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Superposition model analysis on the site symmetry of Fe³⁺ ions doping spinel crystals

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Abstract. The fine-structure spin-Hamiltonian parameters b_2^0 , b_4^0 and b_4^3 of Fe³⁺ in the spinel crystals MgAl₂O₄, ZnAl₂O₄ and ZnGa₂O₄ have been analysed by means of the superposition model. This study indicates that the site symmetry for iron is C_{3v} instead of D_{3d}. Moreover, information on the lattice relaxation around this impurity has been obtained for the three host lattices.

1. Introduction

The fine-structure spin-Hamiltonian parameters b_2^0 , b_4^0 and b_4^3 of Fe³⁺ in various spinel crystals (MgAl₂O₄, ZnAl₂O₄ and ZnGa₂O₄ [1–3]) have been measured in the past using electron paramagnetic resonance (EPR) spectroscopy (table 1). In those studies it is assumed that the spinel (AB₂O₄) structure belongs to the cubic space group $Fd\bar{3}m$, as usually assigned. According to this space group, the EPR spectrum was assigned to Fe³⁺ occupying the trigonally distorted B sites (point symmetry, D_{3d} ($\bar{3}m$)) at the centre of oxygen octahedra (figure 1(a)).

However, during the last two decades the cubic space group $F\bar{4}3m$ has also been proposed for the spinel structure [4–11]. In this case the B sites have point symmetry C_{3v} ($3m$) (figure 1(b)). For instance, in the case of the Cr³⁺ ion in MgAl₂O₄ spinel, which also enters the B sites [12, 13], several workers [9–11] have suggested that chromium ions are shifted along their local trigonal (111) axis, i.e. they propose that the point group at the chromium site is C_{3v} instead of D_{3d}. This can also be expected for the Fe³⁺ ion since the inverse spinel MgFe₂O₄ presents a clear departure from $Fd\bar{3}m$ symmetry, as obtained from electron diffraction studies [4, 7]. Unfortunately, it is not possible to decide between these two alternatives from the angular dependence of the EPR spectrum of Fe³⁺ ions since the constraints imposed on the spin-Hamiltonian of an $S = \frac{5}{2}$ system are identical for D_{3d} and C_{3v} symmetries [14].

In recent years, Newman's [15, 16] superposition model has been used to relate the fine-structure spin-Hamiltonian parameters b_n^m to the coordinates of the ligand ions, i.e. to the first neighbours of the paramagnetic ion. Although controversy exists about the validity of this model for 3d⁵ ions (see the recent review in [17]), it has been used successfully to study crystal-field effects for paramagnetic ions in many systems [17]. Also, the model has proved to be useful in determining the local environment of

Table 1. Coordinates R and θ of the oxygen ions which surround octahedral B sites with D_{3d} symmetry (figure 1(a)), and fine-structure spin-Hamiltonian parameters of Fe^{3+} at room temperature in spinel crystals (with the lattice constant a_0). The b_n^m parameters are those typically used in the superposition model and are related to the other usual spin-Hamiltonian parameters as follows: $b_2^0 = 3B_2^0 = D$, $b_4^m = 60B_4^m$, $b_4^0 = -(a - F)/3$, $b_4^3 = (20/3)\sqrt{2}a$. The fine-structure b_n^m parameters are expressed in the principal defect axes system X, Y, Z shown in figure 1.

	MgAl ₂ O ₄	ZnAl ₂ O ₄	ZnGa ₂ O ₄
a_0 (Å)	8.080	8.086	8.330
$R(\text{Al, Ga-O})$ (Å)	1.928	1.915	1.988
θ (deg)	50.66	49.94	50.66
Reference	[6]	[6]	[22]
b_2^0 (cm ⁻¹)	-0.2467 ± 0.0005	-0.3402 ± 0.0002	-0.2442 ± 0.0002
b_4^0 (cm ⁻¹)	-0.0153 ± 0.0003	-0.0157 ± 0.0001	-0.0118 ± 0.0001
b_4^3 (cm ⁻¹)	0.448 ± 0.012	0.542 ± 0.004	0.419 ± 0.008
Reference	[1]	[2]	[3]

