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# A short review of theoretical and empirical models for characterization of optical materials doped with the transition metal and rare earth ions

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ABSTRACT

In this paper, a brief retrospective review of the main developments in crystal field theory is provided. We have examined how different crystal field models are applied to solve the problems that arise in the spectroscopy of optically active ions. Attention is focused on the joint application of crystal field and density functional theory (DFT) based models, which takes advantages of strong features of both individual approaches and allows for obtaining a complementary picture of the electronic properties of a doped crystal with impurity energy levels superimposed onto the host band structure.



## 1. Introduction

Recent decades have witnessed fast development of optical materials with fascinating applications in technologies pertaining to lasers, lighting, solar cells, non-linear optics, scintillators, bio-imaging etc. The search for custom-made new materials with outstanding characteristics for particular devices as well as attempts to improve the performance of already known and widely used materials is continued. Strategies for developing new optical materials require an understanding of the fundamental electronic properties of the optically active ions. It is the purpose of this paper to show that such understanding can be successfully obtained by using advanced theoretical models that are currently available to us. The results of such modelling can also set direction for the optimized search for new materials.

Numerous theoretical and empirical models are currently available for the description of the optical materials properties. As may be expected, those various models have their own strengths and weaknesses. Therefore, the model must be carefully understood prior to its use in the interpretation of an observation. This will be demonstrated in this paper with examples.

It is hoped that this paper will be useful for the researchers working in the fields of optical materials that are based on the transition metal and rare earth ions. We also hope that the paper can be a good starting point as an introduction to the field to help the readers to go to more advanced and longer books and papers.

## 2. A brief historical time line overview

Many years ago it has been already recognized that the introduction of a small amount of an impurity ion in a solid (very often referred to as a host) can induce dramatic changes in the optical properties of the host. For example, the color of the host can change with the appearance of additional absorption/emission bands. To understand the origin of such changes a special branch of physics, namely the crystal field theory (CFT), has been developed.

In the CFT framework, the main object of study is the embedded impurity ion, which may have unfilled *d*- or *f*-electron shell

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(usually, for optical applications the ions with the 3d and 4*f* unfilled shells are used). Usually, the concentration of such impurity ions is relatively low, in most cases not more than 1–3%, so various interactions between impurity ions can be neglected in the first approximation. The main goal is then to find how the energy levels of such impurity are split and to identify the main factors that determine the splitting pattern. If such a problem is solved, behavior of many impurities in the same host or the same impurity in many hosts can be described, understood and, hopefully, extrapolated to other materials as well.

In 1929, H. Bethe published his famous paper [1], in which he employed the group theory to analyze the splitting of the spectral terms of impurity ions in crystal fields of different symmetries. Later on, Van Vleck [2] formulated the basic ideas of the CFT, which since then has come a long way from the simplest model of point charges in a crystal lattice to more advanced and elaborated models, which take into account the differences in the electronic structure of different ions, spatial distribution of their electron densities, overlap of the wave functions of impurities and nearest neighbors etc.

Further progress in the field was made by Stevens [3] and Judd [4], who introduced the decomposition of the crystal field Hamiltonian into irreducible tensor operators. Such technique, taken together with the Wigner-Eckart theorem, allows for an easy calculation of the matrix elements of the crystal field Hamiltonian with its subsequent diagonalization and comparison of the obtained eigenvalues with the experimentally observed energy levels.

The next development in CFT is linked with the names of Tanabe and Sugano [5], who were able to calculate and plot the energy level diagrams for all $d^n$ ($n = 1–9$) configurations in ideal octahedral and tetrahedral environments (6-fold and 4-fold coordination, respectively). The so-called Tanabe-Sugano diagrams are still widely used to interpret the optical spectra of the *d* ions in crystal fields.

It should be mentioned that these theories were merely phenomenological, i.e. the number of non-zero parameters in the crystal field Hamiltonian was identified from the local symmetry of the impurity site (which often was approximated by a higher symmetry for the sake of simplicity). Then all those non-zero parameters were treated as the fitting parameters and varied until the root-mean-square deviation between the calculated and observed energy levels was minimized. However, such approach – although it can provide very good agreement between the calculated and experimental energy level schemes – employs many parameters (in some cases, more than 10), appears to be a purely mathematical model and cannot distinguish between different physical/structural mechanisms that can be responsible for the formation of optical properties of impurities in crystals.

