MODELING IN EMR SPECTROSCOPY - LOW SYMMETRY ASPECTS

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Paramagnetic centers with orthorhombic, monoclinic, and triclinic site symmetry occur often in various technologically important materials. For such centers intricate low symmetry aspects arise, which bear on meaningful interpretation of electron magnetic resonance (EMR) data and their correlation with structural data. The focus of this paper is on providing an overview of the modeling techniques for analysis and interpretation of EMR data, including the zero-field splitting parameters (ZFSPs) and *g*-factors, for transition ions at low symmetry sites in crystals worked out by us. Illustrative examples taken from our recent studies of low symmetry ion-host systems are discussed. This paper serves as a primer for experimentalists.

INTRODUCTION

Electron magnetic resonance (EMR) studies of paramagnetic centres exhibiting orthorhombic (C_{2v}, D_2, D_{2h}), monoclinic (C_2, C_S, C_{2h}) and triclinic (C_1 and C_i) site symmetry have gained renewed importance, since such centres occur often in various technologically or biologically important systems. The low symmetry aspects arising for such centres bear on meaningful interpretation of EMR data and their correlation with structural data. A review of the modeling techniques for analysis and interpretation of EMR data for transition ions at low symmetry sites in crystals has recently been published (Rudowicz & Gnutek, 2009).

This paper provides a succinct description of the modeling techniques and capabilities of the computer packages worked out by us over the years as well as a listing of most recent applications. For theoretical background underlying EMR and optical spectroscopy of transition ions, including, crystal (ligand) field (CF) theory, effective and microscopic spin Hamiltonian (SH), zero-field splitting parameters (ZFSPs) and *g*-factors, and low symmetry aspects, we refer the readers to (Rudowicz & Gnutek, 2009) and references therein. This paper provides a primer for experimentalists who wish to utilize these modeling techniques for their analysis and interpretation of low symmetry EMR data.

MODELING TECHNIQUES AND COMPUTER PROGRAMS DEALING WITH LOW SYMMETRY ZFS PARAMETERS

Modeling in EMR and optical spectroscopy is defined as (Rudowicz & Gnutek, 2009): *theoretical interpretation of experimental parameters {EPs}, measured by various techniques, in terms of more fundamental microscopic parameters {MPs}, obtainable from other independent experiments as well as comparative analysis of EP datasets from various sources*. This comprises, e.g. derivations of analytical expressions or numerical relationships: *{EPs} ∝ {MPs}*. As a reference notation for SH (Rudowicz & Gnutek, 2009) we utilize the extended Stevens (ES) operators O_k^q (Rudowicz, 1987):

$$H = H_{Ze} + H_{ZFS} = \mu_B \boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \sum B_k^q O_k^q \left(S_x, S_y, S_z \right) =$$
$$\mu_B \boldsymbol{B} \cdot \boldsymbol{g} \cdot \boldsymbol{S} + \sum f_k b_k^q O_k^q \left(S_x, S_y, S_z \right), \quad (1)$$

f_k = 1/3, 1/60, 1/1260 for k = 2, 4, and 6, respectively. For analysis and interpretation of EMR data, several modeling techniques and related computer packages described below were developed (Rudowicz & Gnutek, 2009).

Conversions, standardization, and transformations of ZFS parameters - CST package

For orthorhombic site symmetry a natural symmetry-adapted axis system is formed by three mutually perpendicular symmetry axes or directions, labeling of which as either *x*, or *y*, or *z* may be arbitrary. Different

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choices are interrelated and correspond to specific axes transformations. The intrinsic properties of orthorhombic ZFSPs are described by the rhombicity ratio: $\lambda = E/D$ (conventional) and $\lambda' = B_2^2 / B_2^0$ (ES notation). The standardization idea enables to limit the ratio: λ and λ' to the range $(0, 1/3)$ and $(0, 1)$, respectively. To this end, the six choices of labeling of the orthorhombic symmetry axes and respective transformations Si that depend on the initial value of the ratio λ (λ') were defined w.r.t. an original axis system $S1(x, y, z)$. These transformations yield different yet correlated ZFSP values, which are physically equivalent and yield identical energy levels.

