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COMPUTER PROGRAM SPM-MC AND ITS APPLICATIONS IN EMR STUDIES OF TRANSITION IONS IN CRYSTALS

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Development of computer program for superposition model (SPM) calculations is reported. A novel aspect in this approach is the usage of the Monte Carlo (MC) method to predict the feasible ligands' positions by fitting the experimental electron magnetic resonance (EMR) data to theoretical estimates. The program SPM-MC may be helpful for interpretation of EMR spectra for paramagnetic ions at low (triclinic) symmetry sites and coordinated by up to 13 ligands of arbitrary type. For illustration we consider the case of chromium Cr^{3+} ions in $YAlO_3$ (YAP) crystal, which exhibits orthorhombic structure (*Pbnm* space group), whereas the site symmetry is lower than orthorhombic due to structural distortions.

INTRODUCTION

Interpretation of electron magnetic resonance (EMR) spectra is often cumbersome due to low local site symmetry exhibited by paramagnetic centers. For such cases comparative analysis of data obtained from experimental EMR studies and the structural data may be facilitated by theoretical modeling of the zero-field splitting (ZFS) parameters (ZFSPs) - for a review, see, e.g. (Rudowicz,1987; Rudowicz & Misra, 2001). Various modeling techniques for analysis and interpretation of EMR data for transition ions at low symmetry sites in crystals have recently been discussed in (Rudowicz & Gnutek, 2009). One major technique is the superposition model (SPM) (Newman & Urban, 1975; Newman & Ng, 1989), which enables prediction of ZFSPs based on the assumed structural distortions models for a transition ion (M) surrounded by the nearest neighbour *n* ligands (L) within ML_n complex, see, e.g. (Rudowicz,1987; Yeom, Chang, Choh & Rudowicz, 1994). Comparison of SPM predictions with experimental ZFSP values enables verification of the structural models and thus provides information about the local distortions around paramagnetic ions.

In this paper we present a computer program SPM-MC for modeling and analysis of the structure of ML_n complexes around paramagnetic centers, which utilizes as input the experimental data extracted from EMR spectra. This program is based on the SPM technique and may also be used for prediction of the ZFSPs based on the structural data. A novel aspect in this approach is the usage of the Monte Carlo (MC) method to predict the feasible ligands positions by fitting the experimental EMR data to theoretical estimates. The program has been tested for various types of crystal structures and ML_n complexes. Subsequently, we consider its application for SPM analysis for Cr^{3+} and Fe^{3+} ions in yttrium aluminum perovskite $YAlO_3$ (YAP) crystal. The EMR measurements of YAP single crystals containing Cr^{3+} and Fe^{3+} impurity ions as well as the spin Hamiltonian analysis of EMR spectra (carried out based on triclinic C_i) site symmetry were reported in (Stefaniuk, Rudowicz, Gnutek & Suchocki, 2009). Capabilities of the program SPM-MC and preliminary results of its application for Cr^{3+} ions in YAP are presented here.

SPIN HAMILTONIAN AND SPM ANALYSIS OF EMR SPECTRA

In this study we adopt the spin Hamiltonian (SH) notation (Rudowicz, 1987; Rudowicz & Misra, 2001), outlined in (Stefaniuk, Rudowicz, Gnutek & Suchocki, 2009). For clarity we only define the form of SH suitable for arbitrary low (triclinic) symmetry and expressed in terms of the extended Stevens operators (ESO) O_k^q defined in (Rudowicz, 1985; Rudowicz & Chung, 2004):

$$\begin{aligned} H_s &= \mu_B B\cdot g\cdot S + \sum B_k^q O_k^q (S_X, S_Y, S_Z) \\ &= \mu_B B\cdot g\cdot S + \sum f_k b_k^q O_k^q \quad . \end{aligned} \qquad (1)$$

The ZFSPs B_k^q (b_k^q) with k = 2 only are required for Cr^{3+} (S=3/2), whereas those with k = 2 and 4 for Fe^{3+} (S=5/2) ions (Rudowicz, 1987; Rudowicz & Misra, 2001; Stefaniuk, Rudowicz, Gnutek & Suchocki, 2009). For proper relations between the orthorhombic ZFSPs and the conventional ones (Rudowicz, 1987; Rudowicz & Misra, 2001) as well as pertinent

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references, the readers may refer to (Stefaniuk, Rudowicz, Gnutek & Suchocki, 2009; Rudowicz, 2000).

