Symmetry-Modelling of Rare Earth Compounds with Kramers Ions: II. Erbium(III) in Various Solids

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The »truncated crystal field method« which allows determination of the microsymmetry of the crystal field around Kramers ions is applied to erbium(III) in five different host crystals. The starting data for the calculations are taken from carefully interpreted optical spectra. In the first step, crystal field parameters for various assumed test symmetries are chosen in order to give the best fit to the splitting of the ground state multiplet. Then, a truncated crystal field calculation involving only a limited number of Stark levels is performed. The microsymmetry of the earth ion in the compounds is suggested in terms of the standard deviation between the calculated and experimental Stark splittings. All the calculations including the optimization of parameters have been performed on a personal computer.

Tables of crystal field parameters and standard deviations are given for the following compounds with optical data taken from the literature: $Er(C_2H_5SO_4)_3 \cdot 9H_2O$, Er(III) : $LuPO_4$, Er(III) : $HfSiO_4$, Er(III) : $LaCl_3$ and Er(III) : Y_2O_3.

INTRODUCTION

Interpretation of the optical and magnetic phenomena of single crystals containing rare earth ions is usually done within the framework of crystal field theory. Due to the semiempirical nature of this theory, model-dependent crystal field parameters are introduced. Determination of these parameters is a very difficult task and is based on fitting experimental and theoretical values of the Stark level energies. Information of vital importance in this respect is the knowledge of the local symmetry of the crystal field around the central ions, *i. e.*, the microsymmetry of the rare earth lattice sites in the crystal. Usually, there are three experimental techniques employed to obtain this information, namely the X-ray diffraction methods, ESR measurements, and optical spectroscopy. Each of these supplies supplementary information as compared to the others.

The present contribution deals with microsymmetry determinations based solely upon optical spectra of Er(III) compounds. Recently, the so-called »truncated crystal field method« has been developed by the present authors taking into account the features characteristic of Kramers ions (*i. e.*, ions having an odd number of electrons) in the optical spectra.[1] The method has

been show to give very good results for Nd(III) compounds[1,2] and is applied to crystals containing Er(III) in this work.

THE TRUNCATED CRYSTAL FIELD METHOD (TCFM)

The special nature of Kramers ions is due to their behaviour under time reversal symmetry and was discovered by Kramers [3] and thoroughly investigated by Wigner.[4]

There are two immediate consequences of this symmetry property for the optical spectra of these ions:

1) all possible microsymmetries of the crystal field with the exception of the cubic ones cause a splitting of the free ion states with the total angular momentum quantum number J into $(J+1/2)$ Stark components (J is a half-integer for Kramers systems),

2) in the absence of external magnetic fileds each of the crystal field states remains at least doubly degenerate (it is only in cubic symmetries that fourfold degenerate levels occur).

This means that the usual procedure of counting the crystal field bands in the optical spectra to evaluate the microsymmetry of a crystal fails completely with Kramers ions. The only distinction, which is possible in favourable cases, is the one between cubic and all the other symmetries. Both the number and degeneracies of the Starke levels in cubic symmetries for some J values are given in Table I.

TABLE I

Number and degeneracy (p) of Stark levels with different J values in cubic symmetry

J	1/2	3/2	5/2	7/2	9/2	11/2	13/2	15/2	17/2
p = 2	1	0	1	2	1	2	3	2	3
p = 4	0	1	1	1	2	2	2	3	3
total	1	1	2	3	3	4	5	5	6

The TCFM replaces the counting criterion by a more quantitative treatment without performing a full and cumbersome crystal field analysis.

