and has been investigated by S. Geller and J.L. Darand<sup>[9]</sup>. The cell constants are  $a = 6.10\text{\AA}$ ,  $b = 10.46\text{\AA}$ ,  $c = 4.744\text{\AA}$  and  $\alpha = \beta = \gamma = 90^\circ$ . The crystal structure belongs to space group  $D_{2h}^{16}$ -Pmnb. The Li and Mn ions are ordered and each is surrounded by a highly distorted octahedron of oxygens. The octahedrons of oxygens about an  $\text{Mn}^{2+}$  ion shares only one edge of a  $\text{PO}_4$  tetrahedron. Using the atomic position given for  $(\text{Mg})_2\text{SiO}_4$  with the lattice constants the values of metal – oxygen bond distances, the angle  $\theta_i$  that Metal – oxygen bond makes with the c- axis and  $\phi_i$  are calculated and given in TABLE 1.

The EPR spectrum of  $\text{Mn}^{2+}$  in  $(\text{Mg})_2\text{SiO}_4$  single crystal have been studied by A.Chatelain and R.A.Weeks<sup>[12]</sup> and the value of ZFS parameter $_2^0$  reported is  $-0.0730\text{ cm}^{-1}$ . In order to apply the superposition model for the case considered in this paper, we used the values of  $\bar{b}_2(R_o)$ ,  $R_o$  and  $t_2$  given previously in the literature. Heming and Lehman<sup>[13]</sup> determined the values of  $\bar{b}_2(R_o) \approx -0.05\text{ cm}^{-1}$  and  $t_2 = 7$ . These data were tested by Wen – Chen Zeng<sup>[14]</sup>, who studied the zero – field splitting and a local geometry for  $\text{Mn}^{2+}$  in  $\text{LiTaO}_3$ . He was able to obtain consistent result assuming the data given<sup>[8]</sup> with the reference distance being  $R_o = 0.22\text{ nm}$ <sup>[15]</sup>. We used the above given data in our analysis. As a first step we calculated the value of  $_2^0$  spin – Hamiltonian parameter for the structure data obtained from X – ray measurement done for pure  $(\text{Mg})_2\text{SiO}_4$  or S.Geller and J.L.Darand<sup>[16]</sup>. we obtained the value  $b_2^0 = -0.0730\text{ cm}^{-1}$ . It is certainly same from the value measured by experimentally<sup>[12]</sup> but with opposite sign. Therefore it is obvious that the local symmetry

around  $\text{Mn}^{2+}$  doping  $(\text{Mg})_2\text{SiO}_4$  is modified. The reason for this modification lies, as it seems, in both the same valences between  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  and different ionic radii. In order to obtain some information about local distortions of the crystal lattice around the paramagnetic  $\text{Mn}^{2+}$  ion. The convergence of our calculations were assured by imposing two conditions:

- The structure data for pure  $(\text{Mg})_2\text{SiO}_4$  were taken as a set of starting parameters.
- A minimum  $\text{Mn}^{2+}$  and oxygen distance was assumed to be  $0.22\text{ nm}$  based on the knowledge of the ionic radii of  $\text{Mn}^{2+}$  and oxygen.
- In this way we were able to fit the experimental data on  $b_2^0$  with the structural data given in (TABLE 1) and using  $\bar{b}_2 = -0.0419\text{ cm}^{-1}$ . In these calculations the charge compensation should occur due to the same charge. This may take place locally, in which case the magnetic parameters are affected and the charge compensation take place sufficiently await from the impurity such that magnetic parameters are not affected. We have made SPM calculations by taking into account the charge compensation effect of bond angles only and assuming that bond length to remain unchanged as doping with  $\text{Mn}^{2+}$  in place  $\text{Mg}^{2+}$ . Using equation (3-7) along with the values of  $\theta_i$ ,  $\phi_i$  and M - O bond distances (TABLE 1).  $R_o = 0.22\text{ nm}$ ,  $t_2 = 7$ ,  $t_4 = 10$ , the values of intrinsic parameters  $\bar{b}_2 = -0.0419\text{ cm}^{-1}$  and  $\bar{b}_4 = -0.0106\text{ cm}^{-1}$ , the second and fourth order zero field splitting parameters are calculated and given in TABLE (2). The values of ZFS parameters  $b_2^0$ ,  $b_2^2$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$  and intrinsic parameters  $_2$  and  $_4$  are very close to that of  $\text{Mn}^{2+}$  in other host single crystals<sup>[17-27]</sup> and maintain the inequality  $\bar{b}_2 \geq 4b_4$ <sup>[3,4]</sup>

TABLE 1 : Polar co-ordinates of M-O bond in single crystals

Host	M-O Bond	$R_i$ (nm)	$\theta_i$ (deg.)	$\phi_i$ (deg.)
$(\text{Mg})_2\text{SiO}_4$	Mg(1)-O(1)	2.54	114.40	90
	Mg(1)-O(2)	2.18	52.80	90
	Mg(1)-O(3)	2.07	59.46	49.38
	Mg(2)-O(4)	2.58	116.50	90
	Mg(2)-O(5)	2.12	54.47	90
	Mg(2)-O(6)	2.20	50.38	43

TABLE 2: Spin hamiltonian and intrinsic parameters obtained for  $Mn^{2+}$  in host single crystals

Host	Spin Hamiltonian Parameters in $cm^{-1}$	Intrinsic Parameters in $cm^{-1}$
(Mg) <sub>2</sub> SiO <sub>4</sub>	$b_2^0 = 0.0730$	$\bar{b}_2 = -0.0419$
	$b_2^2 = 0.0736$	$\bar{b}_2 = -0.0419$
	$b_4^0 = 0.0215$	$\bar{b}_4 = -0.0104$
	$b_4^2 = 0.0674$	$\bar{b}_4 = -0.0104$
	$b_4^4 = 0.0412$	$\bar{b}_4 = -0.0104$

## CONCLUSIONS

The ionic radii of  $Mn^{2+}$ ,  $Mg^{2+}$  are comparable, so  $Mn^{2+}$  on substituting the  $Mg^{2+}$  cation site perhaps does not cause appreciable local distortion in  $(Mg)_2SiO_4$  single crystals. Hence by using SPM theory suggested by Newman and Urban<sup>[3]</sup>, it is possible to reproduce ZFS parameters  $b_2^0$ ,  $b_2^2$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$  for  $Mn^{2+}$  doped in these single crystals at room temperature using the values of intrinsic parameters of  $\bar{b}_2$  and  $\bar{b}_4$  calculated in the present study. The superposition model analysis shows that for large values of ZFS parameters  $b_2^0$ ,  $b_2^2$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$ , intrinsic parameters  $b_2$  and  $b_4$  can be estimated with suitable errors but for small values of these spin – Hamiltonian parameters it is very difficult to predict the correct sign and magnitude. Hence we can conclude from the present study that superposition model is very useful to get information about the zero field splitting of parameter ions in host single crystals.

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