Crystal-field analysis for RE^{3+} ions in laser materials: III. Energy levels for Nd^{3+} and Er^{3+} ions in LaAlO$_3$, YAlO$_3$, and LaGaO$_3$ single crystals – Combined approach to low symmetry crystal field parameters

M. Karbowiak [a,*], P. Gnutek [b], C. Rudowicz [b]

[a] Faculty of Chemistry, University of Wrocław, ul. F. Joliot-Curie 14, 50-383 Wrocław, Poland
[b] Institute of Physics, West Pomeranian University of Technology, Al. Piastów 17, 70-310 Szczecin, Poland

ABSTRACT

Crystal field (CF) analysis of energy levels for Nd^{3+} and Er^{3+} ions in LaAlO$_3$, YAlO$_3$, and LaGaO$_3$ single crystals is presented. It is shown that a combined approach comprising the ascent/descent in symmetry (ADS) method combined with superposition model (SPM) analysis can be successfully used for analysis of low-symmetry systems. The present ADS/SPM approach is less labor and time consuming as compared, e.g., with Monte-Carlo method and it also allows maintaining the relationship between the crystallographic axis system and the nominal axis systems of fitted CFP sets. For orthogallates and orthoaluminates the actual C$_s$ symmetry, resulting from distortion of perovskite structure, may be successfully approximated for both systems by the ADS chain C$_{4v}$ ↔ C$_3$ (D$_3$) ↔ C$_s$ or C$_3$ (D$_3$) ↔ C$_s$ symmetry. The possibility of using of approximated symmetries for orthogallates or orthoaluminates can be useful for interpretation of energy levels for this family of compounds of technological importance, particularly in the case when the number of available experimental energy levels is insufficient for full C$_s$ parameterization. The novel aspect of the combined ADS/SPM approach is that possible higher symmetry approximations employing also the axis systems oriented differently than for the actual symmetry are searched for, taking advantages of the transformation properties of CF parameters sets.

1. Introduction

The crystals of the general formula ABO$_3$ (A = a rare-earth (RE) ion, B = Al, Ga, Fe, Cr, or V ion) have a distorted perovskite structure: LaAlO$_3$, YAlO$_3$, and LaGaO$_3$ [1]. These crystals activated by various RE^{3+} ions are of interest due to their physical properties useful for technological applications. Rare-earth orthogallates AGaO$_3$ are considered as good substrates for making thin films of high-T_c superconductors as well as semiconductors [2,3]. Orthoaluminates AAlO$_3$ and AGaO$_3$ have favorable optical, thermal, and mechanical properties attractive for solid state laser hosts [4,5]. Spectroscopic properties of the RE^{3+}-doped ABO$_3$ crystals were investigated, e.g., for LaAlO$_3$ doped with Nd^{3+} [6], Eu^{3+} [7], Ho^{3+} [8], and Er^{3+} [9,10] as well as YAlO$_3$:Nd^{3+} [11], LuAlO$_3$:Nd^{3+} [12], and LaGaO$_3$ doped with Nd^{3+} [13–15] and Er^{3+} [16].

The theoretical modeling of energy levels of RE^{3+} ions in AAlO$_3$ and AGaO$_3$ hosts are rather scarce. Based on analysis of 117 Stark levels of NdAlO$_3$, the crystal-field parameters (CFPs) for Nd^{3+} ion at trigonal D$_3$ sites were determined [17]. CF analysis [18] for

Nd^{3+} and Er^{3+} ions at monoclinic C$_s$ sites in YAlO$_3$ was recently extended in [19]. CF modeling was also carried out for energy levels of Tb^{3+} ions at monoclinic C$_s$ sites in TbAlO$_3$ [20,21].

To evaluate the performance of the ground state terminated lasers, the thermal population of the upper and lower Stark levels must be known. Also the important parameter relevant to laser operation, i.e. the emission cross-section, must be determined, e.g., using the reciprocity method [22], which requires knowledge of the partition functions for lower and upper states. To calculate the partition functions, the knowledge of energies of all CF states arising from splitting of various multiples that are involved in laser transitions is indispensable. Often it is not possible to determine experimentally all energy levels due to restrictions on the selection rules or overlapping transitions. Hence, the CF analysis and simulations of energy levels prove especially useful, since they yield reliable fitted CF parameter sets, which may be employed for predictions of the experimentally yet unobserved levels. The calculated wave functions may be also used for predictions of, e.g., transition intensities or magnetic properties of the activator ion in a given host [19,20].