Implications of orthorhombic and lower symmetry standardization for analysis and modeling of ZFSPs may be summarized as follows: (1) fitted rhombicity ratio may be obtained in various ranges; (2) large non-standard values of λ or λ' do not indicate large orthorhombic distortions in crystals, misunderstanding of this aspect may lead to wrong physical conclusions, (3) fitted and/or theoretical ZFSPs or CF parameters (CFPs) may be meaningfully compared only if expressed in the same region of the parameter space – the most convenient choice is to adopt the standard range of the ratio λ (λ'); (4) the alternative ZFSP sets (standard and non-standard) generated by orthorhombic standardization transformations may be utilized in the multiple correlated fitting technique; this technique utilizes independent fittings starting from various regions of parameter space to improve the reliability of final fitted ZFSPs (CFPs). Pertinent calculations are facilitated by the package CST, which includes modules for conversions, standardization, and transformations of ZFS and CF parameters.

Superposition model of ZFS (CF) parameters – SPM package

The superposition model (SPM) enables separation of the geometrical and physical information contained in ZFS parameters for transition ions at arbitrary symmetry sites in crystals. Hence, the H_{ZFS} (as well as H_{CF}) can be expressed as the sum of separate axially symmetric contributions from all nearest neighbour ligands of the transition metal ion. Thus for a given ML_n complex of the central metal (M) ion surrounded by n ligands (L), the ZFSPs may be parameterized, in the ES notation, as:

$$B_k^q = \sum_{i=1}^{n} \overline{B}_k(R_i) \cdot K_k^q(\theta_i, \varphi_i), \qquad (2)$$

where $(R_i, \theta_i, \varphi_i)$ are the polar coordinates of the ith ligand. The intrinsic parameters $\overline{B}_k$ represent the strength of the kth-rank ZFS contributions from ligands of a given type located at the distance R_i, whereas the coordination factors K_k^q describe the geometrical information. The distance dependence of $\overline{B}_k$'s is assumed as the adjustable power-law dependence: $\overline{B}_k(R_i) = \overline{B}_k(R_0)(R_0 / R_i)^{t_k}$, where R_0 is the reference distance, which in practice is fixed arbitrarily as the standard average M-L distance for a particular cation, whereas t_k is the power-law exponent. Assumption that the value of R_0 should be applicable for SPM calculations for a particular cation enables meaningful comparisons of the results and prediction of ZFSPs for other structurally similar ion-host systems.

SPM enables to simplify, especially for low symmetry cases, the set of adjustable parameters to a smaller set than that formed by the original ZFSPs (CFPs) for a given site symmetry. SPM is useful for modeling of ZFSPs for transition ions in undistorted hosts as well as structural distortions of ML_n complex. SPM has predictive powers - the model parameters obtained semi-empirically for one ion-host system may be used to calculate ZFSPs for the same ion in structurally similar crystals where the model parameters were not yet determined. The package SPM is suitable for arbitrary symmetry and facilitates modeling. It includes the transformations module adopted from the package CST. SPM modeling may be combined with the crystal field analysis (CFA) package to provide input CF parameters for the CFA/MSH modeling (Gnutek, Yang & Rudowicz, 2009) as well as with the techniques 3DD and PAM (see below).

Diagonalization of 2nd-rank ZFS and other terms - 3DD package

The method 3DD is based on diagonalization of a 3x3 matrix:

$$R_z(\gamma)^T \cdot R_y(\beta)^T \cdot R_z(\alpha)^T \cdot \begin{pmatrix} D_{xx} & D_{xy} & D_{xz} \\ D_{yx} & D_{yy} & D_{yz} \\ D_{zx} & D_{zy} & D_{zz} \end{pmatrix} \cdot R_z(\alpha) \cdot R_y(\beta) \cdot R_z(\gamma) = \begin{pmatrix} D_{XX} & 0 & 0 \\ 0 & D_{YY} & 0 \\ 0 & 0 & D_{ZZ} \end{pmatrix}$$

$$(3)$$

$R_z(\alpha), R_y(\beta), R_z(\gamma)$ are the rotation matrices; Euler angles are defined in the R.H.S. axis system as: (α/z, β/new y', γ / final z''). Utilizing the relations between the ZFSPs expressed in the conventional and ES notation, the package 3DD has enabled applications, for the first time, to monoclinic and triclinic CFPs. The package 3DD finds: (1) Euler angles (α, β, γ) of the principal axis system, (2) the principal values of any 2nd-rank terms, and (3) the transformed 4th- and 6th- rank parameters.

