Crystal-Field Analysis

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Comment on the Crystal-Field Analysis Underlying "Breakdown of Crystallographic Site Symmetry in Lanthanide-Doped $NaYF_4$ Crystals"

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Recently, Tu et al.[1] analyzed the high-resolution photoluminescence (PL) spectra of Eu^{3+} ions doped into cubic (α) and hexagonal (β) $NaYF_4$ and attempted to resolve the questions concerning the number of sites and local site symmetry of Eu^{3+} emitters in $NaYF_4$. The authors[1] have proposed breakdown of crystallographic site symmetry in lanthanide-doped α- and β-$NaYF_4$, which is independent of the dopant concentration. Accordingly, they asserted that the highest spectroscopically determined site symmetry of Eu^{3+} descends from the crystallographically determined O_h to C_s in α-$NaYF_4$, whereas it descends from C_{3h} to C_s in β-$NaYF_4$ upon doping. To further verify these assertions and confirm the actual local site symmetry, calculations of the Eu^{3+} energy levels have been carried out assuming the crystal-field (CF) Hamiltonian H_{CF} with C_s symmetry. The obtained small root-mean-square (rms) deviations between the calculated and experimental energy levels were considered[1] as confirmation of the validity of the asserted breakdown of the crystallographic site symmetry from O_h or C_{3h} to the spectroscopically assigned C_s. The major conclusion, quote:[1] "*Both sets of reliable CF parameters are determined for the first time, which can be used as an important reference to deduce CF and local structures of other Ln^{3+} ions in $NaYF_4$ phosphors*" has motivated us to reanalyze the respective findings. Our reanalysis of the methodology[1] reveals several evident drawbacks and pitfalls in the CF analysis,[1] which are discussed below.

Only 41 and 58 energy levels for α- and β-$NaYF_4$:Eu^{3+}, respectively, were taken into account[1] in the CF analysis. These energy levels were experimentally determined assuming that all levels may be assigned to Eu^{3+} ions located at one type of crystallographic sites. The number of energy levels of 41 or 58 is rather small for Eu^{3+} ions at low site symmetry. Out of 360 energy levels that are theoretically expected in the energy range 0 to 36000 cm^{-1}, only a few single energy levels were assigned[1] in the case of several multiplets (Supporting Information, Tables S3 and S4).[1] Moreover, although it was not explicitly specified,[1] it may be presumed that according to the commonly accepted practice the experimental levels were assigned to the nearest calculated values. Our experience based on numerous fittings shows that it is relatively easy to obtain small rms deviations when fitting for such limited sets of the experimental energy levels based on an arbitrary, to a certain extent, assignment of these levels to the calculated ones. Hence, the supposedly good agreement between the experimental and calculated energy levels proves neither the correctness of the given CF parameterization nor the assumed site symmetry of Ln^{3+} ions.

One major drawback of the CF analysis[1] is the adoption of the crystal field parameter (CFP) set obtained earlier for Eu^{3+} ions in Gd_2O_3[2] as the starting CFPs for fittings. This is unacceptable in view of the structural incompatibility of Gd_2O_3 and β-$NaYF_4$. The dopant Eu^{3+} ions are located at the C_2 symmetry sites in Gd_2O_3, whereas C_s symmetry is assumed for Eu^{3+} in both α- and β-$NaYF_4$. Although the monoclinic H_{CF} forms involve the same symbolic CFPs[3] for C_2 and C_s symmetry (Supporting Information, Equation (S3)), it does not mean that the CFP values for Eu^{3+} ions in the two hosts would be close to each other.

Comparing the respective polyhedra (Figure 1), it turns out that the ML_n complex in Gd_2O_3 is GdO_6 with the actual site symmetry C_2, whereas YF_8 in α-$NaYF_4$ with site symmetry O_h and YF_9 in β-$NaYF_4$ with site symmetry C_{3h}.

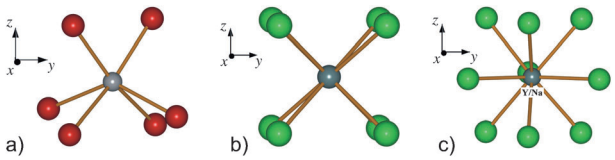

Figure 1. The coordination polyhedra: a) GdO_6 in Gd_2O_3 (space group $Ia\bar{3}$),[4] b) YF_8 in α-$NaYF_4$ (space group $Fm\bar{3}m$),[5] and c) YF_9 in β-$NaYF_4$ (space group $P6_3/m$)[6] represented in the Cartesian axis systems (*x*, *y*, *z*) with the *z*-axis taken along the highest-order symmetry. In all cases the *z*-axis is parallel to the crystallographic *c*-axis, and the *x*-axis is parallel to the crystallographic *a*-axis.