The CF analysis is also useful for appropriate assignment of observed energy levels. In Judd–Ofelt intensity analysis, the

---

* Corresponding author.
E-mail address: miroslaw.karbowiak@chem.uni.wroc.pl (M. Karbowiak).

absorption bands are integrated to obtain the transition intensities. The erroneous assignment of observed lines may result in wrong determination of multiplet barycenters and multiplet to multipet transition intensities. Examples of wrong assignments for systems under consideration are discussed in Section 3.1. Importantly, for low-symmetry systems, due to the possible existence of multiple minima on the error surface of the parameter space, reliable fittings of the energy levels are rather hard to achieve, see, e.g. [23,24]. Moreover, fitted CFP sets may correspond to a local minimum rather than to the global minimum. The Monte-Carlo method has been used in CF energy level fittings to achieve a global minimum. It employs large number of random starting parameter sets [25] in order to find all existing minima and discriminate the global minimum from the local minima. Its drawback is that different local minima may correspond to different ordering of Stark components. Hence, only for systems where the group-theoretical irreducible representations may be assigned unambiguously to each experimental energy level, the expected number of local minima is small. Otherwise numerous local minima result from fittings and selection of the global minimum requires confidence in the correctness of the ordering of Stark components used in fittings. Moreover, as in the case of any fittings based on non-directional experimental data [26], i.e. here the CF energy levels, the Monte-Carlo method does not provide information about orientation of the nominal axis system which may be assigned to a given fitted CFPs set. Besides, the Monte-Carlo fittings are labor and time consuming, since up to 100,000 calculations must be performed [20].

An alternative procedure based on prior evaluation of reliable starting CFP values seems preferable [23,24], since then the single CFP set or a few well-determined CFPs sets need to be tested. If the starting point is sufficiently well determined, fittings should converge to the global minimum. There are several methods enabling theoretical determination of starting CFPs for fittings from crystal structure, e.g., superposition model, angular overlap model, and simple overlap model – succinctly overviewed in [27], and exchange charge model defined in [28]. The combined procedure employing the ascent/descent in symmetry (ADS) method with the superposition model (SPM) analysis and/or the pseudosymmetry axes method (PAM) [23,24] could be successfully applied for analysis of low symmetry systems, thus allowing determination of reliable CFP sets. The other advantage of this approach over the Monte-Carlo method is that, since it is based on consideration of ligands' coordination around the central metal ion, it is possible to assess more easily possible higher symmetry approximations and structural relationships between different systems.

The combined ADS/SPM strategy [23] improves the overall reliability and compatibility of the CFP sets reported in literature. This strategy may be further validated by comparing the results of such calculations with those obtained by other independent methods. For this purpose we have chosen $YAlO_3$:Er^{3+} system [19]. Er^{3+} ions doped into $YAlO_3$ occupy C_s symmetry sites. A comprehensive experimental data set comprising 134 energy levels exists, and a global minimum was determined in [19] using the Monte-Carlo method for $YAlO_3$:Er^{3+}. Hence, $YAlO_3$:Er^{3+} serves as a suitable test of the ADS/SPM approach, which is the main aim of this paper. For this purpose, first we analyze the energy levels of $LaAlO_3$:Nd^{3+}, which exhibits higher point symmetry D_3 at the cation site, and then carry out CF analysis based on the ADS/SPM approach. The results show the usefulness of this approach for assignment of experimentally determined energy levels. An additional advantage is that the CFPs determined for this higher symmetry ion-host system may be used as starting in analysis for RE^{3+} ions at low symmetry sites - as a case study we use $YAlO_3$:Er^{3+}. Finally, the results obtained for $YAlO_3$:Er^{3+} are employed for analysis of experimental energy levels of Er^{3+} ion at C_s sites in $LaGaO_3$.

