

Computer program superposition model-Monte Carlo (SPM-MC) and its applications in EMR studies of transition ions at low symmetry sites Fe³⁺ doped YAP crystals

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Abstract. An extension of the computer program superposition model-Monte Carlo (SPM-MC), designed for modelling of the spectroscopic and structural properties of transition ions at low symmetry sites in crystals, is presented. Special focus is put on two aspects. The first aspect concerns the effects of variation of the superposition model (SPM) parameters, i.e. the intrinsic parameters (\bar{b}_2, \bar{b}_4) and power law exponents (t_2, t_4), on the quality of fittings of experimental data and theoretical predictions. This enables to increase the reliability of the modelling results. The second aspect concerns the implications of low site symmetry on modelling of the pertinent properties. Applications of the program SPM-MC to Fe³⁺ ions at the triclinic (C_i) symmetry sites in YAlO₃ (YAP) crystals are considered.

Key words: superposition model (SPM) • spin Hamiltonian (SH) • yttrium aluminum perovskite (YAP) • YAlO₃

Introduction

The low local site symmetry exhibited by paramagnetic centres in several crystals makes interpretation of electron magnetic resonance (EMR) spectra difficult. To facilitate comparative analysis of data obtained from experimental EMR studies, i.e. the zero-field splitting (ZFS) parameters (ZFSPs) [7, 12] and the structural data, various modelling techniques have been developed [11]. One major technique is the superposition model (SPM) [4, 5]. SPM enables (i) prediction of ZFSPs based on the assumed structural distortions models for a transition metal (M) ion surrounded by the nearest neighbour n ligands (L) within ML_n complex, see, e.g. [8, 16] and (ii) verification of the structural models by comparison of SPM predictions with experimental ZFSP values.

In this paper we present an extension of the computer program superposition model-Monte Carlo (SPM-MC) [14] designed for modelling of the spectroscopic and structural properties of transition ions at low symmetry sites in crystals. This program is based on the SPM [4, 5] and the Monte Carlo (MC) method, and utilizes the crystallographic and EMR data. Two capabilities of the program are as follows. The first capability is prediction of the structure of ML_n complexes around paramagnetic transition ions at low symmetry sites in crystals, i.e. the feasible ligands' positions distorted by an impurity. This is achieved by fitting the theoretical estimates to the experimental ZFSPs obtained from EMR spectra. The second capability is estimation of the ZFSPs based on the structural data and a suitable choice of the SPM parameters, i.e. the intrinsic parameters (\bar{b}_k) and the power law exponents (t_k). The preliminary program

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SPM-MC [14] has been extended to incorporate the 4th and 6th-rank ZFS terms as well as to improve the graphical presentation of modelling results. For illustration, applications of the program SPM-MC to Fe^{3+} ions at the triclinic (C_i) symmetry sites in YAIO_3 (YAP) crystals are considered.

Spin Hamiltonian and SPM analysis of EMR spectra

Analysis of EMR spectra was performed using spin Hamiltonian (SH) suitable for transition ions [1]. For arbitrary low (triclinic) symmetry SH [7, 12] is best expressed in terms of the extended Stevens operators (ESO) O_k^q [6, 10]

$$(1) \quad H_s = \mu_B B \cdot g \cdot S + \sum B_k^q O_k^q (S_x, S_y, S_z) \\ = \mu_B B \cdot g \cdot S + \sum f_k b_k^q O_k^q$$

where g represent the Zeeman electronic tensor, B is the external magnetic field, S_i are the spin operators, and B_k^q (b_k^q) are the ZFSPs. The ‘scaling’ factors f_k in Eq. (1) are most commonly defined as [7, 12] $f_2 = 1/3$; $f_4 = 1/60$; $f_6 = 1/1260$. For proper relations between the conventional ZFSPs and B_k^q (b_k^q) in Eq. (1), see [7, 9, 12]. For Cr^{3+} ($S = 3/2$) ions only the ZFSPs with $k = 2$ are required, whereas for Fe^{3+} ($S = 5/2$) ions with $k = 2$ and 4.