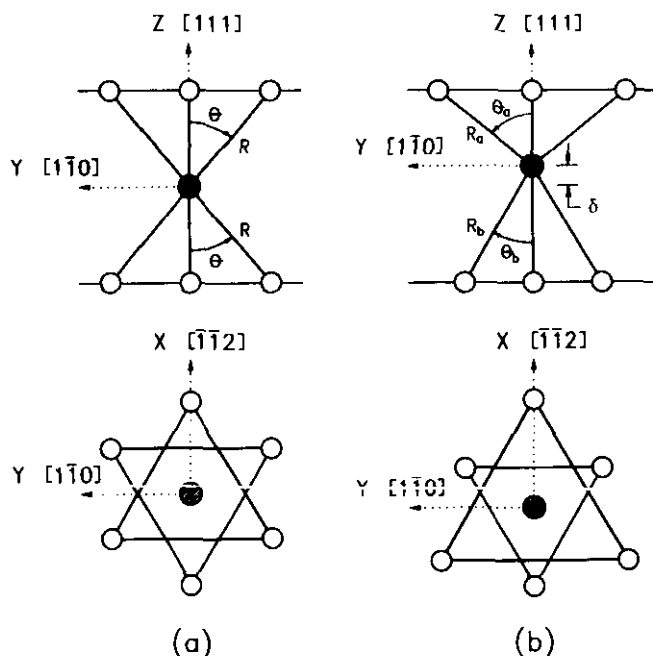


Figure 1. Arrangement of O^{2-} ions (\circ) around Fe^{3+} (\bullet) at the B sites of spinel crystals in the case of (a) D_{3d} or (b) C_{3v} symmetry.

the impurity ion when there is a set of very similar simple ions as nearby neighbours of the paramagnetic ion.

In this work, the fine-structure spin-Hamiltonian parameters b_2^0 , b_4^0 and b_4^3 for Fe^{3+} doping three spinel crystals (MgAl₂O₄, ZnAl₂O₄ and ZnGa₂O₄) have been analysed by means of the superposition model in order to ascertain which Fe^{3+} site symmetry (D_{3d} or C_{3v}) is more plausible, as well as to obtain information about the relaxation of the host lattices in the neighbourhood of the impurity.

2. Superposition model analysis for D_{3d} site symmetry

Recently, Zheng [18] has used Newman's superposition model to analyse solely the second-order parameter b_2^0 of Fe^{3+} for the same spinel crystals. In that work, D_{3d} site symmetry as well as no lattice relaxation were *a priori* assumed to obtain different values of the intrinsic parameter \bar{b}_2 . On the contrary, we think that relaxation should occur to some extent because the ionic radius of Fe^{3+} (0.64 Å) is larger than that of Al^{3+} (0.50 Å), although rather similar to that of Ga^{3+} (0.62 Å). Furthermore, we have also taken into account the fourth-order parameters b_4^0 and b_4^3 . As will be shown, they are essential in this analysis.

The superposition model provides the following equations for Fe^{3+} at B sites with D_{3d} symmetry (figure 1(a)):

$$\begin{aligned} b_2^0 &= 3\bar{b}_2(R_0)(R_0/R)^{t_2}(3\cos^2\theta - 1) \\ b_4^0 &= \frac{3}{4}\bar{b}_4(R_0)(R_0/R)^{t_4}(35\cos^4\theta - 30\cos^2\theta + 3) \\ b_4^3 &= 210\bar{b}_4(R_0)(R_0/R)^{t_4}\cos\theta\sin^3\theta. \end{aligned} \quad (1)$$