The mathematics employed by the TCFM is based fully on the tensor operator formalism of crystal fields as developed by Judd and Wybourne.[5,6]

The crystal field operator $\hat{H}_{cf}$ is represented by the following expansion:

$$\hat{H}_{cf} = \sum_{k,q} B_{kq} \hat{C}_{kq}, \tag{1}$$

where the B_{kq} are crystal field parameters and the $\hat{C}_{kq}$ are spherical tensor operators related to the ordinary spherical harmonics $\hat{Y}_{kq}$ considered as operators by:

$$\hat{C}_{kq} = [4\pi/(2k + 1)]^{1/2} \hat{Y}_{kq}. \tag{2}$$

The number of terms in the expansion of Eq. 1 depends on the symmetry of the crystal field. Table II gives the most common microsymmetries for

rare earths, the related point groups and the corresponding non-vanishing crystal field parameters, respectively.

TABLE II

Crystal field symmetries, their point groups and corresponding non-vanishing crystal field parameters

microsymmetry	point groups	crystal field parameters
cubic	T_h, T_d, T, O_h, O	B_{40}, B_{60}
hexagonal	$C_{3h}, C_6, C_{6h}, D_6,$ D_{3h}, C_{6v}, D_{6h}	$B_{20}, B_{40}, B_{60}, B_{66}$
tetragonal	$S_4, C_4, C_{4h}, D_{2d},$ C_{4v}, D_4, D_{4h}	$B_{20}, B_{40}, B_{44}, B_{60}, B_{64}$
trigonal	$C_3, C_{3i}, C_{3v},$ D_3, D_{3d}	$B_{20}, B_{40}, B_{43}, B_{60}, B_{63},$ B_{66}
rhombic	C_{2v}, D_2, D_{2h}	$B_{20}, B_{22}, B_{40}, B_{42}, B_{44},$ $B_{60}, B_{62}, B_{64}, B_{66}$

In order to compute the Stark level energies to the first order of perturbation theory, matrix elements between $\hat{H}_{cf}$ and the zero order free ion wavefunctions of the rare earth ions must be calculated. With the Wigner-Eckart theorem these matrix elements can be factored into products of coupling coefficients and reduced matrix elements. Computational details are given elsewhere.[1,5,6] The starting point for the TCFM is the spectroscopically observed crystal field splitting of the ground state multiplet $^4I_{15/2}$ for the Er(III) ion in the lattice. This splitting can be determined from optical fluorescence data or by investigation of hot band systems at various temperatures.[2] The four non-cubic symmetries in Table II are taken as test symmetries in succession. For each of them a different set of crystal field parameters has to be determined in such a way that an optimal fit to the observed ground state splitting is obtained. The repeated diagonalizations of crystal field matrices necessary in the course of the optimization procedure are performed by using standard algorithms. The electron-hole equivalence in atomic shells makes Er(III) with configuration $4f^{11}$ equivalent to Nd(III) with configuration $4f^3$. Therefore, the energy matrices for Nd(III) given in Ref. [1] can be used here too when the sign of the spin-orbit coupling constant is reversed. The optimization procedures were carried out with the routine MAXMUM of the software package GAUSS^{TM} (version 1.49B, 1988) on a standard personal computer. The algorithms employed by MAXMUM are the positive definite secant Broyden-Fletcher-Goldfarb-Shano and Davidon-Fletcher-Powell algorithms, both of which are general purpose optimization routines efficient for a variety of problems.[7] The quantity which is minimized in all calculations is the standard deviation σ in the following form:

$$\sigma = \left(\frac{\Sigma_i \, (obs_i - calc_i)^2}{\text{No. of levels} - \text{No. of parameters}} \right)^{1/2}, \tag{3}$$

where the summation is taken over all Stark levels of the ground state multiplet and where obs$_i$ and calc$_i$ denote the i-th observed and calculated Stark level energies, respectively.

The second step of the TCFM is the calculation of the crystal field splittings for two other multiplets using the same parameter sets that have been optimized for the ground state in different test symmetries. Additional multiplets $^4F_{9/2}$ and $^4G_{11/2}$ were selected for the erbium case. They fulfil the important conditions of being both well separated from each other and simultaneously from other multiplets having the same J-value. This is crucial because the assumption of negligible inter-multiplet interactions is implied by the form of the crystal field matrices.[1]

Here again, the standard deviation σ of Eq. 3 is used as a measure of the quality of the fit. In this case the summation must be carried over all Stark levels of the three multiplets $^4I_{15/2}$, $^4F_{9/2}$, and $^4G_{11/2}$.