Later on, Newman [6,7] developed the so-called superposition model of crystal field, which allows *to calculate* the crystal field parameters (CFPs) based on the coordinates of the nearest – at least – neighbors of an impurity ion. It reduces considerably the number of fitting parameters and gives a possibility of a direct quantitative analysis of the structural effects on the energy level scheme of impurities in terms of the point group symmetry of an impurity center in a crystal lattice. A recent detailed review of the superposition model can be found in Ref. [8]. Another important step forward was made by Prof. B.Z. Malkin [9] by developing the so-called exchange charge model of crystal field, which is based even on a smaller (sometimes only one!) fitting parameter. The overlap integrals between the wave functions of an impurity ion and ligands are included into the expressions for the CFPs, and by doing so the effects of the covalent bond formation between the impurities and nearest neighbors can be readily taken into account. All CFPs can be calculated from the crystal structure, the number of ions taken for such calculation is practically unlimited and can include contributions of ions from large distances, up to 100 Å, to ensure proper convergence of the oscillating sign-changing crystal lattice sums.

It is interesting that simultaneously with the development of CFT, it was recognized that interaction of the crystal lattice vibrations with impurity ions considerably affects the electronic energy levels. Moreover, interaction of the crystal lattice vibrations with the electronic energy levels of impurity appears to be essential for the formation of the luminescence/absorption spectra. The so called single-coordinate configurational coordinate model, which had been developed in this connection, was successful in explanation of the Stokes and anti-Stokes emission, thermal losses, non-radiative relaxation processes etc [10].

It should be mentioned that in the first years of the CFT development, the calculations of the energy levels splitting were often performed in the truncated (not complete) basis, without taking into account the high-lying energy levels. To some extent, it was caused by modest computational facilities (if compared with the modern ones) available at that time for the calculations. Recent development of computational facilities not only allowed to diagonalize the crystal field Hamiltonians in the complete basis sets, but to take into account the configurations of opposite parity, like $4f^{n-1}5d$, $4f^{n-1}6s$ etc [11–14] (here n is the number of the electrons in the unfilled shell), which increases enormously the rank of the crystal field matrixes.

A very important characteristic of the experimental spectra is the intensity of the absorption lines, which is of paramount importance for the lighting applications, for example. The theory of the *d-d* transition intensities is not developed so far. At the same time, intensities of the *f-f* transitions in the spectra of the rare earth ions and radiative lifetimes of the emitting levels can be successfully modelled in the framework of the Judd-Ofelt theory [15–17].

By now, large arrays of the experimental data on the optical properties of various optical materials under various conditions have been accumulated. Critical considerations of those data resulted in creation of various empirical models that give systematic overview of the luminescence and emission spectra of different optical materials, which allowed to predict certain spectroscopic characteristics in similar materials and/or their structural properties [18–23].

Another prominent direction towards progress in optical materials is related to the density functional theory (DFT) based computational techniques, which become extremely popular in the last years. However, the vast majority of the available programs are based on the one-electron approximation, whereas most of the impurity ions actively used in applications have several electrons in their unfilled electron shells. This means that it is simply impossible to take into account the multielectron effects in the DFT-based methods of calculations. Nevertheless, useful information can still be obtained by applying these methods to the calculations of various properties of optical materials, e.g. optimized structure around impurity, location of the lowest impurity state in the band gap, distribution of electron densities etc. Moreover, even in the framework of the single-electron calculations, Du [24,25] was able to identify certain trends in emission of the $Mn^{4+}$ ions based on the spin-forbidden $^2E_g \rightarrow {}^4A_{2g}$ transition, thus marking significant development of the red phosphors for the solid state lighting.

Several other papers which dealt with the analysis of the impurity multiplets can be mentioned here as well [26–31].

In the next sections we shall put main emphasis on the CFT and the first principles calculations while giving a few examples of calculations of energy levels of impurities in crystals with proper references and/or discussions.