



### Superposition model analysis for the zero-field splitting of $Mn^{2+}$ in $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$

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#### ABSTRACT

The Newman superposition model has been applied to second-order zero-field splitting parameter  $b_2^0$  for  $Mn^{2+}$  in  $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$ . It is shown that calculated value of  $b_2^0$  is in agreement with the experimental value if local lattice relaxations are taken into account.

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#### KEYWORDS

Superposition model;  
Electron paramagnetic resonance;  
 $Mn^{2+}$ ;  
Zero-field splitting.

#### INTRODUCTION

Since the electron paramagnetic resonance (EPR) of  $S$ -state ions is easily detectable even at room temperature, many EPR investigations resulting in the determination of zero-field splitting (ZFS) parameters in single crystals have been reported in the literature. In most of these systems the  $S$ -state ions were coordinated by oxygen and the ZFS parameter  $b_2^0$  is quite sensitive with respect to small structure changes. The calculations of ZFS follow two approaches. In the first, which is referred to as *ab-initio* calculation, the ZFS is generally calculated using an electrostatic model of the crystal field, together with one or more of the splitting mechanisms. The second method of estimating the ZFS is by the Newman empirical superposition model (SPM) relating the fine structure constants to the actual arrangements of ligands around the impurity<sup>[1]</sup>. The SPM has proved to be a very powerful tool in probing the local structure of  $S$ -state ions in a variety of compounds<sup>[2]</sup>. In

particular, the method has been successfully applied to gain very detailed information on the lattice site and crystalline environment of  $Mn^{2+}$  in a number of systems. This paper describes the SPM analysis of the trigonal spectra of  $Mn^{2+}$  in  $Nd_2Mg_3(NO_3)_{12} \cdot 24H_2O$  (NMN) at room temperature. The EPR data have been taken from the literature<sup>[3]</sup> and the analysis is restricted to the largest ZFS parameter  $b_2^0$ .

#### SUPERPOSITION MODEL

The SPM is based on two assumptions: (i) the total ZFS experienced at an ion in a crystal is due to the close neighbour ions only and (ii) the ZFS at one ion caused by the second ion is intrinsic to that ion pair, i.e. is dependent upon exactly what ions are present and the distance between them, irrespective of the other surrounding. In the SPM, the total ZFS at the central ion is therefore given by a sum of axially symmetric contributions of the ligands  $i$  of  $MX_i$  unit only. The contri-

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butions of more distant neighbours as well as the interactions between the ligands are ignored<sup>[4]</sup>. Two sources of ZFS may be distinguished (i) contribution of the overlap and covalency and (ii) contribution of the crystal field. The former mechanism was shown to be superimposable as long as charge transfer and overlap remain small<sup>[4]</sup>. The analysis of the superimposability of the crystal field contribution to ZFS is very complicated. The SPM must hold for crystal field itself and second the spin-Hamiltonian parameter must be linear in crystal field. The analysis of Gd<sup>3+</sup> ion ZFS indicated that contribution to  $b_2^m$  nonlinear in the crystal field is indeed small and the same hold for Mn<sup>2+</sup> ion<sup>[5]</sup>. The above conclusion justifies the assumptions of SPM quite satisfactorily. However, it is very unlikely that SPM postulates hold precisely. There may be significant contribution from ions more distant than the neighbouring ligands. Zhou<sup>[6]</sup>, has shown, using point charge model, that in BaZnF<sub>4</sub>:Mn<sup>2+</sup>, contribution to ZFS from next nearest Zn<sup>2+</sup> and Ba<sup>2+</sup> ions are too small to be taken into consideration. The main limitation in applying SPM is to determine exactly the position of the ligands<sup>[1,4]</sup> EPR study is usually done on the paramagnetic ion diluted with diamagnetic host lattice. One has to use the positional parameters of the pure host lattice, but the true bond distances and distortions for the impurity ion may differ appreciably. However, the relaxation effects are likely to be smallest for pairs of host and impurity ion having the same valency and similar ionic radii.

The ZFS parameter  $b_2^0$  is written as

$$b_2^0 = \sum K_2^0(\theta_i, \varphi_i) b_2(R_i) \quad (1)$$

where  $K_2^0 = (1/2)(3 \cos^2 \theta - 1)$  is the coordination factor, the summation runs over all ligands,  $R_i$ ,  $\theta_i$ ,  $\varphi_i$  are the spherical coordinates of the  $i$ -th ligand (paramagnetic ion is placed at the origin).  $b_2(R_i)$  is a scalar quantity, called the second-order intrinsic ZFS parameter. It depends on the ionicity of ligands and is generally agreed to be approximately constant for different compounds with the same metal-ligand combination<sup>[4]</sup>. In the SPM framework it is assumed<sup>[1]</sup>, that the change of  $b_2(R_i)$  on going from a reference distance  $R_0$  to another  $R_1$  is given by the empirical power law<sup>[4]</sup>.

$$b_2(R_i) = b_2(R_0) (R_0/R_i)^{t_2}$$

where the power law exponent  $t_2$  is  $7 \pm 1$  for Mn<sup>2+</sup>.  $R_0 = 0.22$  nm is the reference distance for Mn<sup>2+</sup> sur-

rounded by six oxygens<sup>[4]</sup>. The value of  $b_2(R_0) = -0.05$  cm<sup>-1</sup> is used<sup>[4]</sup>. This value is obtained experimentally from the analysis of the spin-Hamiltonian parameter  $b_2^0$  corresponding to Mn<sup>2+</sup> placed in different lattices, all of which have same ligands (oxygen or water) and the same coordination number 6<sup>[4]</sup>.