In these equations, R is the bonding length ($Fe^{3+}-O^{2-}$ distance) and θ is the angle between the Fe-O bond and the trigonal fine-structure Z axis (which is a $\langle 111 \rangle$ crystal direction), as illustrated in figure 1(a). The values of R and θ for the Al-O bond in $MgAl_2O_4$ and $ZnAl_2O_4$, and the Ga-O bond in $ZnGa_2O_4$ are shown in table 1. The intrinsic parameters $\bar{b}_2(R_0)$ and $\bar{b}_4(R_0)$ and the exponents t_2 and t_4 were given by Siegel and Müller [19] and Newman and Siegel [20] for Fe^{3+} in MgO at the reference distance $R_0 = 2.101$ Å:

$$\begin{aligned} \bar{b}_2(R_0) &= -(0.412 \pm 0.025) \text{ cm}^{-1} & t_2 &= 8 \pm 1 \\ \bar{b}_4(R_0) &= 0.00291 \text{ cm}^{-1} & t_4 &= 14. \end{aligned} \quad (2)$$

Thus, our aim is to use equations (1) with the parameters (2) and the experimental parameters b_n^m given in table 1 to obtain the relaxed values R and θ for Fe^{3+} in the three host lattices.

First, the experimental ratio b_4^3/b_4^0 provides directly the value of θ without use of $\bar{b}_4(R_0)$ and t_4 . The results are $\theta = (55.4 \pm 0.9)^\circ$, $(58.2 \pm 0.2)^\circ$ and $(58.7 \pm 0.4)^\circ$ for Fe^{3+} in $MgAl_2O_4$, $ZnAl_2O_4$ and $ZnGa_2O_4$, respectively. Here the errors are due only to the uncertainty in the experimental values of b_4^0 and b_4^3 . It is to be noted that, if D_{3d} symmetry is assumed, the experimental values of b_4^0 and b_4^3 imply a considerable relaxation of the surroundings of the Fe^{3+} ion, as seen by comparison of the above θ -values with those given in table 1 for the undistorted host lattices.

In order to estimate the distance R , we can use equations (1) for b_4^0 and b_4^3 , with $\bar{b}_4(R_0)$ and t_4 given in (2) and the values of θ obtained above. The results are $R = 1.978$ Å, 1.954 Å and 1.991 Å, respectively. These values are quite reasonable, taking into account that the ionic radius of Fe^{3+} is larger than those of Al^{3+} and Ga^{3+} . Moreover, these values for R are related between themselves in a similar way to the Al-O and Ga-O distances in the three host lattices (table 1). However, if one calculates b_2^0 with the coordinates (R, θ) obtained in this way, and $\bar{b}_2(R_0)$ and t_2 given in (2), the results ($b_2^0 = +0.068 \text{ cm}^{-1}$, $+0.372 \text{ cm}^{-1}$ and $+0.359 \text{ cm}^{-1}$, respectively) are very different from the experimental values.

On the other hand, during the last decade, different sets of values have been proposed for the intrinsic parameters and exponents. These proposals arise from

Table 2. Results for the coordinates of the six oxygen ions surrounding Fe^{3+} in spinel crystals, obtained from the superposition model for C_{3v} site symmetry (figure 1(b)) with two different sets of intrinsic parameters.

	MgAl_2O_4	ZnAl_2O_4	ZnGa_2O_4
The Newman-Siegel-Müller set (equation (2))			
R_a (Å)	1.93 ± 0.02	1.89 ± 0.01	1.92 ± 0.02
R_b (Å)	2.03 ± 0.02	2.01 ± 0.02	2.05 ± 0.02
θ_a (deg)	58.0 ± 1.4	60.0 ± 0.7	60.5 ± 0.8
θ_b (deg)	44.3 ± 1.4	39.0 ± 0.8	39.3 ± 0.9
δ (Å)	0.22 ± 0.01	0.31 ± 0.01	0.32 ± 0.01
The Yeung set (equation (3))			
R_a (Å)	1.71 ± 0.05	1.69 ± 0.03	1.72 ± 0.04
R_b (Å)	1.91 ± 0.02	1.87 ± 0.02	1.90 ± 0.03
θ_a (deg)	55.8 ± 1.2	57.4 ± 0.6	57.8 ± 0.7
θ_b (deg)	38.1 ± 1.8	31.2 ± 2.0	31.2 ± 1.7
δ (Å)	0.27 ± 0.02	0.35 ± 0.01	0.35 ± 0.01