According to the philosophy of this kind of symmetry modelling the agreement between the observed and calculated Stark splittings is the best, i. e., σ assumes its smallest value when the actual microsymmetry of the crystal is either identical or very close to the test symmetry selected for the optimization procedure. Therefore, the σ-values obtained by the TCFM constitute a sensitive criterion for the microsymmetry around the Kramers ion in the crystal.

RESULTS AND DISCUSSION

In order to test the TCFM, five compounds with known microsymmetries of the Er(III) sites have been chosen. All of them have well resolved optical spectra reported in literature.[8-11] The results of the calculations together with the optimized parameters and the σ-values for the various test symmetries are given in Tables III—VII.

For all compounds the correct microsymmetries were reproduced by the TCFM as the most probable ones. Therefore, this kind of symmetry modelling

TABLE III

Optimized crystal field parameters and σ-values resulting from a TCFM treatment of Er(III) : LuPO$_4$. Optical data from Ref [8]

Er(III):LuPO$_4$			microsymmetry: D$_{2d}$	
test symmetry	hexagonal	tetragonal	trigonal	rhombic
crystal field parameters optimized for the ground state $^4I_{15/2}$	B_{20} = 979 B_{40} = -203 B_{60} = -198 B_{66} = 352	B_{20} = - 99 B_{40} = -197 B_{44} = -639 B_{60} = 682 B_{64} = -100	B_{20} = -408 B_{40} = -176 B_{43} = 171 B_{60} = -634 B_{63} = - 32 B_{66} = -257	B_{20} = 253 B_{22} = -296 B_{40} = -342 B_{42} = 117 B_{44} = -429 B_{60} = - 70 B_{62} = - 2 B_{64} = -450 B_{66} = -170
σ	35.82	11.65	31.05	20.82

TABLE IV

Optimized crystal field parameters and σ-values resulting from a TCFM treatment of Er(III) : HfSiO₄. Optical data from Ref. [8]

Er(III):HfSiO$_4$		microsymmetry: D$_{2d}$		
test symmetry	hexagonal	tetragonal	trigonal	rhombic
crystal field parameters optimized for the ground state $^4I_{15/2}$	$B_{20} = 308$ $B_{40} = 155$ $B_{60} = -250$ $B_{66} = -530$	$B_{20} = -187$ $B_{40} = -934$ $B_{44} = -517$ $B_{60} = -362$ $B_{64} = 355$	$B_{20} = 467$ $B_{40} = -41$ $B_{43} = -878$ $B_{60} = -201$ $B_{63} = 424$ $B_{66} = -141$	$B_{20} = 370$ $B_{22} = -172$ $B_{40} = 29$ $B_{42} = 411$ $B_{44} = -273$ $B_{60} = -59$ $B_{62} = -252$ $B_{64} = -189$ $B_{66} = -437$
σ	35.66	16.07	25.63	25.22

TABLE V

Optimized crystal field parameters and σ-values resulting from a TCFM treatment of Er(III) : Y₂O₃. Optical data from Ref. [9]

Er(III):Y$_2$O$_3$		microsymmetry: C$_{2v}$		
test symmetry	hexagonal	tetragonal	trigonal	rhombic
crystal field parameters optimized for the ground state $^4I_{15/2}$	$B_{20} = 778$ $B_{40} = 1326$ $B_{60} = -596$ $B_{66} = -702$	$B_{20} = -1241$ $B_{40} = 2225$ $B_{44} = -96$ $B_{60} = 721$ $B_{64} = 239$	$B_{20} = 994$ $B_{40} = -290$ $B_{43} = 1292$ $B_{60} = 172$ $B_{63} = -620$ $B_{66} = 412$	$B_{20} = 39$ $B_{22} = -554$ $B_{40} = 744$ $B_{42} = -1402$ $B_{44} = -861$ $B_{60} = -15$ $B_{62} = 347$ $B_{64} = -507$ $B_{66} = -87$
σ	52.04	37.25	35.18	12.59