Low symmetry aspects observed in EMR spectra of Cr^{3+} and Fe^{3+} ions in YAP arise due to structural distortions. YAP has a distorted perovskite structure with the orthorombic centrosymmetric *Pbnm* space group (Geller & Wood, 1956; Vasylechko L., Matkovskii A., Savytski D., Suchocki A. & Wallrafen F., 1999). The YAP structure forms as a grid of tilted AlO_6 regular octahedra with Y ions occupying voids between them. The YO_8 dodecahedra are considerably distorted since the Y-O bond-length varies from 0.2284 nm to 0.2597 nm for YAP-Nd (Vasylechko *et al.*, 1999). The cation ionic radii are: $R_Y = 0.102$ nm and $R_{Al} = 0.053$ nm. The Cr^{3+} ($R_{Cr} = 0.062$ nm), Ti^{3+} ($R_{Ti} = 0.067$ nm), Mn^{4+} ($R_{Mn} = 0.053$ nm), and Fe^{3+} ($R_{Fe} = 0.065$ nm) ions are found to substitute the Al cations in YAP host (Yamaga M., Takeuchi H., Han T. J. & Henderson B., 1993; Belt *et al.*, 1974; Rakhimov R. R., Wilkerson A. L., Loutts G. B., Noginov M. A., Noginova N., Lindsay W. & Ries H. R., 1998; Yamaga M., Yosida T., Henderson B., O'Donnell K. & Date M., 1992).

Superposition model represents the ZFSPs in the form of linear combinations of products of the intrinsic parameters and coordination factors – for definitions, see, e.g. (Newman & Urban, 1975; Newman & Ng, 1989; Rudowicz, 1987; Yeom, Chang, Choh & Rudowicz, 1994). The intrinsic parameters depend only on the kind of ligands and their distances from the central ion. The coordination factors $K_k^q(\theta_i,\phi_i)$ depend only on the angular positions of ligands in the coordinate system associated with the paramagnetic ion. Full listing of $K_k^q(\theta_i,\phi_i)$ obtained using the transformation properties of the ESOs for arbitrary symmetry and k = 2, 4, and 6 has been provided in (Rudowicz, 1987). For illustration we provide the SPM expressions used for the orthorhombic ZFSPs b_k^q suitable for Cr^{3+} ions (Müller & Berlinger, 1983; Müller, Berlinger & Albers, 1985; Kuriata J., Baker J. M., Sadlowski L., Stefaniuk I. & Bodziony T., 1998):

$$b_2^0 = \sum_i \left(-A\left(\frac{R_0}{R_i}\right)^n + B\left(\frac{R_0}{R_i}\right)^m \right) \cdot \frac{1}{2}\left(3\cos^2\theta - 1\right) \tag{2}$$

$$b_2^2 = \sum_i \left(-A\left(\frac{R_0}{R_i}\right)^n + B\left(\frac{R_0}{R_i}\right)^m \right) \cdot \frac{3}{2}\left(\sin^2\theta\cos 2\phi\right)$$

and Fe^{3+} ions (Siegel & Müller, 1979; Müller & Berlinger, 1983):

$$b_2^0 = \sum_i \left((-A + B)\left(\frac{R_0}{R_i}\right)^{t_2} \right) \cdot \frac{1}{2}\left(3\cos^2\theta - 1\right) \tag{3}$$

$$b_2^2 = \sum_i \left((-A + B)\left(\frac{R_0}{R_i}\right)^{t_2} \right) \cdot \frac{3}{2}\left(\sin^2\theta\cos 2\phi\right)$$