taking into account local relaxation effects around the impurity. This implies changes in the metal-ligand interaction distances with respect to those for the undistorted host lattices. Consequently, different values for the intrinsic parameters and exponents are obtained. In particular, Yeung [21] has recently employed a lattice relaxation model to calculate the distorted positions of the ligands for Mn^{2+} and Fe^{3+} ions in cubic sites of some alkaline-earth metal oxides. The set of intrinsic parameters and exponents given by Yeung for the $\text{Fe}^{3+}-\text{O}^{2-}$ system at a typical reference distance $R_0 = 2 \text{ \AA}$ is

$$\begin{aligned} \bar{b}_2(R_0) &= -(0.1552 \pm 0.0048) \text{ cm}^{-1} & t_2 &= 16 \\ \bar{b}_4(R_0) &= (0.00099 \pm 0.00008) \text{ cm}^{-1} & t_4 &= 16 \pm 4. \end{aligned} \quad (3)$$

By using the previous procedure with this new set of parameters, the calculated distances which fit b_4^0 and b_4^3 are $R = 1.774 \text{ \AA}$, 1.755 \AA and 1.784 \AA for MgAl_2O_4 , ZnAl_2O_4 and ZnGa_2O_4 , respectively, the values for θ being the same as above. These distances are less reliable than the preceding values obtained with set (2). Moreover, the corresponding calculated values for b_2^0 ($b_2^0 = +0.108 \text{ cm}^{-1} + 0.635 \text{ cm}^{-1}$ and $+0.548 \text{ cm}^{-1}$) are also very different from the experimental values.

Therefore, we conclude that D_{3d} site symmetry for Fe^{3+} in spinel crystals does not hold, according to the superposition model, for the two sets of intrinsic parameters and exponents considered above. The alternative is to analyse the fine-structure parameters to check C_{3v} symmetry with this model.

3. Superposition model analysis for C_{3v} site symmetry

The superposition model provides the following equations for Fe^{3+} with C_{3v} symmetry (figure 1(b)):

$$\begin{aligned} b_2^0 &= \frac{3}{2} \bar{b}_2(R_0) [(R_0/R_a)^{t_2} (3 \cos^2 \theta_a - 1) + (R_0/R_b)^{t_2} (3 \cos^2 \theta_b - 1)] \\ b_4^0 &= \frac{3}{8} \bar{b}_4(R_0) [(R_0/R_a)^{t_4} (35 \cos^4 \theta_a - 30 \cos^2 \theta_a + 3) \\ &\quad + (R_0/R_b)^{t_4} (35 \cos^4 \theta_b - 30 \cos^2 \theta_b + 3)] \\ b_4^3 &= 105 \bar{b}_4(R_0) [(R_0/R_a)^{t_4} \cos \theta_a \sin^3 \theta_a + (R_0/R_b)^{t_4} \cos \theta_b \sin^3 \theta_b] \end{aligned} \quad (4)$$

where the parameters have the same meaning as in equations (1).

In this case we have to deal with four unknowns R_a , R_b (θ_a and θ_b) but only the three equations (4). However, an assumption can be made about these four coordinates, which consists in imposing the constraint that the distance between the two oxygen planes in figure 1(b) must lie in the interval going from the values for $MgAl_2O_4$ (2.445 Å) [6], $ZnAl_2O_4$ (2.465 Å) [6] and $ZnGa_2O_4$ (2.521 Å) [22] to those for $MgFe_2O_4$ (2.483 Å) [23] and $ZnFe_2O_4$ (2.554 Å) [6]. This condition is reasonable since it has been shown that the structure parameters around a magnetic ion substituting in a host crystal are between those of the host crystal and those of the crystal where the impurity ion is a proper constituent [24, 25].

