Plenary lecture

EMR OF TRansition Ions: An Overview of Theoretical Aspects Posing Problems in Interpretation of Experimental EMR Data

Czeslaw RUDOWICZ

Department of Physics and Materials Science, City University of Hong Kong, Kowloon Tong, Hong Kong SAR, China

The aim of this presentation is to bring about a better understanding of the intricacies of the spin Hamiltonian (SH) theory, which underlies Electron Magnetic Resonance (EMR - encompassing EPR, ESR and related techniques) studies. Various theoretical aspects of EMR underpinning the interpretation of experimental EMR data, are critically reviewed. A number of aspects concerning EMR studies of transition ions with the spin $S \geq 1$, which require a thorough clarification, has been identified. Examples drawn from EMR literature are presented in order to illustrate the possible consequences, i.e. serious problems and misinterpretation of experimental EMR data.

The major problems concern the following aspects: (1) inconsistent notations for the operators and the zero-field splitting (ZFS) parameters, (2) misleading nomenclature for various terms appearing in SH, (3) conceptual problems with crucial notions underlying the SH theory, (4) incorrect relations for ZFS parameters, (5) incompatible ZFS parameter sets arising from the usage of (i) non-standard or (ii) mixed axis systems for orthorhombic symmetry sites, (6) lack of full understanding of the symmetry properties of SH for monoclinic symmetry sites, (7) incorrect admission of the odd-order SH terms, (8) truncated forms of ZFS Hamiltonian, and (9) confusion concerning derivation of the microscopic SH.

Specific questions to be considered include: (a) Does EMR measure the *'crystal-field'* parameters?; (b) How is the *effective* spin related to the real electronic spin?; (c) What is the difference between the *fictitious* spin and the *effective* spin?; (d) Why do some authors measure a very large *'rhombicity'*?; (e) To what extend the ZFS parameter values listed in some review articles are reliable?; (f) Which conversion relations are correct or incorrect?

The roots of these problems, their possible consequences, and the proposed solutions will be discussed in a nutshell. It is hoped that making the spectroscopists, working in the EMR and related areas, aware of the major problems will help reducing the proliferation of the incorrect relations and misinterpretations.