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The program (Section 3.1) handles also the general SPM expressions for k = 2 and 4 (Newman & Ng, 1989; Rudowicz, 1987; Gnutek, Acikgoz & Rudowicz, 2010):

$$b_k^q = \sum_i \bar{b}_k(R_i)\cdot K_k^q(\theta_i,\phi_i),$$

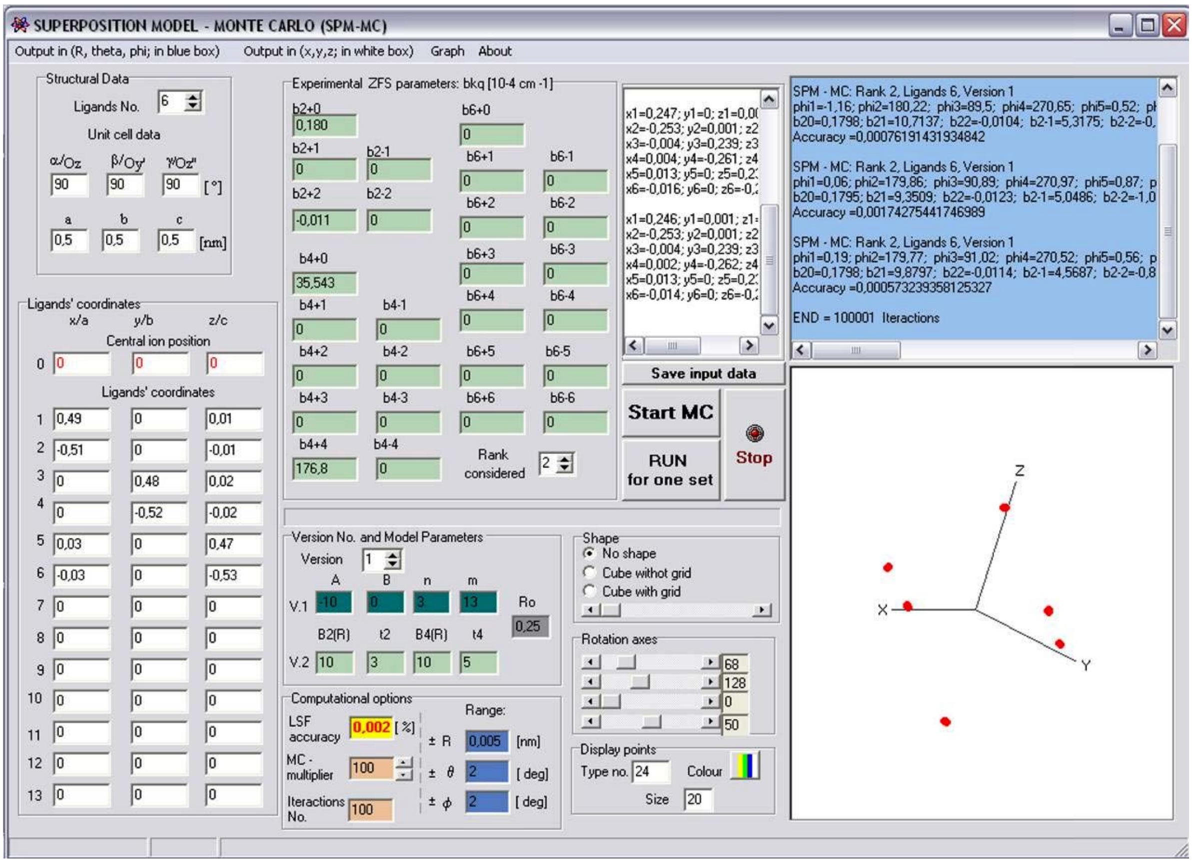
$$\bar{b}_k(R_i) = \bar{b}_k(R_0)\left(\frac{R_0}{R_i}\right)^{t_k} \tag{4}$$

