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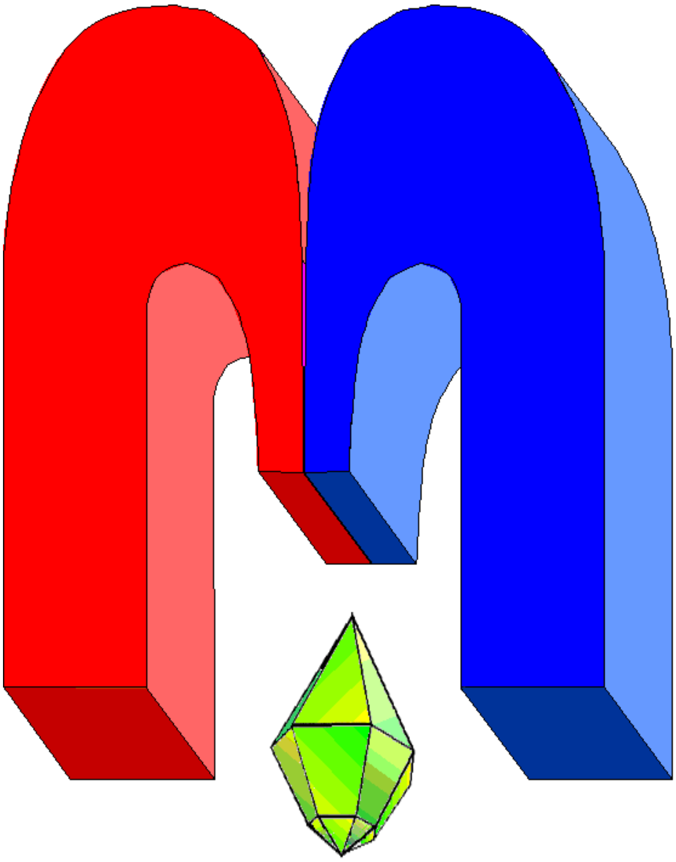

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Advances of crystal field theory and exchange charge model

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A short overview of the exchange charge model of crystal field is given. Several most important applications of the model to the calculations of the crystal field parameters, energy levels of impurity ions, parameters of the electron-vibrational interaction and transition intensities supported by the recent literature publications are discussed.

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Preface

This short article was written on occasion of the 80th anniversary of the author of *exchange charge model* (ECM), Professor Boris Zalmanovich Malkin from Kazan University. The authors of this article are honored to know Boris Zalmanovich personally. We would like to congratulate him sincerely on occasion of his jubilee, which marks his bright scientific career and profound contribution to the development of crystal field theory and deeper understanding of properties of the impurity ions in solids. Happy 80th anniversary, and a lot of joy, good health and happiness, dear Boris Zalmanovich!

1. Introduction

Fascinating variety of colors of gemstones, crystals and glasses has always admired people through the whole long history of different civilizations. Since ancient times people could tune the colors of glasses by changing their constituting elements and/or preparation conditions (of course, without having realized what was happening on the microscopic level), which resulted in a qualitative understanding of the relations between the colors and chemical composition. Still a very long way was left to be gone through until it became possible to get a quantitative description of optical properties of solids, understand the role played by the impurities – both intentional or unintentional – in the formation of those optical properties and learn how to control amount of those impurities (or defects) to produce crystals of high optical quality for numerous applications.

Development of quantum mechanics, theory of free atoms/ions spectra and group theory created all required conditions and set the stage for emerging crystal field theory (CFT) that allowed to uncover the main physical mechanisms responsible for varying optical properties of impurities and calculate their energy levels splitting.

Historically, the CFT takes its roots from 1929, when H. Bethe published his famous paper [1], in which he linked the group theory and splitting of the spectral terms of impurity ions in crystal fields (CF) of different symmetries. The next developments were made by Van Vleck [2].

