

Investigating the zero-field splitting parameters of $3d^5$ ions (Mn^{2+} and Fe^{3+}) doped $\alpha-Al_2O_3$ crystal

Muhammed Açıkgöz*

Faculty of Arts and Sciences, Bahcesehir University, Beşiktaş 34353, İstanbul, Turkey

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ABSTRACT

The characteristics of the local environment around paramagnetic centers formed by $3d^5$ ions (Mn^{2+} and Fe^{3+}) in $\alpha-Al_2O_3$ crystal are investigated using theoretical analysis. The zero-field splitting (ZFS) parameters (ZFSPs) for Mn^{2+} and Fe^{3+} ions located at the substitutional Al^{3+} sites and the interstitial sites are modeled using several modelling approaches through superposition model (SPM) and the fourth-order perturbation theory (PT) formula. The possible structural distortions resulting from Mn^{2+} and Fe^{3+} ions are determined around Al^{3+} sites with C_{3v} symmetry and interstitial sites with D_{3d} symmetry. The results are discussed in respect to the potential of the sites to be located by $3d^5$ ions and modelling approaches.

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1. Introduction

Corundum ($\alpha-Al_2O_3$) is the thermodynamically stable morph of aluminum oxide (alumina, Al_2O_3). The single crystal form of $\alpha-Al_2O_3$ known as sapphire finds very significant role in a wide variety of important applications, i.e. [1–3]. Also it is broadly used as a catalyst for diverse processes [4]. When Al_2O_3 , as an oxide ceramic material, is doped with the transition-metal ions (Fe^{3+} , Mn^{2+} , etc.), its magnetic, electric and mechanical properties may be changed significantly [5].

In order to describe electron paramagnetic resonance (EPR) spectra of $3d^5$ paramagnetic ions and analyze its results, both second b_2^q (D and E) and fourth-rank b_4^q (a and F) zero-field splitting (ZFS) parameters (ZFSPs) have great importance in low symmetry fields.

Some different local structural distortion models around the transition ions Ni^{2+} [6], Cr^{4+} [7], Co^{2+} [8], Fe^{3+} [9], and Mn^{2+} [10] in $\alpha-Al_2O_3$ were reported. Mainly, transition ions are expected to occupy the Al^{3+} ion center as a substitutional site. Apart from [8], in [6,7,9,10], the authors considered only the Al^{3+} sites for the doped transition ions to replace. However, this substitution was considered not as an exact replacement but a displacement along threefold axis towards the empty octahedral site [11,12]. The local lattice structures around impurity Mn^{2+} [10] and Fe^{3+} [9] ions at Al^{3+} sites were previously studied using the same theoretical method, which depended on the diagonalization of the energy matrices.

In this study, different from the previous reports [9,10], we take into account the possibility of location of $3d^5$ ions not only at the substitutional Al^{3+} site but also at the interstitial site. Superposition model (SPM) and the fourth-order perturbation theory (PT) formula are employed to determine the pertinent ZFSPs for the transition metal centers located either at the Al^{3+} site or the interstitial site in $\alpha-Al_2O_3:Fe^{3+}$ and $\alpha-Al_2O_3:Mn^{2+}$. We achieve a detailed SPM analysis using reasonable ranges of the values from the relevant model parameters in literature. Theoretical predictions of both the second-rank b_2^0 and fourth-rank ZFS parameters b_4^q ($q = 0, 3$) for Mn^{2+} and Fe^{3+} ions in $\alpha-Al_2O_3$ are carried out.