Superposition model [4, 5, 8, 16] represents the ZFSPs as linear combinations of products of the intrinsic parameters (\bar{b}_k), depending on the kind of ligands and their distances from the central ion, and the coordination factors (K_k^q), depending on the angular positions of ligands. Full listing of K_k^q obtained using the transformation properties of the ESOs for arbitrary symmetry and $k = 2, 4$, and 6 may be found in [8]. The SPM calculations for the 2nd-rank ZFSPs may be carried out in two ways as described for Cr^{3+} :YAP in [15].

Program SPM-MC and its applications

Basic capabilities of the program SPM-MC and a sample interface showing illustrative input and output data have been outlined in [14]. In brief, the input data, i.e. the unit cell parameters and the number of ligands is first entered in the field ‘Structural data’ (Fig. 1 in [14]). The experimental EMR data are provided in the field ‘Experimental ZFS parameters’, whereas the rank of ZFSPs to be used for calculations is selected via ‘Rank considered’. At present, two options for the input of the model parameters, named ‘Version #1’ and ‘Ver-

sion #2’, are available based on the relations described in [14, 15]. The values of the model parameters ($A, B, n, m, t_k, \bar{b}_k, R_0$) [14, 15] are entered in the field ‘Version No. and Model Parameters’. The required range and accuracy of calculations are specified in the field ‘Computational options’. The results of calculations based on the Monte Carlo (MC) method, represented in the spherical and Cartesian coordinates together with the values of all EMR parameters, are displayed in the two upper-right windows. Additionally, the graphical 3-D (three-dimensional) representation of the ligands positions and the axis systems appears in the lower-right window. The program enables to obtain one set of the values of the ZFSPs b_k^q by clicking on the button ‘Run for one set’. All numerical output results may be saved into a text file, whereas the graphs are saved as *.bmp files.

The program has been thoroughly tested by the applications to various types of crystal structures and ML_n complexes for which reliable input and output data exist. As a practical case study, we consider yttrium aluminum perovskite YAIO_3 (YAP) single crystals containing Cr^{3+} and Fe^{3+} impurity ions. For the present SPM-MC study, we utilize the EMR measurements on Fe^{3+} :YAP and the SH analysis for the actual triclinic (C_i) site symmetry reported earlier [15].

The parameters A, B (for the 2nd-rank), and R_0 for Fe^{3+} ions, which replace Al^{3+} in YAIO_3 , were obtained from the data in [3, 13] whereas the crystallographic data from [2]. For Fe^{3+} :YAP, we adopt: $R_0 = 0.195$ nm, $n = 10$, $m = 13$, $A = -10.6$ cm^{-1} , and $B = -8.2$ cm^{-1} , as well as the SPM parameters: $\bar{b}_2 = 1.4$, $\bar{b}_4 = -0.63$ and $t_2 = 3$, $t_4 = 5$.

Using the ZFS parameters and the pertinent conversion relations provided in [9, 15] the program SPM-MC computes the feasible positions of the oxygen ligands in a given unit cell volume that yield the SPM-predicted ZFSPs consistent with the experimental ZFSPs. The numerical calculations and analysis were carried out for the complex FeO_6 in YAIO_3 . The angles θ_i and ϕ_i were varied in the range of several degrees from the starting values reported for the undistorted AlO_6 octahedron, whereas the minimum distances R_i were computed from the ionic radii. The averaged values (θ_i, ϕ_i, R_i) obtained from the program SPM-MC are listed in Table 1 together with the crystallographic data for the AlO_6 octahedron in pure crystal [14]. These values were used to construct the FeO_6 octahedron in YAIO_3 (Fig. 1). Similar analysis for Cr^{3+} :YAP will be presented elsewhere.

The effects of variation of the SPM parameters: R_0 , (\bar{b}_2, \bar{b}_4) and (t_2, t_4) on the quality of fittings of experimental data and theoretical predictions are presented in Figs. 2, 3 and 4.