Major applications of the 3DD module concern monoclinic and triclinic symmetry cases and consist in: (i) determination of the orientation of the principal axis system of 2nd-rank ZFS 'tensors' and respective

principal values, (ii) standardization of ZFSPs for triclinic symmetry, (iii) reduction of the number of parameters for fittings, (iv) generation of alternative ZFSP sets for the multiple correlated fitting technique to increase reliability of final parameter sets. The implication of triclinic standardization of ZFSPs is the correct interpretation of the 4th- and 6th-rank ZFSPs in the principal axis system of the 2nd-rank parameters. Note that the rhombicity ratio $\lambda' = B_2^2 / B_2^0 \in (0,1)$ is not meaningful for triclinic ZFSP sets. Only after reduction of low symmetry ZFSPs to zero: $B_2^1, B_2^{-1}, B_2^{-2} = 0 \Rightarrow \alpha, \beta, \gamma \neq 0$ and bringing the 2nd-rank ZFS terms to the orthorhombic-like form, this ratio is meaningful.

Pseudo-symmetry axes method – PAM package

The pseudo-symmetry axes method (PAM) searches for the minimum of the factor ε_{sym} defined as:

$$\varepsilon_{sym} = \sum_{q \neq q(sym)} \left(B_k^q (\alpha, \beta, \gamma) / c_q^k \right)^2 \Big/ N_k \, ,$$

$$N_k = \sum_q \left(B_k^q / c_q^k \right)^2 \, . \tag{4}$$

The minimal value of ε_{sym} yields the Euler angles (α, β, γ), defined w.r.t. the original axis system, which determine a new pseudo-symmetry axis system of the 4th- and 6th-rank ZFSPs corresponding to a given higher symmetry approximation. An important feature of the ZFSPs expressed in these approximated pseudo-symmetry axes is that the higher symmetry ZFS parameters adopt maximal values, while the lower symmetry ones are reduced to nearly zero.

Applications of PAM enable to extract physical information concerning the nearest surrounding of transition ion in crystals, i.e. the local site symmetry and the nature and strength of structural distortion. For triclinic local site symmetry all ZFSPs exist in any axis system, whereas the PAM orthorhombic approximation yields the best approximated pseudo four-fold axes. Importantly, all ZFSP sets transformed by the Euler angles (α, β, γ) arising from PAM are physically equivalent, i.e. they yield the same energy levels and thus EMR spectra. Higher symmetry approximations adopted within PAM enable relating ZFSP sets with the local site symmetry of transition ion and determining the orientation of the local site symmetry axes w.r.t. the crystallographic axis system. The 4-, 3-, 2-fold axes determined in this way may be compared with the ion-ligands bonds in crystals. The quantities $S_k = \sqrt{N_k / (2k+1)}$ are rotational invariants w.r.t. any rotation of the axis system. Hence, a useful quantity is the difference between the rotational ZFSP invariants:

($S_k - S_k$*), where S_k contains the full ZFSP set, whereas S_k* contains only components with $q = q_{sym}$ (including $q = 0$) for the rank $k = 4$ and 6 representing the chosen higher symmetry PAM approximation. The quantity ($S_k - S_k$*) provides a 'measure' of the strength of low symmetry effects.

Comparison of datasets in n-D space - CF/NR package

The closeness factors C_k for a given rank k and the global ones C_{gl} reflect the 'angles' between 'vectors' in multidimensional space for the 2nd-, 4th-, and 6th-rank ZFSPs (CFPs), whereas the norms ratios R_k (R_{gl}) compare the 'magnitudes' of 'vectors'. The usefulness of the quantities C_k and R_k stems from their limiting values: $C \in \{-1, 1\}$ and R or $1/R \in \{0, 1\}$, which indicate how any two 'vectors', e.g. $\{ B_k^q \}$ and $\{ B_k^q \}$', are close (or otherwise) to each other. If these quantities tend to 1, the two sets are numerically very close, whereas if they differ significantly from 1, the two sets are disparate. The closeness factors and norms ratios facilitate quantitative comparison of compatible data sets from various sources, as well as identification of similar data sets of compatible type. These quantities are applicable also for other types of data, e.g. sets of energy levels.