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Even if the proposed[1] distortion of the actual crystallographic site symmetry in α- and β-$NaYF_4$ from O_h and C_{3h}, respectively, to the supposedly spectroscopically observed C_s (see Ref. [1], Figure 1) is taken into account, reasonable structural compatibility between the ML_n complexes in Gd_2O_3 and α- or β-$NaYF_4$ cannot be achieved. Thus, in view of the above arguments, the CFP fittings[1] for $NaYF_4$:Eu^{3+} appear to have been carried out based on a randomly selected starting CFP set, which are not suitable for the ion-host system under investigation. Hence, in view of the structural incompatibility, the adoption[1] for $NaYF_4$:Eu^{3+} of the starting CFPs suitable for Gd_2O_3:Eu^{3+} diminishes significantly the reliability of the fitted CFPs. Consequently, the fitted CFPs in Ref. [1], Table 1 cannot be considered as valid and properly fine-tuned final CFPs. This assertion is supported by the following observations arising from analysis of the numerical results.[1]

First, the starting CFP values (Ref. [2], Table 2)[2] differ significantly from the fitted ones[1] (Supporting Information, Table S1). In general, this indicates that the starting CFPs were poorly determined for the system in question. Moreover, in their four-stage fitting strategies the authors have resorted at the third stage to the following procedure, quote:[1] "*relocate or reassign those uncertain CF levels that resulted in anomalously large root-mean-square (rms) deviation of the fit, and simultaneously vary the parameters to fit all CF levels we observed.*" Only then the energy levels in α- or β-$NaYF_4$:Eu^{3+} were fitted to "*all the freely varied parameters*". To assess reliability of such procedure, it must be kept in mind that each assignment of the experimental energy levels to the calculated ones yields specific local minimum (or minima). The above quote indicates that the assignments[1] were, to a large extent, arbitrary, as the only criterion employed was minimalization of the rms deviations between the calculated and experimental energy levels. However, achieving the lowest rms value does not necessarily guarantee reaching the global minimum. Importantly, for other energy levels assignments, different CFP values could be obtained with comparable or even smaller rms deviations. The procedure employed by Tu et al.[1] has evidently been based on optimalization of the CFPs with respect to the experimental energy levels as well as combined with simultaneous identification in the spectra of the experimental levels and their assignment to the calculated ones in such a way as to minimize the rms values. Such procedure is acceptably reliable only if the CFP space of feasible solutions is restricted by adoption of physically most suitable starting CFP values. Otherwise, in the case of lack of such starting CFP values, fittings carried out in an unrestricted CFP space would most likely yield unreliable fitted CFPs. Alternative method to adopt in such cases, which would enable reaching the best global minimum, is the Monte Carlo method[7,8] that requires tremendously large number of fittings. This method enables determination of all possible local minima that exist on the error surface of the parameter space, simultaneously for different feasible assignments, that is, ordering of Stark component within given LSJ multiplet. Evidently, the procedure[1] does not satisfy the above criteria, since the starting CFPs were not well determined as well as no method to locate all possible local minima has been used. Thus, instead of a global minimum, the fitted CFPs[1] may likely represent at worst a false minimum, or at best one specific local minimum out of a large number of such minima.

Second, the same starting CFPs were used for energy levels calculations for Eu^{3+} ions in cubic α-$NaYF_4$ (CN = 8) and hexagonal β-$NaYF_4$ (CN = 9). This procedure would be justified only if the structural compatibility would be obtained in both cases as a result of the distortions induced by Ln^{3+}-doping. As H_{CF} parameterizes the effect of the electric field due to the surrounding n ligands (L) acting on a paramagnetic ion (M) in a given ML_n complex in crystal or in a molecule, the angular part of the CF interaction is related to the symmetry of the ML_n complex, that is, with the spatial distribution of ligands around the central ion. To ensure compatibility of CFPs for two complexes, these complexes must be structurally similar, that is, the same number of ligands should be distributed around the central ion in geometrically similar arrangements. This means that, in the spherical polar coordinates (θ, ϕ, R), the respective angles (θ_L, ϕ_L) and the relative M–L distances must be comparable in the two ML_n complexes. This condition is neither satisfied in the case of Gd_2O_3 and α-$NaYF_4$ nor Gd_2O_3 and β-$NaYF_4$, because the respective coordination numbers and thus the distributions of ligands are very different in the two complexes being compared. The proposed breakdown of site symmetry will also not lead to the fulfillment of the required condition as may be seen by comparing Figure 1 in Ref. [1] with our Figure 1. In consequence, the fitted CFP sets obtained for Eu^{3+} in α-$NaYF_4$ and β-$NaYF_4$ differ from each other as well as each set differs from the starting CFP set (Supporting Information, Table S1). The above observations confirm that the methodology[1] does not guarantee reliable fitting outcomes. Thus the fitted CFP values[1] represent rather a sets of random numbers, which have little physical significance.