Table 1. The positions of the oxygen ligands ($i = 1$ to 6) in the MO_6 octahedra in the polar coordinates

Ligand's number i		1	2	3	4	5	6
AlO_6 [2]	R_i (nm)	0.1901	0.1901	0.1910	0.1910	0.1921	0.1921
	θ_i ($^\circ$)	14.2	165.8	80.2	99.8	80.2	99.8
	ϕ_i ($^\circ$)	196.7	16.7	56.0	236.0	324.4	144.4
FeO_6	R_i (nm)	0.243	0.256	0.239	0.26	0.235	0.266
	θ_i ($^\circ$)	87.51	92.47	85.61	92.15	2.664	175.5
	ϕ_i ($^\circ$)	2.646	181.6	91.69	267.8	-1.949	181.3

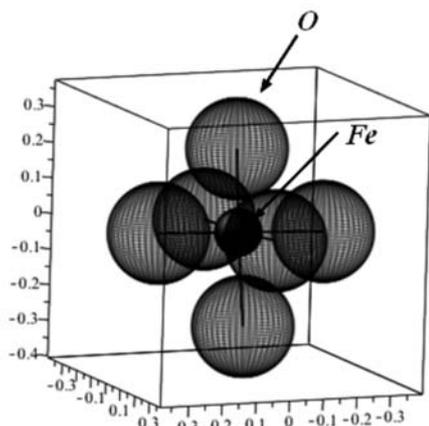


Fig. 1. The FeO₆ octahedra for the structural data listed in Table 1.

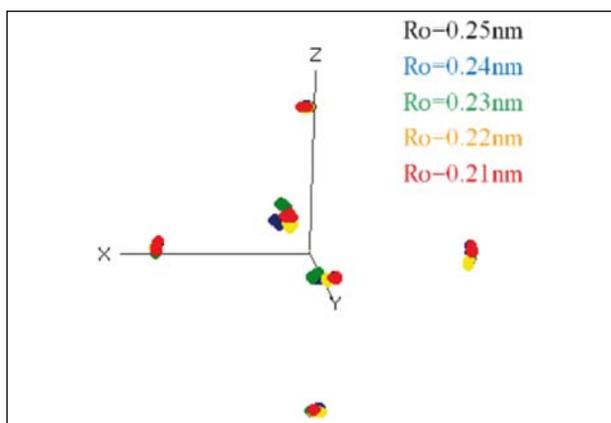


Fig. 2. Simulated FeO₆ octahedron for different R₀.

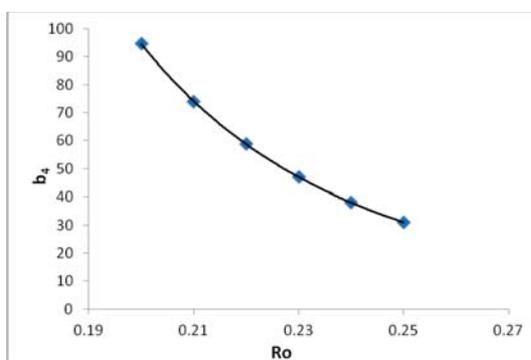


Fig. 3. Variation of the intrinsic parameter \bar{b}_4 with R₀ (the line may be approximated by equation $y = 0.0302x^{-5}$).

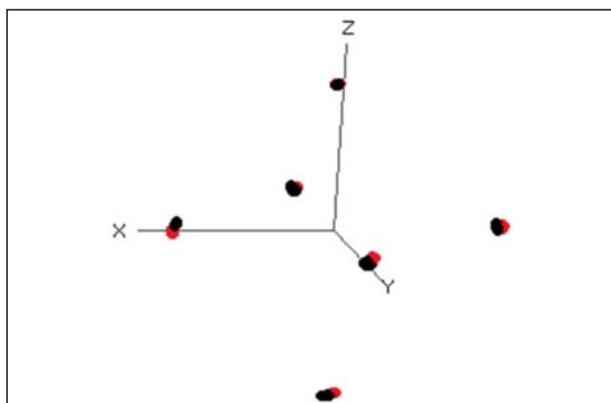


Fig. 4. Calculated FeO₆ octahedron for the version #1 (black points) and #2 (red points) using $b_2^0 = 0.0255$, $b_2^2 = -0.0244$.