## RESULTS AND DISCUSSION

The crystal structure of Ce<sub>2</sub>Mg<sub>3</sub>(NO<sub>3</sub>)<sub>12</sub>·24H<sub>2</sub>O (CMN) isomorphous to NMN has been studied by Zalkin *et al*<sup>[7]</sup>. The primitive cell of NMN containing one formula unit is rhombohedral. The space group is  $R\bar{3}$ . The lattice parameters in hexagonal setting are  $a = 1.1$  nm,  $c = 3.459$  nm<sup>[7]</sup>. The unit cell parameters for CMN are  $a = 1.1004$  nm,  $c = 3.4592$  nm. The rhombohedral unit cell contains three divalent ions situated at two different lattice sites. One occupies the C<sub>3i</sub> point symmetry site (site I) and the other two occupy the C<sub>3</sub> point symmetry site (site II). The divalent ions are surrounded by six water molecules forming a nearly octahedral complex. Each Nd<sup>3+</sup> is coordinated with twelve oxygen ions belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron.

The EPR of Mn<sup>2+</sup> in NMN shows the presence of two inequivalent Mn<sup>2+</sup> centres of unequal intensity. The Mn<sup>2+</sup> substitutes for Mg<sup>2+</sup> and shows the spectrum of two Mn<sup>2+</sup> complexes. It was found that the principal  $z$  axes of two [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> complexes are along the  $c$  axis and  $x$  axis is perpendicular to the  $c$  axis. The zero-field splitting parameter  $b_2^0(D)$  of Mn<sup>2+</sup> at site I is and II are  $-187.2 \times 10^{-4}$  cm<sup>-1</sup> and  $19.4 \times 10^{-4}$  cm<sup>-1</sup>, respectively<sup>[3]</sup>. Mg<sup>2+</sup> in NMN at site I is surrounded by six water molecules at a distance of 0.2058 nm. The detailed crystal structure of NMN has not been determined. However, it is expected that bond lengths of Mg<sup>2+</sup>-H<sub>2</sub>O in NMN would not be very different from that of Mg<sup>2+</sup>-H<sub>2</sub>O in CMN. In the SPM analysis the structural data of CMN is used. Mg<sup>2+</sup> in NMN at site I is surrounded by six water molecules at a distance  $R = 0.2058$  nm and at site II is surrounded by two sets of three water molecules each as nearest neighbours at distances 0.2056 nm and 0.2058 nm<sup>[7]</sup>. The angle  $\theta$  that Mg-O makes with the  $c$  axis at site I is  $54.10^\circ$  and for site II are  $54.83^\circ$  and  $123.69^\circ$ . The calculated value

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of ZFS parameter  $D$  is  $-75.7 \times 10^{-4} \text{ cm}^{-1}$  and  $104.8 \times 10^{-4} \text{ cm}^{-1}$ . The SPM predicts the correct sign. The calculated value of  $D$  for site I is smaller than the experimental value and larger for site II.

In these calculations, the assumption has been made that the crystalline structure in the vicinity of the magnetic ion is unchanged from those of the host lattice. The difference in calculated and experimental values of  $D$  may be, in principle, due to local relaxation. It has been shown that if  $R$  (metal-ligand bond distance)  $>$  normal Mn-ligand bond distance, the introduction of substitutional  $\text{Mn}^{2+}$  gives rise to an inward relaxation while the opposite occurs for  $R <$  Mn-ligand bond distance<sup>[9]</sup>. The ionic radii of  $\text{Mg}^{2+}$  and  $\text{Mn}^{2+}$  are 0.066 nm and 0.080 nm<sup>[8]</sup>. Therefore,  $\text{Mn}^{2+}$  substitution for  $\text{Mg}^{2+}$  would allow some expansion of  $\text{O}^{2-}$  octahedron around manganese. A movement of oxygen along the  $c$  axis is assumed such that Mn-oxygen bond length increases from that Mg-oxygen. This causes a change in the value of  $\theta$ . It is found that an increase of about 1.454% in bond lengths (from 0.2058 to 0.2088 nm) causes the angle  $\theta$  to change to  $53^\circ$  for site I. An increase of about 0.9% in bond length for site II causes  $\theta$  to change to  $54.33^\circ$  and  $124.33^\circ$ . These values of  $R$  and  $\theta$  leads to  $b_2^0$  values  $-187 \times 10^{-4} \text{ cm}^{-1}$  and  $19.5 \times 10^{-4} \text{ cm}^{-1}$  for site I and II respectively. A change of bond lengths of about 3%-4% is observed from EXAFS measurements in  $\text{KZnF}_3$  and  $\text{KCdF}_3$  doped with  $\text{Mn}^{2+}$ <sup>[9]</sup>.

In conclusion, with the use of the SPM, it is possible to obtain the ZFS parameter  $b_2^0$  for  $\text{Mn}^{2+}$  in host lattice studied from crystal structure data by taking into account the local relaxation effects.

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