2. Crystal structure

The $\alpha-Al_2O_3$ structure is on the basis of hexagonal close-packed (hcp) arrangement of oxygen anions, which represented by the α (trigonal) phase [13]. The elementary cell with $Z = 6$ includes two formula units consisting of four Al atoms and six O atoms. Even though the primitive unit cell of $\alpha-Al_2O_3$ is rhombohedral (space group $R-3c$ (No. 167)), it is commonly used to be described with the hexagonal symmetry in the literature [14]. Several hexagonal parameters have been reported for the lattice constants of $\alpha-Al_2O_3$ as tabulated in Table 1. As shown in Fig. 1, they correspond to six oxygen layers along the c -axis [13]. Structural parameters of the host lattice, bond lengths between cations–anions and the angular positions of the oxygens ligands with respect to trigonal axis, for both the Al^{3+} sites and the interstitial sites of the $\alpha-Al_2O_3$ are given in Table 2 as well. When a $3d^5$ transition ion substitutes for Al^{3+} cation, the distance of a ligand is different from

* Tel.: +90 212 3810307; fax: +90 212 3810300.

E-mail address: macikgoz@bahcesehir.edu.tr

Table 1
Lattice constants of α -Al₂O₃.

Lattice constants		Refs.
<i>a</i> (Å)	<i>c</i> (Å)	
4.785	12.991	[11]
4.759208	12.99202	[18]
4.75	12.97	[19]
4.7433	12.9763	[20]
4.7628	13.0032	[21]
4.7586	12.9897	[22]
4.7640	13.0091	[23]

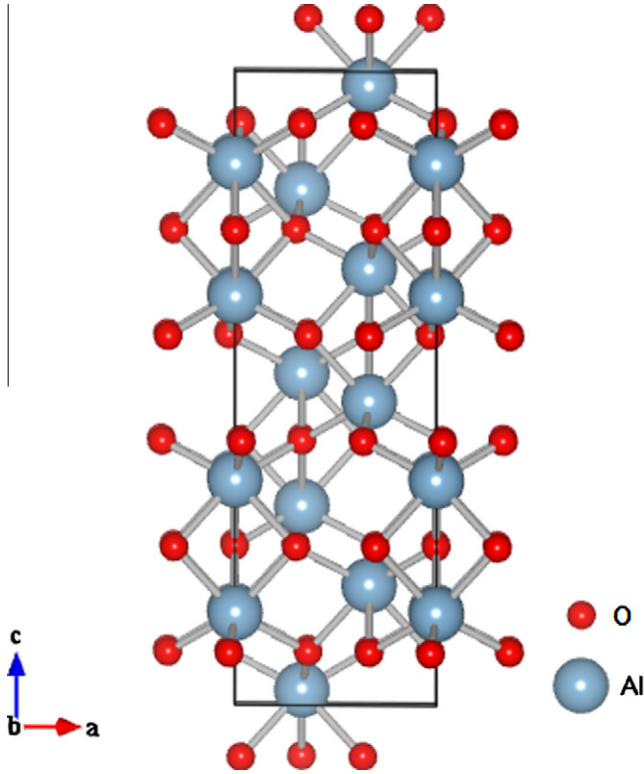


Fig. 1. Single unit cell of α -Al₂O₃ crystal. Orientation of the crystallographic axes *a*, *b*, and *c* are shown.

the cation–anion distance in the host lattice due to the fact that the radius of the substitution atom r_s differs from that of the host atom r_h . In order to take this fact into account in the calculations we reasonably approximate ligand distances using the following formula [15]: $R_i \approx R_{hi} + \frac{1}{2}(r_s - r_h)$, where R_i and R_{hi} represent the ligand and cation–anion distances, respectively. So, using the cation–anion distances in Table 2 and the ionic radii of the substitutional and host ions, $r_s(\text{Mn}^{2+}) = 0.80$, $r_s(\text{Fe}^{3+}) = 0.63$, and $r_h(\text{Al}^{3+}) = 0.54$ [16,17] (in Å), we obtain R_i values as given in Table 2.

Table 2
The structural properties of α -Al₂O₃ at room temperature.