APPLICATIONS

Recent applications of the packages outlined above in the area of optical spectroscopy concern reanalysis of crystal field (CF) parameter sets for several ion-host systems: Pr^{4+} in $BaPrO_3$ (Rudowicz & Gnutek, 2008a), Ho^{3+} in $HoCl_3 \cdot 6H_2O$ (Karbowiak, Rudowicz, Gnutek & Mech, 2008a), Nd^{3+} in Nd_2BaCuO_5 and Nd_2BaZnO_5 (Rudowicz, Gnutek & Karbowiak, 2007), Tm^{3+} in $TmBa_2Cu_4O_8$ and and $TmBa_2Cu_3O_{7-\delta}$ (Rudowicz, Gnutek, Lewandowska & Orłowski, 2009c), Cr^{4+} in Li_2MgSiO_4 and Nd^{3+} in β-BaB_2O_4 (Gnutek, & Rudowicz, 2008), Nd^{3+} in $[Nd(hfa)_4(H_2O)](N(C_2H_5)_4)$ (Mech, Gajek, Karbowiak & Rudowicz, 2008), Eu^{3+} and Er^{3+} in RE_2BaXO_5 (RE = rare-earth, X = Co, Cu, Ni, Zn) (Rudowicz, Gnutek & Lewandowska, 2009b), Er^{3+} and Nd^{3+} in $YAlO_3$ (Gnutek & Rudowicz, 2009), Tb^{3+} in $TbAlO_3$ (Rudowicz, Gnutek & Brik, 2009a), Er^{3+} and Tm^{3+} ions at C_2 symmetry sites in hexahydrated trichloride crystals (Karbowiak, Gnutek & Rudowicz, 2010b), Tm^{3+} ions in Tm_2BaXO_5 (X = Co, Cu, Ni) (Rudowicz, Lewandowska & Gnutek, 2010), and Tm^{3+} in $KGd(WO_4)_2$ and $KLu(WO_4)_2$, and Ho^{3+} and Er^{3+} ions in $KGd(WO_4)_2$ (Rudowicz & Gnutek, 2010).

Applications for analysis and modeling of low symmetry aspects inherent in EMR data considered so far comprise: PAM analysis for Fe^{3+} and Gd^{3+} in monoclinic zirconia (Rudowicz & Gnutek, 2008b),

EMR studies of orthorhombic to monoclinic structural phase transition in hexagonal $BaTiO_3$ doped by Fe^{3+} ions (Rudowicz, Gnutek & Budzyński, 2008), standardization of ZFSP sets for Mn^{2+} ions in various hosts exhibiting orthorhombic symmetry (Kripal, Yadav, Gnutek & Rudowicz, 2009), SPM/CFP and CFA/MSH modeling of the local structure using CF and SH parameters for the tetragonal Fe_K^{3+}-O_I^{2-} defect centre in $KTaO_3$ (Gnutek et al., 2009), and SPM analysis of low symmetry aspects inherent in the structural and ZFS parameters for Fe^{3+}: $TlInS_2$ (Gnutek, Acikgoz & Rudowicz, 2010) and $TlGaS_2$ (Acikgoz, Gnutek & Rudowicz, 2010). Currently in progress is analysis and modeling of ZFS parameters for: Cr^{3+} and Fe^{3+} ions in pure and Co^{2+}-doped $YAlO_3$, Gd^{3+} ions at triclinic sites in $CsSrCl_3$, and Fe^{3+} ions in $LiNbO_3$.

CONCLUSIONS

The modeling techniques for analysis and interpretation of EMR data for transition ions, which are especially useful for low symmetry cases, are reviewed. These modeling techniques enable deeper analysis and interpretation of the low symmetry aspects involved in the fitted and theoretical ZFSPs. The computer packages, which facilitate extracting useful structural information inherent in orthorhombic, monoclinic, and triclinic ZFSP sets, are available from the authors upon request.

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