One of the CFT keystones is the possibility of decomposing the CF Hamiltonian into irreducible tensor operators [3, 4] as

$$H = \sum_{p=0,2,4,6} \sum_{k=-p}^{p} B_p^k O_p^k, \tag{1}$$

where O_p^k are the linear combinations of the irreducible tensor operators acting on the angular parts of the impurity ion wave functions. The first term B_p^k stands for the crystal field parameters (CFPs). They have dimension of energy, and all information about the point symmetry of the crystal lattice site occupied by an impurity center is "hidden" in those CFPs. The term with $p = 0$ can be dropped since it just produces the overall shift of the whole energy level scheme and does not affect the relative intervals between the calculated energy levels. In the case of the impurity ions with the d-electron shell $p = 2, 4$, and in the case of the impurity ions with the f-electron shell $p = 2, 4, 6$.

If the calculations of the O_p^k matrix elements are reasonably easy to be performed, the CFPs are harder to evaluate. The first model of CFT was the so-called the point charge model (PCM), which considered only the Coulomb or point charge interaction between the impurity ion and all surrounding crystal lattice ions. The PCM equations allow to calculate the splitting of the impurity ions spectral terms. However, it has been recognized immediately that these splittings are severely underestimated and there was an urgent need in the development of more advanced models capable of taking into account more interactions between impurity ions and their neighbors, differences in the electronic structure of different ions, nature of ligands, spatial distribution of their electron densities, formation of chemical bonds between the impurities and ligands etc.

The number of non-zero CFPs in Hamiltonian (1) depends on the point symmetry around an impurity ion; the lists on those non-zero CFPs for different point groups can be found in the literature [5, 6].

There are two possible ways to get the numerical values of the CFPs. The first one is based on the non-linear fit of the calculated eigenvalues of the Hamiltonian (1) to the experimentally observed energy levels. In this case, the information about the point symmetry of the impurity ion site should be known before the calculations – this will determine which CFPs are not zero. Then the initial values of those non-zero CFPs should be taken as an input for the fitting procedure. After that the root-mean-square (rms) deviation between the calculated and experimental energy levels should be minimized by varying the CFPs values. This approach is rather mathematical; it allows to get a very small rms value (of the order of 10-20 cm^{-1} in the case of the rare earth ions, for example). There are, of course, certain disadvantages of this method. First of all, the number of fitting parameters is very large, because *all* CFPs are treated as independent parameters to be varied freely. Secondly, it may be difficult to get really *global* rms deviation minimum, since the fitting procedure may end up in one of possible *local* rms deviation minima. In addition, it may happen – especially when the CF has a rather low symmetry – that several CFPs sets result in the same or very close rms values, making them mathematically indistinguishable and hindering their physical analysis.

The second method of getting the CFPs numerical values is to *calculate* them from the known crystal structure. This approach is more physical than the previously described one because it does not imply any a priori knowledge of the point symmetry of the impurity ion site. Moreover, it would allow to decrease considerably the number of the fitting parameters and establish clear trends that link together symmetry of the crystal lattice site occupied by an impurity ion and its spectroscopic properties.

One of the CFT models that give a possibility of calculating CFPs values is the so-called superposition model developed by Newman [7,8]. With the positions of the nearest neighbors of the impurity ion, it is possible to calculate the CFPs. The superposition model if applied to the d- or f-ions employs at least four and six fitting parameters, respectively, the so-called intrinsic parameters $\overline{B_p}$ and power-law exponents t_p ($p = 2, 4$ for the d-ions and $2, 4, 6$ for the f-ions). Detailed description of this model can be found in a review chapter by Y.Y. Yeung [9].

The exchange charge model (ECM) of crystal field was developed by B.Z. Malkin [10]. It is based even on a smaller (sometimes only one!) number of fitting parameters. The model contains explicit expressions that allow to calculate all CFPs from the crystal structure without any a priori assumption about the CF symmetry. The number of ions taken for such calculations is practically unlimited and can include contributions of ions located very far from the impurity ion site, which allows to achieve convergence of the oscillating sign-changing crystal lattice sums.