In Eqs. (2)-(4) (θ, ϕ) are the polar angles, R_i - the distance between the central ion and i^{th}-ligand; the constants $A, B, n, m, t_k, \bar{b}_k$ and the reference distance R_0 depend on the kind of impurity ions and their valence (Rudowicz, 1987; Müller & Berlinger,1983; Müller, Berlinger & Albers, 1985; Kuriata *et al.*, 1998; Siegel & Müller, 1979). The SPM calculations for the 2nd-rank ZFS terms may be carried out in two ways: (i) based on the method (Müller & Berlinger, 1983) using Eqs. (2) or (3) and (ii) using general expressions, Eqs. (4), for all 5 triclinic ZFSPs. For the 4th-rank ZFS terms Eqs. (4) are used together with the selected way for the 2nd-rank ZFS terms. Development of the extended version of the program SPM-MC based on the general SPM expressions for k = 6, see, e.g. (Gnutek, Acikgoz & Rudowicz, 2010) and references therein, is in progress.

PROGRAM SPM-MC AND ITS APPLICATIONS

Program SPM-MC

Basic capabilities of the program SPM-MC are outlined below. The input data, i.e. the unit cell parameters and the number of ligands is first entered in the field 'Structural data' (see, Fig. 1). Next, in the field 'Ligands' coordinates' the positions of up to 13 distinct ligands may be entered. The experimental EMR data are provided in the field 'ZFS parameters', whereas the rank of ZFSPs to be used for calculations is selected via 'Rank considered'. The values of the model parameters ($A, B, n, m, t_k, \bar{b}_k$, R_0) are entered in the field 'Model parameters'. At present two calculation options, i.e. 'Version' #1 and #2, are available based on the relations (2) or (3) and (4), respectively. The required range and accuracy of calculations are specified in the field 'Computational options'. Finally, the program may be activated by clicking on the button 'Start MC'. 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 3D representation of the ligands positions and the axis systems appears in the lower-right window. 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.



Structural Data
Ligands No. 6
Unit cell data
α/Oz 90; β/Oy' 90; γ/Oz'' 90 [°]
a 0,5; b 0,5; c 0,5 [nm]

Ligands' coordinates

	x/a	y/b	z/c
Central ion position			
0	0	0	0
Ligands' coordinates			
1	0,49	0	0,01
2	-0,51	0	-0,01
3	0	0,48	0,02
4	0	-0,52	-0,02
5	0,03	0	0,47
6	-0,03	0	-0,53
7	0	0	0
8	0	0	0
9	0	0	0
10	0	0	0
11	0	0	0
12	0	0	0
13	0	0	0

Experimental ZFS parameters: bkq [10-4 cm -1]
b2+0 0,180
b2+1 0; b2-1 0
b2+2 -0,011; b2-2 0
b4+0 35,543
b4+1 0; b4-1 0
b4+2 0; b4-2 0
b4+3 0; b4-3 0
b4+4 176,8; b4-4 0
b6+0 0
b6+1 0; b6-1 0
b6+2 0; b6-2 0
b6+3 0; b6-3 0
b6+4 0; b6-4 0
b6+5 0; b6-5 0
b6+6 0; b6-6 0
Rank considered 2

```
x1=0,247; y1=0; z1=0,0(
x2=-0,253; y2=0,001; z2
x3=-0,004; y3=0,239; z3
x4=0,004; y4=-0,261; z4
x5=0,013; y5=0; z5=0,2:
x6=-0,016; y6=0; z6=-0,:

x1=0,246; y1=0,001; z1=
x2=-0,253; y2=0,001; z2
x3=-0,004; y3=0,239; z3
x4=0,002; y4=-0,262; z4
x5=0,013; y5=0; z5=0,2:
x6=-0,014; y6=0; z6=-0,:
```

```
SPM - MC: Rank 2, Ligands 6, Version 1
phi1=-1,16; phi2=180,22;  phi3=89,5;  phi4=270,65;  phi5=0,52;  pł
b20=0,1798; b21=10,7137;  b22=-0,0104;  b2-1=5,3175;  b2-2=-0,
Accuracy =0,00076191431934842

SPM - MC: Rank 2, Ligands 6, Version 1
phi1=0,06; phi2=179,86;  phi3=90,89;  phi4=270,97;  phi5=0,87;  p
b20=0,1795; b21=9,3509;  b22=-0,0123;  b2-1=5,0486;  b2-2=-1,0
Accuracy =0,00174275441746989

SPM - MC: Rank 2, Ligands 6, Version 1
phi1=0,19; phi2=179,77;  phi3=91,02;  phi4=270,52;  phi5=0,56;  p
b20=0,1798; b21=9,8797;  b22=-0,0114;  b2-1=4,5687;  b2-2=-0,8
Accuracy =0,000573239358125327

END = 100001  Iteractions
```