The solutions of equations (4) and the imposed constraint which fit exactly the three experimental b_n^m -values are shown in table 2 for the three spinel crystals and both sets of superposition model parameters considered (equations (2) and (3)). The errors for these coordinates have been obtained from the uncertainties in the experimental b_n^m -values, and in the intrinsic parameters and exponents, as well as from the intervals considered for the distance between oxygen planes. Such results allow us to calculate the Fe^{3+} displacement δ along a $\langle 111 \rangle$ direction (figure 1(b)), which is also included in table 2.

We have also solved equations (4) by using the spin-Hamiltonian data for Fe^{3+} in $ZnGa_2O_4$ [3] measured at 4.5 K. The b_2^0 parameter is about 1.5% larger than at room temperature and the fourth-order parameters are larger by about 5%. The polar coordinates are similar to those at room temperature, but the solutions for the distances are slightly lower, indicating a reduction of about 0.5% at 4.5 K.

4. Discussion

The coordinates for C_{3v} symmetry in table 2 show an important relaxation of the impurity neighbourhood and a non-negligible displacement of the Fe^{3+} ions along their local trigonal $\langle 111 \rangle$ axis. Both sets of intrinsic parameters used here provide similar qualitative results, but the values for the distances obtained with set (2) are more reliable because of the ionic radii considerations already pointed out. The values obtained for R_a and R_b are quite similar for the three materials, although they show a modulation due to the host lattice into which iron is embedded, as observed by comparison with the crystal structure data in table 1.

Reliable information, which cannot be ascertained only from the b_2^0 values, is obtained when comparing the superposition model results for the three host crystals. In table 2 it is observed that oxygen ions around Fe^{3+} in $ZnAl_2O_4$ and $ZnGa_2O_4$ present the same angular arrangement within uncertainty, and that Fe^{3+} undergoes a similar displacement, in spite of its different b_n^m parameters in $ZnAl_2O_4$ and $ZnGa_2O_4$. However, such relaxation data are somewhat different for $MgAl_2O_4$. This result shows a strong influence of next-nearest cations for iron (zinc for both $ZnAl_2O_4$ and $ZnGa_2O_4$, and magnesium for $MgAl_2O_4$). In fact, in the perfect lattice case, next-nearest cations of B sites are directly responsible for the trigonal expansion of the oxygen octahedra around these sites [26].

On the other hand, in a recent electron nuclear double-resonance (ENDOR) study of Cr^{3+} in $MgAl_2O_4$ spinel [27] it was determined that Cr^{3+} ions have D_{3d} symmetry. Although ENDOR studies have not been performed on Fe^{3+} in $MgAl_2O_4$ spinel, we have seen in this case that the superposition model analysis predicts C_{3v}

symmetry, which is also supported by the departure from $Fd\bar{3}m$ symmetry obtained for $MgFe_2O_4$ from electron diffraction studies [4, 7]. The displacements of iron along a $\langle 111 \rangle$ trigonal axis can be accounted for on the basis that the conventional lattice site (with D_{3d} symmetry) is not a potential minimum [8]. According to Grimes [10], large impurity ions are held at the high-symmetry site by repulsive interactions, while smaller ions are able to move closer to positions of minimum energy. Therefore, it is reasonable that a displacement of Fe^{3+} takes place, as its ionic radius (0.64 Å) is smaller than that of Cr^{3+} (0.69 Å). Moreover, this argument is in agreement with the larger displacement of Fe^{3+} in $ZnAl_2O_4$ and $ZnGa_2O_4$ than in $MgAl_2O_4$ (table 2), since the lattice constant a_0 (table 1) is larger for the zinc spinels than for the magnesium spinel, providing more room for the Fe^{3+} ion to move closer to the potential minimum.

In conclusion, we have obtained that the complete set of experimental b_n^m parameters of Fe^{3+} in various spinel crystals can be accounted for by means of the superposition model considering C_{3v} site symmetry, and that this is not possible for D_{3d} symmetry. Furthermore, the relaxation around the impurity has been calculated, showing an appreciable displacement of Fe^{3+} along the $\langle 111 \rangle$ axes. The consistency of the various results in this work makes it a reliable example of the usefulness of the superposition model.

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