The ECM has such a wide potential of applications to different systems/phenomena, that it makes it one of the most successful CF models developed so far. In the next paragraph we briefly discuss the model and its usage.

2. A short description of ECM and examples of its applications

The main ECM idea is to represent the CFPs as a sum of two terms:

$$B_p^k = B_{p,q}^k + B_{p,S}^k. \tag{2}$$

The first term $B_{p,q}^k$ describes the electrostatic interaction between an impurity ion and ions of crystal lattice, which, at this point, are considered as the point charges with the electrical charges equal to the formal valences of the ions. The second term $B_{p,S}^k$ is proportional to the overlap integrals between the wave functions of an impurity ion and ligands. Its proper calculation implies the quantum-mechanical treatment of both central ion and ligands, to distinguish between the overlap integrals corresponding to the electron orbitals with different l and m quantum numbers. This term models the effects of the covalent bond formation and considerably improves the original point charge model of CF. As a result, good agreement between the ECM calculated and experimentally observed energy levels of the impurity ions can be obtained. The analytical expressions for calculating both terms are as follows [10]:

$$B_{p,q}^k = -K_p^k (1 - \sigma_p) e^2 \langle r^p \rangle \sum_i q_i \frac{V_p^k(\theta_i, \phi_i)}{R_i^{p+1}}, \tag{3}$$

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{2l+1} \sum_i \left(G_s S_i^2(s) + G_\sigma S_i^2(\sigma) + G_\pi S_i^2(\pi) \right) \frac{V_p^k(\theta_i, \phi_i)}{R_i}. \tag{4}$$

The summation in both equations is performed over the crystal lattice ions denoted by index i with charges q_i. The spherical coordinates of the i-th ion of crystal lattice in the coordinate system, whose origin coincides with the impurity ion position, are denoted as R_i, θ_i, ϕ_i. The averaged values $\langle r^p \rangle$ of p-th power of the impurity ion electrons coordinate can be found in the literature [11]. Alternatively, they can be calculated numerically using the corresponding ions' radial wave functions. The values of the numerical factors K_p^k and expressions for the polynomials V_p^k are given in Ref. [10]. The value of l in Eq. (4) is 2 (3) for the d-(f-) electrons, respectively. The shielding constant σ_p is required only for the f ions, to take into account the screening effects of the filled $5s$ and $5p$ orbitals; it is identically zero for the d-electrons, since the d-shells are the outer ones. The overlap integrals between the d-functions of the central ion and p-, s-functions of the ligands are denoted by S_s, S_σ, S_π. In the $\langle lm|l'm'\rangle$ notation: $S_s = \langle d0|s0\rangle$, $S_\sigma = \langle d0|p0\rangle$, $S_\pi = \langle d1|p1\rangle$. These integrals can be calculated numerically; the main mathematical difficulty is that the wave functions involved are centered on different ions, and a coordinate transformation should be made to express all coordinates in one common system of reference [12]. The ECM dimensionless adjustable parameters are denoted by G_s, G_σ, G_π. Their numerical values are determined by matching the positions of three lowest in energy experimentally observed spectral bands to the corresponding calculated energy levels. Very often they can be taken equal: $G_s = G_\sigma = G_\pi = G$. In this case, the number of the ECM fitting parameters is reduced to one only, and only the lowest in energy absorption band is required to determine the value of G by adjusting the corresponding calculated energy level to its experimental counterpart. The numerical factors γ_p are $\gamma_2 = 1$, $\gamma_4 = -4/3$ for the d-electrons and $\gamma_2 = 3/2$, $\gamma_4 = 1/3$, $\gamma_6 = -3/2$ for the f-electrons [10].

