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Review

Modeling techniques for analysis and interpretation of electron magnetic resonance (EMR) data for transition ions at low symmetry sites in crystals—A primer for experimentalists

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ABSTRACT

Electron magnetic resonance (EMR) studies of paramagnetic centers exhibiting monoclinic and triclinic local site symmetry have gained renewed importance, since such centers occur often in various technologically important materials and biological systems. The intricate low symmetry aspects, which arise for such centers, bear on meaningful interpretation of EMR data and their correlation with structural data. This review provides a primer for experimentalists who wish to utilize efficiently the modeling techniques for analysis and interpretation of EMR data for transition ions, especially ions located at low symmetry sites in crystals. This requires proper understanding of the low symmetry effects observable in EMR spectra as well as related theoretical questions concerning, e.g., (i) existence of physically equivalent zero-field splitting (ZFS) parameter sets, (ii) clear definitions of the axis systems, (iii) proper forms of spin Hamiltonians, and (iv) distinction between *apparent* and *actual* low symmetry cases. The question (i) involves consideration of the orthorhombic standardization, which provides basis for standardization of monoclinic and triclinic ZFS parameters. Thus, the aspects pertaining to orthorhombic site symmetry are also outlined. To solve other questions several modeling techniques have been utilized and related computer packages have recently been developed in our group: (1) the superposition model calculations of the zero-field splitting parameters (ZFSPs) in arbitrary symmetry, (2) the procedure for diagonalization of the 2nd-rank ZFSPs and transformation of respective 4th- and 6th-rank ZFSPs, (3) the pseudosymmetry axes method for approximation of the 4th- and 6th-rank ZFSPs to higher symmetry, and (4) the closeness factors and norm ratios for quantitative comparisons of various ZFSP sets. These modeling techniques enable deeper analysis and interpretation of the low symmetry aspects involved in the fitted and theoretical ZFSPs. The computer packages facilitate extracting useful structural information inherent in monoclinic and triclinic ZFSP sets. Illustrative examples taken from recent studies of low symmetry ion-host systems are discussed.

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1. Introduction

This review aims at providing a primer for experimentalists who wish to utilize efficiently the modeling techniques and the related computer packages developed in our group, which may facilitate analysis and interpretation of electron magnetic resonance (EMR) data for transition ions, especially ions located at orthorhombic and lower symmetry sites in crystals. For this purpose the conceptual and theoretical framework indispensable for proper understanding and interpretation of pertinent experimental and theoretical EMR data is presented in a nutshell. The modeling techniques in question are relevant for optical spectroscopy, for which the underlying concept is the crystal (or ligand) field (CF) theory [1–6], as well as magnetic measurements and EMR spectroscopy—which includes electron paramagnetic resonance (EPR), electron spin resonance (ESR), and other related techniques—for which the underlying concept is the spin Hamiltonian (SH) theory [7–11]. The major focus of this review is on the applications of the modeling techniques in the area of EMR spectroscopy. Pertinent applications in the area of optical spectroscopy would require a separate review.

The meaning of 'low' site symmetry varies in literature. Here, by low local site symmetry [12] we mean the following cases: triclinic (C_1, C_i) and monoclinic (C_2, $C_{1h}\equiv C_S$, C_{2h}) as well as the continuous rotational symmetry cases [13]: tetragonal II (C_4, S_4, C_{4h}), trigonal II (C_3, S_6), hexagonal II (C_6, C_{3h}, C_{6h}). The respective point symmetry groups (denoted below as PSG) are given in brackets. Importantly, the local site symmetry, and not the symmetry of the whole crystal given by a space group, determines the form of CF and spin Hamiltonians [1–11]. The orthorhombic site symmetry is not 'low' in the sense defined above, since the respective Hamiltonians involve only real CF and zero-field splitting (ZFS) terms. However, the peculiar features of orthorhombic Hamiltonians [14–17] bear significantly on interpretation of EMR spectra also for monoclinic and triclinic cases.