2. Crystallographic data and the axis systems

$LaAlO_3$, $YAlO_3$, and $LaGaO_3$ crystallize in a distorted perovskite structure and RE^{3+} ion is coordinated by 12 oxygen ions. The smallest lattice distortion occurs in $LaAlO_3$, having R-3c space group and the unit cell parameters: $a = b = 0.53647$ nm and $c = 1.31114$ nm [29]. In this crystal lanthanide ions occupy trigonal D_3 symmetry sites. $LaGaO_3$ crystallizes in the orthorhombic space group *Pbnm* with the unit cell parameters (in nm): $a = 0.5523$, $b = 0.5493$, and $c = 0.7773$ [30]. The site symmetry of La^{3+} ion is monoclinic C_s. $YAlO_3$ crystallizes in the orthorhombic structure with *Pnma* space group symmetry with the unit cell parameters (in nm): $a = 0.5180$, $b = 0.5330$, and $c = 0.7375$ [31]. The point symmetry of Y^{3+} ion is also C_s.

2.1. Axis system for LaAlO₃

For $LaAlO_3$, instead of the crystallographic axis system (CAS) (a, b, c), which is non-Cartesian, the modified CAS* (a^*, b, c) is chosen with the a^* axis perpendicular to the b–c plane and forming with the a axis the angle 30°. For CF analysis we adopt a Cartesian axis system (x, y, z) defined w.r.t. the CAS* as: ($x = a^*$, $y = b$, $z = c$). The spherical polar coordinates of ligands (R_i, θ_i, ϕ_i), $i = 1–12$, are listed in Table 1 for the polyhedron LaO_{12} in the $LaAlO_3$, whereas this polyhedron is depicted in Fig. 1a.

2.2. Axis systems for YAlO₃

For $YAlO_3$ we adopt the Cartesian axis system (x, y, z) defined w.r.t. the CAS (a, b, c) as: ($x = a$, $y = b$, $z = c$). In this axis system the z-axis is perpendicular to the σ_h plane, hence it is most suitable for the C_s symmetry of Y sites. The spherical polar coordinates of ligands (R_i, θ_i, ϕ_i), $i = 1–12$, expressed the CAS are listed in Table 2 (set $YAlO_3$-C_s) for the polyhedron YO_{12} in the $YAlO_3$, whereas this polyhedron is depicted in Fig. 1b. Rotating the axis system $YAlO_3$-C_s by Euler angles $\alpha = -1.7°$, $\beta = -54.8°$, and $\gamma = 0°$, an alternative axis system (denoted as $YAlO_3$-C_1) is obtained, in which the approximated C_3 axis is revealed – Fig. 1c. The ligands' coordinates in the axis system $YAlO_3$-C_1 are also listed in Table 2. In order to symmetrize the polyhedron YO_{12} to obtain an idealized one which exhibits an approximated higher symmetry system with C_3 axis, the average shift in the bond lengths ΔR_{av} of 0.034 nm, and the average changes in the angles $\Delta\theta_{av}$ of 4.08° and $\Delta\phi_{av}$ of 8.80°, are required. For this purpose, we have used the program SYMMOL [32] included in the computer package WinGX [33]. It turns out that to obtain more idealized polyhedron with even higher D_3 symmetry of Y site, only small additional adjustments in the ligands' positions are necessary. The ligands' coordinates for the idealized polyhedron YO_{12}

Table 1
The spherical polar coordinates (R_i, θ_i, ϕ_i) of oxygen ligands in the polyhedron LaO_{12} in $LaAlO_3$ in the CAS*.

Ligands	$LaAlO_3$-D_3		
	R_i [nm]	θ_i [°]	ϕ_i [°]
O1	0.2548	90.0	150.0
O2	0.2548	90.0	−90.0
O3	0.2548	90.0	30.0
O4	0.2817	90.0	−30
O5	0.2817	90.0	90
O6	0.2817	90.0	−150
O7	0.2682	144.6	65.0
O8	0.2682	144.6	−175.0
O9	0.2682	144.6	−55.0
O10	0.2682	35.4	−125.0
O11	0.2682	35.4	−5.0
O12	0.2682	35.4	115.0