Host structure		Ligand distances				Angular positions	
R_{h1}	R_{h2}	$R_{i1} - \text{Mn}^{2+}$	$R_{i1} - \text{Fe}^{3+}$	$R_{i2} - \text{Mn}^{2+}$	$R_{i2} - \text{Fe}^{3+}$	$\theta_1(^{\circ})$	$\theta_2(^{\circ})$
		<i>Al³⁺ site</i>					
1.966 [11]	1.857 [11]	2.096	2.011	1.987	1.902	47.64 [11]	63.06 [11]
1.975 [24]	1.853 [24]	2.105	2.020	1.983	1.898	47.74 [24]	63.12 [24]
1.970 [25]	1.860 [25]	2.100	2.015	1.990	1.905	47.56 [25]	63.50 [25]
		<i>Interstitial Site</i>					
1.978 [11]	1.978 [11]	2.108	2.023	2.108	2.023	56.85 [11]	56.85 [11]

3. Basic theory and analysis

Transition metal ions Mn²⁺ and Fe³⁺ belong to 3d⁵ electronic configuration. They are expected to substitute for Al³⁺ in α -Al₂O₃ structure. However, doped transition ions may occupy the interstitial sites, which are the center of vacant oxygen octahedron with the trigonal D_{3d} symmetry [11]. The aluminum cations occupy octahedrally coordinated sites where the local site symmetry may be approximated as C_{3v} [12]. Also, for the site symmetry of the Al sites, C₃ has been proposed in [26].

3.1. Superposition model analysis

The energy levels of the ground spin state of transition metal ions with the spin $S = 5/2$ systems at trigonal type I symmetry site (C_{3v}) in α -Al₂O₃ can be described by the spin Hamiltonian of the form [27–30]:

$$H = H_{Ze} + H_{ZFS} = g_{\perp} \mu_B (B_x S_x + B_y S_y) + g_{\parallel} \mu_B B_z S_z + \frac{1}{3} b_2^0 O_2^0 + \frac{1}{60} (b_4^0 O_4^0 + b_4^3 O_4^3) \quad (1)$$

where the first term represents the Zeeman electronic (Ze) and the second term represents the ZFS contribution consisting of ZFSPs associated with the extended Stevens operators O_k^q . We can derive the following explicit SPM expressions for the ZFSPs of a sixfold coordinated 3d⁵ ion in a ligand complex exhibiting trigonal symmetry [31,32]:

$$D_{(SPM)} = b_2^0 = \frac{3\bar{b}_2(R_0)}{2} \left[\left(\frac{R_0}{R_1} \right)^{t_2} (3 \cos^2 \theta_1 - 1) + \left(\frac{R_0}{R_2} \right)^{t_2} (3 \cos^2 \theta_2 - 1) \right] \quad (2)$$

$$b_4^0 = \frac{3\bar{b}_4(R_0)}{8} \left[\left(\frac{R_0}{R_1} \right)^{t_4} (35 \cos^4 \theta_1 - 30 \cos^2 \theta_1 + 3) + \left(\frac{R_0}{R_2} \right)^{t_4} (35 \cos^4 \theta_2 - 30 \cos^2 \theta_2 + 3) \right]$$

$$b_4^4 = 105\bar{b}_4(R_0) \left[\left(\frac{R_0}{R_1} \right)^{t_4} \sin^3 \theta_1 \cos \theta_1 \cos 3\varphi_1 + \left(\frac{R_0}{R_2} \right)^{t_4} \sin^3 \theta_2 \cos \theta_2 \cos 3\varphi_2 \right] \quad (3)$$

where R_0 is the reference distance, $\bar{b}_k(R_0)$ are the intrinsic parameters and t_k are the power law exponents. In our calculations, for both Mn²⁺ and Fe³⁺ ions, three model parameter sets including $\bar{b}_k(R_0)$ and t_k are adopted from the source data given in [33,34] and [35,36] respectively suitable for the Mn²⁺ ions and Fe³⁺ ions surrounded by oxygen ligands with coordination number 6 (Table 3). These sets

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