Version No. and Model Parameters
Version 1

	A	B	n	m	Ro
V.1	-10	0	3	13	0,25
	B2(R)	t2	B4(R)	t4	
V.2	10	3	10	5	

Computational options
LSF accuracy 0,002 [%]
MC - multiplier 100
Iteractions No. 100
Range:
± R 0,005 [nm]
± θ 2 [deg]
± ϕ 2 [deg]

Shape
● No shape
○ Cube withot grid
○ Cube with grid

Rotation axes
68
128
0
50

Display points
Type no. 24
Colour
Size 20

Fig. 1. Sample interface for the program SPM-MC showing illustrative input and output data.

Applications

For Cr^{3+} ions, which replace Al^{3+} in $YAlO_3$, the parameters *A, B*, and R_0 were obtained from the data in (Müller & Berlinger, 1983; Siegel & Müller, 1979), whereas the crystallographic data from (Diehl & Brandt, 1975). For illustration, we adopt the following values: $R_0 = 0.\ 195$ nm, $n = 10$, $m = 13$, $A = -10.\ 6$ cm^{-1}, and $B = -8.2$ cm^{-1}. Using the ZFS parameters and the pertinent conversion relations provided in (Stefaniuk, Rudowicz, Gnutek & Suchocki, 2009; Rudowicz, 2000) 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 $Cr(Al)O_6$ in $YAlO_3$.

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
Host AlO_6 (Diehl & Brandt,1975)	R_i [nm]	0.1901	0.1901	0.1910	0.1910	0.1921	0.1921
	θ_i [°]	14.2	165.8	80.2	99.8	80.2	99.8
	ϕ_i [°]	196.7	16.7	56.0	236.0	324.4	144.4
$Cr(Al)O_6$ our work	R_i [nm]	0.2010	0.1967	0.2041	0.2033	0.2088	0.2162
	θ_i [°]	16.3	86.5	88.1	101.2	175.6	100.1
	ϕ_i [°]	205.1	57.2	331.7	241.6	22.0	154.1

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. These values were used to construct the $Cr(Al)O_6$ octahedron in $YAlO_3$ (not shown here).

CONCLUSIONS

Computer program SPM-MC based on the superposition model (SPM) approach and incorporating the Monte Carlo (MC) method has been developed for interpretation of EMR spectra for paramagnetic ions coordinated by up to 13 ligands of arbitrary type. The extended version of this program will be suitable for low (triclinic) symmetry sites. This program enables prediction of the feasible ligands' positions by fitting the experimental EMR data to the theoretical estimates. Preliminary results for the impurity Cr^{3+} ions in $YAlO_3$ are presented. SPM analysis confirms the most probable model of distortions around Cr^{3+} ions occupying the Al positions. The predicted small radial distortions of the $Cr(Al)O_6$ complex correlate well with the size of the ionic radii of the dopant ions.

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