The usage[1] of the obtained small rms deviations as the sole criterion to assess the validity of the results, including the correctness of the interpretation of spectra, is questionable. This criterion is badly insufficient in view of the discussed above drawbacks and pitfalls inherent in the CF analysis.[1] A common experience is that for systems with low site symmetry a multitude of local minima exists,[7,8] which yield very close rms values but disparate fitted CFPs. This renders incorrect and unphysical most of the fitted CFP sets that correspond to local minima. To distinguish between such sets and the sets that likely correspond to global minima, other criteria must be utilized. An important criterion for a correct CF parameterization is agreement of the second moments $\sigma_2(SLJ)$[9,10] determined using the experimental values of the splitting of a given SLJ-multiplet (σ_2(expt)), and the CFP values B_{kq} (σ_2(calc)). Appropriate expressions are provided in Equations (S4)–(S6) in the Supporting Information. Calculations for the multiplet $^7F_1$ of Eu^{3+} in β-$NaYF_4$ yield: $(\sigma_2(\text{expt}))^2 = 2207\ cm^{-2}$ using the data in Table S4,[1] whereas $(\sigma_2(\text{calc}))^2 = 5108\ cm^{-2}$ using the CFPs from Ref. [1], Table 1. Analogous values for the same multiplet of Eu^{3+} in α-$NaYF_4$ are: $(\sigma_2(\text{expt}))^2 = 6427\ cm^{-2}$ using the data in Table S3,[1] whereas $(\sigma_2(\text{calc}))^2 = 5358\ cm^{-2}$ using the CFPs from Ref. [1], Table 1. For the multiplet $^7F_2$ of Eu^{3+} in β-$NaYF_4$ the obtained value of

$(\sigma_2(\text{expt}))^2 = 2126\ \text{cm}^{-2}$ is also much smaller than $(\sigma_2(\text{calc}))^2 = 4954\ \text{cm}^{-2}$. The disparity between σ_2(expt) and σ_2(calc) is unreasonably large and indicates that the CF parameterization[1] is unphysical. The values of $(\sigma_2(\text{calc}))^2$ could not be verified for other multiplets of Eu^{3+} in α- or β-$NaYF_4$, as the respective experimental splittings have not been determined.[1]

The problems outlined above call for a thorough revision of the methodology.[1] In our opinion, to achieve a correct CF parameterization, the starting CFPs for fittings should be estimated based on the crystallographic structure and the ligand positions, which may be taken either as those determined for the pure host crystal or obtained from considerations of suitable distortion models. The combined approach comprising the ascent/descent in symmetry (ADS) method and the superposition model (SPM) analysis,[11,12] can be successfully used for CF analysis of low-symmetry systems. The recent study[13] provides an illustrative example of SPM calculations dealing with the Ln^{3+} coordinated compounds with fluoride ligands. Prior to this, however, further experimental studies are required to obtain more comprehensive and reliable sets of experimental data suitable for carrying out SPM analysis of CFPs and subsequent calculations of the energy levels of Eu^{3+} in α- and β-$NaYF_4$. Moreover, it would be beneficial to extend both experimental data sets and energy level calculations for other Ln^{3+} ions, for example, Er^{3+} or Nd^{3+}, that are amenable for reliable CF analysis. Results of our experimental spectroscopic studies as well as theoretical analysis will be presented in a forthcoming paper.

We conclude that the arguments exposed above render the methodology used for CFP fittings[1] as highly inappropriate. Consequently, the fitted CF parameters reported by Tu et al.[1] have little physical significance and must be considered as incorrect and unreliable. The H_{CF} parameterization[1] reproduces the energies of Stark sublevels, but it completely fails to reproduce the multipolar structure of the central-ion surroundings in crystals.[9,10] This is a direct consequence of incompatibility of the crystal structure of Gd_2O_3 and that of $NaYF_4$, which prevents adoption of CFPs optimized for the former system as the starting parameters in fittings for the latter one. Utilizing the CFP sets[1] for analysis of spectra of Eu^{3+} for other trivalent lanthanide ions in the host $NaYF_4$ may lead to completely erroneous interpretation of experimental data, which would yield incorrect correlations between the spectra and the energy level structure. Moreover, the risk of such pitfalls is greater, because the lanthanide-doped $NaLnF_4$ crystals belong to a group of important materials with significant application potential. Thus, these crystals have generated considerable interest, especially among experimentalists. This paper provides the underlying theoretical background, which shall help the researchers working in this field to avoid similar pitfalls as those revealed in the analysis.[1] This, in turn, could reduce the number of cases of erroneous interpretations of future experimental data.

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