With the exception of triclinic case, there exists a unique symmetry axis **u** (or direction) for monoclinic and axial type II point symmetry groups. For these low symmetry cases, the so-called 'imaginary' CF terms (defined in Section 2.1) as well as ZFS terms (defined in Section 2.3) are admissible by group theory. These terms are responsible for the low symmetry effects observable experimentally in EMR spectra thoroughly reviewed by Pilbrow and Lowrey [18] and Roitsin [19]. Here, by 'low symmetry aspects' we mean not only the low symmetry effects [18,19] but also related theoretical questions concerning, e.g. existence of physically equivalent zero-field splitting parameter (ZFSP) sets, definitions of the axis systems, forms of spin Hamiltonians, distinction between *apparent* or *actual* low symmetry cases. These aspects and questions will be dealt with in details in a separate review [20].

This review is organized as follows. In Section 2 the scope of modeling in EMR and optical spectroscopy of transition ions as well as fundamentals of crystal field theory and spin Hamiltonian theory are briefly presented at a conceptual level. A nutshell overview of low symmetry aspects involved in EMR studies is provided in Section 3. Section 4 presents the modeling techniques utilized by us and the related computer programs developed in our group, which facilitate analysis and interpretation of EMR data for transition ions, and which are particularly useful for ions located at low symmetry sites in crystals. Illustrative examples taken from recent studies of low symmetry ion-host systems are also discussed. Summary and conclusions are provided in Section 5.

2. Modeling in EMR and optical spectroscopy of transition ions

Succinctly, modeling in EMR and optical spectroscopy may be described as: 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. Achieving these general objectives of modeling involves, among others, derivation of analytical expressions or numerical relationships amenable for computer programing, which in the case of spin Hamiltonian parameters measured by EMR may be symbolically represented as

$$\{\mathrm{EPs}\} \equiv \{B_k^q(\mathrm{ZFS}),\ g_{ij}(\mathrm{Ze})\} \propto \{\text{free ion (FI)} : B,\ C;\ \text{spin}-\text{orbit (SO)} : \lambda;\ \mathrm{CF} : B_{kq}\} \equiv \{\mathrm{MPs}\} \quad (1)$$

The physical meaning of the respective parameters used in Eq. (1) is indicated, while definitions of CF Hamiltonian and spin Hamiltonian, together with related parameters, are provided in Sections 2.1–2.3, respectively. The free ion parameters (denoted below as FIP) may be obtained from atomic spectroscopy. Fittings of the energy levels E_α for a given ion with nl^N configuration in crystal observed using optical spectroscopy techniques enable determination of the crystal field parameters (CFPs) B_{kq}. Importantly, CFPs may be related directly to the crystal structure parameters (denoted below as CSP) via various modeling techniques. Apart from the historically first, so notoriously unreliable, point charge model (PCM), theoretical models developed for modeling of CFPs comprise, e.g. superposition model (SPM), angular overlap model (AOM), exchange charge model (ECM), and simple overlap model (SOM); see, e.g. Refs. [2–6]. A succinct comparative overview of these models (denoted below by respective abbreviations) and their applications to CFPs has been provided by Porcher et al. [21]. Out of these models, only SPM approach (outlined in Section 4.2) may be used not only for modeling CFPs [5] but also for modeling ZFSPs, so independently, i.e. using different model parameters even for the same ion-host system [22]. Note that the attempts utilizing PCM to caclulate ZFSPs directly, which ocassionally appear in literature, see e.g. [23,24], seem doubtful if not invalid.

Analytical equations, symbolically represented by Eq. (1), belong to the domain of the microscopic spin Hamiltonian (MSH) theory; for review, see, Refs. [25,26]. Among others, explicit analytical equations have been derived using tensor algebra in perturbation theory (denoted below as PT) for $3d^4$ and $3d^6$ ions with spin $S = 2$ within the ^5D multiplet split by axial and orthorhombic CF [27–30]. MSH theory [27–30] has enabled prediction of the 2nd- and 4th-rank ZFSPs and the g_i components for, e.g. Cr^{2+}, Mn^{3+}, Fe^{4+} ($3d^4$), and Fe^{2+} ($3d^6$) ions in various crystals; see, Refs. [31–36] and references therein. Pertinent examples are discussed in Section 2.2. However, for more cumbersome cases that involve diagonalization of large matrices, instead of analytical equations various numerical procedures have

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