Full discussion of the results in Figs. 2 to 5 will be given elsewhere. Here we mention only that the simulation of ZFSPs depicted in Fig. 5 may be utilized in various ways, e.g. (i) for checking the correctness of the parameters b_k^q determined from EMR spectra and (ii) for direct determination of the intrinsic parameter \bar{b}_2 (\bar{b}_4) based on known values of the parameters b_2^q (b_4^q).

Conclusions

The preliminary program SPM-MC [14] has been extended to incorporate the 4th and 6th-rank ZFS terms

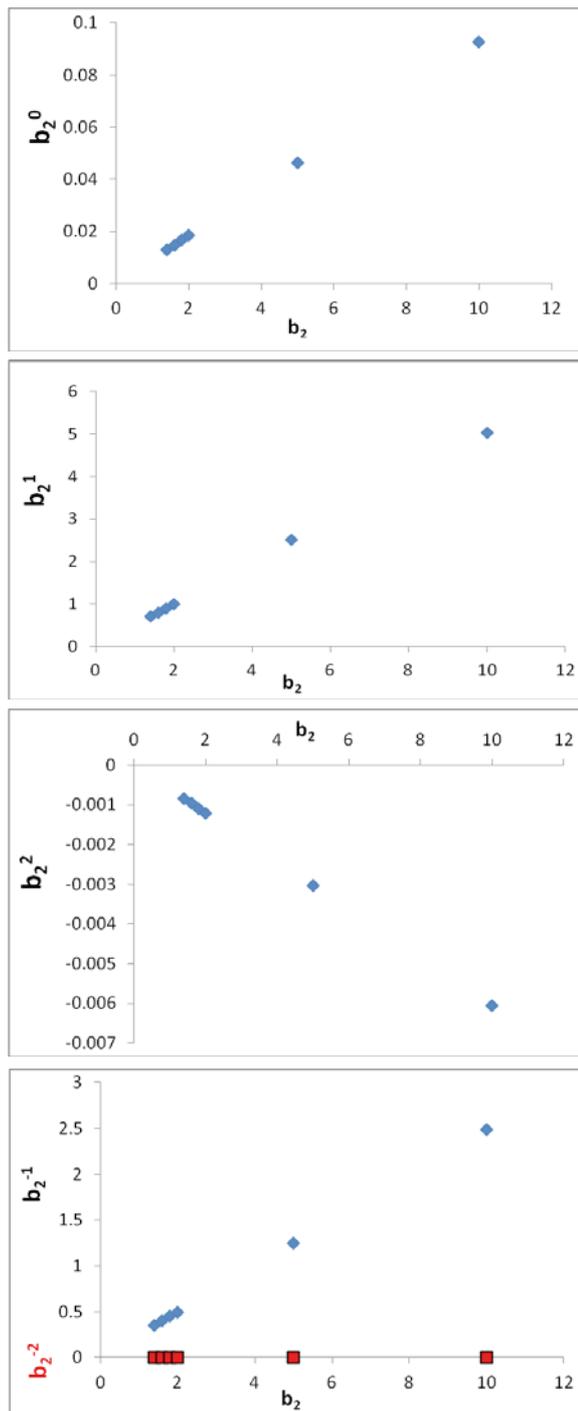


Fig. 5. Variation of the simulated ZFSPs with the intrinsic parameter \bar{b}_2 .

as well as to improve the graphical presentation of the modelling results. The effects of variation of the SPM parameters: R_0 , (\bar{b}_2, \bar{b}_4) and (t_2, t_4) on the quality of fittings of experimental data and theoretical predictions are considered in this paper. For illustration, the calculated results for FeO_6 octahedron ions obtained using both options for the model parameter input (version #1 and #2), which yield compatible results, are presented. After final testing, the program SPM-MC will be available to other researchers on collaborative basis from one of us (IS).

Preliminary results for the impurity Fe^{3+} ions occupying the Al positions in YAlO_3 are presented. SPM analysis enables prediction of the most probable model of distortions around Fe^{3+} ions in YAlO_3 . The predicted small radial distortions of the $\text{Fe}(\text{Al})\text{O}_6$ complex correlate well with the size of the ionic radii of the dopant ions.

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