Crystal-field Analysis of Tb^{3+}:LaF_3 and Gd^{3+}:LaF_3 in C_{2v} Site Symmetry*

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The absorption spectrum of Tb^{3+}:LaF_3 represents a particularly challenging case for energy level structure analysis. Most of the observed extensive band structure occurs in the 26 000–40 000 cm^{-1} range. At higher energies the transitions in our ~1% doped crystals were too weak to be observed in absorption. Since the $^7F_6$ ground state is a very pure septet, and the amount of septet character in the higher energy states decreases rapidly with increasing energy, increasingly weaker transition strengths are expected. The weak intensities and high density of levels have also been cited as problems in interpreting the spectrum of Tb^{3+}:$LaCl_3$ where 'safe' crystal-field analysis did not extend above ~26 000 cm^{-1} [1]. A summary of the free-ion states consistent with the present results has been reported [2].

A crystal-field analysis of the spectrum of Gd^{3+}:LaF_3 to ~37 000 cm^{-1} demonstrated that good agreement with experiment could be achieved assuming a hexagonal site symmetry [3]. However, it has since been shown [4] that the eigenvectors computed in this approximation may not be useful in the interpretation of magnetic measurements, whereas the C_{2v} approximation can be used to correlate both types of results. We extended the previously published experimental results for Gd^{3+}:LaF_3 to include the ^6D and ^6G groups in the 39 000–49 000 cm^{-1} range [5], but we have not previously attempted to analyse all of the available data via a complete free-ion and crystal-field matrix element diagonalization in C_{2v} symmetry.

Experimental

The details of the high resolution spectroscopic methods are summarized in refs. 1 and 5. Spectra taken at ~4 K were used as the basis for analysis.

Results and Discussion

The approach we have taken to the analysis of the spectra of Ln^{3+}:LaF_3 has been illustrated in the previous publications in this series which discussed the analyses where Ln = Pr^{3+}, Tm^{3+}, Er^{3+}, Ho^{3+} and Dy^{3+} [6–8]. Details of the calculations are given there. The purpose of the investigations has been to develop independent complete free-ion and crystal-field parameter analyses for as many of the lanthanides as possible, since in this way trends in parameters can be assessed and non-physical variations are more easily recognized. The spectra in LaF_3 represent the best approximation to true free-ion spectra, which are usually unavailable, that can be obtained in condensed phase.

For the heavy lanthanides, the model crystal-field parameters were derived for Er^{3+}:LaF_3. Starting with Onopko's insight into the structure of the ground state in D_{3h} site symmetry [9], we could derive an excellent correlation between theory and experiment over the entire range of observation for Er^{3+}:LaF_3. Because of the very large number of assignments, we were subsequently able to determine the crystal-field parameters for C_{2v} symmetry using all of the earlier assignments. The Er^{3+}:LaF_3 system is unique in the number of distinct free-ion states that are well separated in energy and in which the number of prominent crystal-field components corresponds to the expected number of crystal-field levels. Projecting the Er^{3+} crystal-field parameters towards the center of the series has resulted in excellent correlations with observed spectra over entire regions of observation. Each ion considered has provided the basis for some modification of the original parameter set, which in turn forms the 'model' for the next member of the series. Thus the initial 'model' for Tb^{3+} was based on the analysis of Dy^{3+}:LaF_3 [8]. This model provided an excellent correlation with the observed levels in Tb^{3+}, making it possible to distinguish vibronic from electronic transitions when the latter were very weak. Thus even though the level structure is rather dense, an extensive correlation between theory and experiment was possible, and 146 crystal-field levels could be assigned. The final parameter set is shown in Table I.

A preliminary set of crystal-field parameters for Tb^{3+} was taken, together with previously established free-ion parameters for Gd^{3+}:LaF_3 [5], for a model

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TABLE I. Parameter Values for $Tb^{3+}:LaF_3$ and $Gd^{3+}:LaF_3$[a]

Parameter	$Tb^{3+}:LaF_3$[b,c] (cm^{-1})	$Gd^{3+}:LaF_3$[b,c] (cm^{-1})
F^2	89204(603)	85675(57)
F^4	63707(567)	[61429]
F^6	47220(532)	45051(30)
ζ	1713(1)	1505(2)
α	19.4(0.8)	20.4(0.1)
β	−578.2(72)	[−600]
γ	1456(148)	1431(21)
T^2	303(73)	[330]
T^3	[40]	[41.5]
T^4	56(31)	[62]
T^6	−294(52)	[−295]
T^7	362(57)	[400]
T^8	326(82)	[350]
M^0	[3.610]	[3.320]
M^2	[2.020]	[1.850]
M^4	[1.370]	[1.260]
P^2	684(17)	596(8)
B_0^2	−254(23)	[−233]
B_0^4	659(48)	[590]
B_0^6	306(36)	[283]
B_2^2	−101(15)	[−94]
B_2^4	365(31)	[402]
B_4^4	436(28)	[407]
B_2^6	−710(28)	[−708]
B_4^6	−225(28)	[−174]
B_6^6	−504(32)	[−528]
Levels fit	146	61
σ	12	7

[a]Errors in individual parameter values are shown in parentheses. Brackets indicate parameter values that were not varied. For definition of parameters see ref. 7. [b]The values of M^K were computed using *ab initio* methods. P^2 varied freely, but P^4 and P^6 were constrained by the ratios $P^4 = 0.75P^2$, $P^6 = 0.50P^2$. [c]The average deviation $\sigma = \Sigma(\Delta_i^2/n-p)^{1/2}$ where Δ_i is the difference between the observed and calculated transition energy, n is the number of levels used in the fitting procedure and p is the number of parameters freely varied.

calculation to determine the extent of correlation with the observed crystal-field structure in $Gd^{3+}:LaF_3$. The comparison revealed that in each free-ion group, all deviations from observed band energies were less than 12 cm^{-1}. The data set is that given in ref. 5. It could be concluded that any adjustment in parameters should be restricted to the free-ion set. Several of the latter parameters were poorly determined when they were freely varied, but fixing values consistent with series averages for some of these maintained an overall excellent degree of correlation. As shown in Table I, it was possible to impose a series-consistent value of F^4, since when this was done the adjusted values of F^2 and F^6 were also consistent with well-established trends over the series, and 60 of the 66 levels between 32 000 and 49 250 cm^{-1} were fitted with an average deviation of 7 cm^{-1}. It is apparent that even with the inclusion of levels near 50 000 cm^{-1}, we observe such a small portion of the $4f^7$ configuration that multiparameter fits to the data in this case are only meaningful in the context of testing predictions based on trends established for the series as a whole.

Supplementary Material

The extensive tables of experimental band energies and computed energy levels for $Gd^{3+}:LaF_3$ and $Tb^{3+}:LaF_3$ are available from W. T. Carnall.

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