Further details of the ECM and description of its application can be readily found in the relevant literature. For the sake of brevity, we just mention the main applications of the ECM, supporting those examples by the corresponding references, where the reader can get more information.

i) The first and the most obvious application of the ECM is the calculation of the CFPs with subsequent diagonalization of the CF Hamiltonian and comparison of the calculated energy levels with the experimental absorption spectra of the corresponding systems. The coordinates of the crystal ions can be obtained from the structural data; the overlap integrals between the impurity ions and ligands can be calculated numerically for different interionic distances and extrapolated then by the exponential or linear decreasing functions of distance. Remarkably, even with one ECM fitting parameter, the agreement between the calculated and observed energy levels is very good. Energy levels of both d- and f-ions can be calculated with the ECM. Examples of ECM application to the d-ions can be given as follows: $\mathrm{Li_2MgSiO_4{:}Cr^{4+}}$ and $\mathrm{Li_2ZnSiO_4{:}Cr^{4+}}$ [13], $\mathrm{MgAl_2O_4{:}Ni^{2+}}$ [14], $\mathrm{Mn^{4+}}$ in a number of red-light emitting phosphor materials such as $\mathrm{Mg_2TiO_4}$ [15], $\mathrm{Ba_2LaNbO_6}$ [16], $\mathrm{LaAlO_3}$ [17] etc. Spectra of many crystals doped with f-ions or containing them as a part of their chemical formula and crystal lattice were analyzed by B.Z. Malkin et al: $\mathrm{LiYF_4{:}Tm^{3+}}$ [18], $\mathrm{LiYF_4{:}Ho^{3+}}$ [19], $\mathrm{Pr^{4+}}$ in $\mathrm{BaPrO_3}$ [20], $\mathrm{Er^{3+}}$ in $\mathrm{(Er_xY_{1-x})_2BaNiO_5}$ [21], $\mathrm{Pr^{3+}}$ in $\mathrm{CsCdBr_3}$ [22], $\mathrm{Tb^{3+}}$ in $\mathrm{Tb_2Ti_2O_7}$ [23] etc.

ii) As an additional result of the CF diagonalization, it is possible to get the wave functions of all CF split levels, which allows to make a few more steps when analyzing the spectroscopic properties of impurities in crystals. For example, magnetic susceptibilities of trivalent lanthanides in rare earth titanate pyrochlores in Ref. [24] and in $\mathrm{NdFe_3(BO_3)_4}$ [25] were calculated in the ECM framework. Intensities of the lanthanide $5d$-$4f$ transitions were successfully modeled in Refs. [26, 27].

iii) Explicit expressions for calculating CFPs allow for finding their derivatives with respect to the Cartesian coordinates (or, finally, in terms of the normal modes), which immediately opens a way to study the phenomena related to the electron-vibrational interaction. Examples of such an analysis can be found in Refs. [28, 29].

iv) Equations for the calculations of the CFPs can be used to get the CFPs numerical values for the decreased or increased interatomic distances, which allows to model the pressure effects on the behavior of the calculated energy levels. In particular, it can be possible to find the dependence of the CF strength on the interatomic distance and estimate the bulk modulus of the host material, parameters of the electron-vibrational interaction, Stokes shift and the Jahn-Teller stabilization energy [30–32].

v) Calculations of the CFPs in the framework of the ECM allow to link the model with other CF models. Thus, the superposition model intrinsic parameters and power exponents for the Co^{2+} ions were extracted from the distance dependence of the CFPs calculated by application of the ECM equations in Ref. [33].

vi) Finally, the unified method of CFPs and energy levels calculations that is offered by the ECM allows for meaningful comparison of the CFPs sets and calculated energy levels of dopants for isostructural crystals and isoelectronic/isovalent impurity ions. The trends in variation of these properties are very important for smart search for new materials with desired characteristics.

3. Conclusions

Success of the ECM is determined by its firm physical grounds, rigorous derivation of all necessary equations and clear meaning of each term in all mathematical expressions. Wide applicability of the model, its ability to tackle complicated crystal systems and physical phenomena make the ECM to be at the top of the CF models developed and used so far.

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