TABLE VI

Optimized crystal field parameters and σ-values resulting from a TCFM treatment of Er(III) : LaCl₃. Optical data from Ref. [10]

Er(III):LaCl$_3$		microsymmetry: D$_{3h}$		
test symmetry	hexagonal	tetragonal	trigonal	rhombic
crystal field parameters optimized for the ground state $^4I_{15/2}$	$B_{20} = 104$ $B_{40} = -30$ $B_{60} = -402$ $B_{66} = 281$	$B_{20} = 523$ $B_{40} = -74$ $B_{44} = 58$ $B_{60} = 104$ $B_{64} = -328$	$B_{20} = 156$ $B_{40} = 526$ $B_{43} = -395$ $B_{60} = -28$ $B_{63} = 361$ $B_{66} = -14$	$B_{20} = 371$ $B_{22} = -363$ $B_{40} = 231$ $B_{42} = 402$ $B_{44} = 25$ $B_{60} = 176$ $B_{62} = 76$ $B_{64} = 98$ $B_{66} = 130$
σ	8.91	14.28	24.26	24.43

TABLE VII

Optimized crystal field parameters and σ-values resulting from a TCFM treatment of Er(C₂H₅SO₄)₃ · 9H₂O. Optical data from Ref. [11]

$Er(C_2H_5SO_4)_3 \cdot 9H_2O$		microsymmetry:	D_{3h}	
test symmetry	hexagonal	tetragonal	trigonal	rhombic
crystal field parameters optimized for the ground state $^4I_{15/2}$	$B_{20} = 113$ $B_{40} = -373$ $B_{60} = -489$ $B_{66} = 436$	$B_{20} = -246$ $B_{40} = -130$ $B_{44} = -647$ $B_{60} = 718$ $B_{64} = 99$	$B_{20} = 683$ $B_{40} = -349$ $B_{43} = -168$ $B_{60} = -323$ $B_{63} = 423$ $B_{66} = 16$	$B_{20} = 4$ $B_{22} = 74$ $B_{40} = -64$ $B_{42} = -592$ $B_{44} = 277$ $B_{60} = 281$ $B_{62} = 83$ $B_{64} = 69$ $B_{66} = -439$
σ	9.63	17.02	19.48	20.06

presented for Er(III) compounds works equally well as for Nd(III) compounds. It is a valuable technique to find the symmetry of the crystal field surrounding the central Kramers ions from optical spectra alone and is thus a useful tool in cases where either insufficient or no structural data are available for the crystals under study. It is worth mentioning that Auzel and Malta[13] have proposed, in a different context, multiplets $^4F_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ as »crystal field probes«. Thus, a replacement of $^4G_{9/2}$ by $^4I_{11/2}$ and $^4I_{13/2}$ might further improve the results of the TCFM for Er(III). The influence of this replacement is presently under investigation.

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SAŽETAK

Modeliranje simetrije spojevima rijetkih zemalja s Kramerovim ionima: II. Erbijum(III) u različitim čvrstim tjelima

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»Truncated crystal field method«, koja omogućuje određivanje mikrosimetrije kristalnog polja u sredini Kramerovih iona, primjećuje se na erbijumu(III) u pet različite pokusne simetrije izabrani su tako, da dolazi do optimalne skladnosti s diso-interpretiranih optičkih spektara. Na samom početku parametri kristalnog polja za različite pokusne simetrije izabrani su tako, da dolazi do optimalne skladnosti s disocijacijom multipleta osnovnog stanja. Zatim se skraćeno izračunava kristalno polje uključujući ograničeni broj Starkovih nivoa. Model pokazuje stvarnu mikrosimetriju spoja pomoću standardnih devijacija proračunatih i eksperimentalno promatranih Starkovih cijepanja. Sva proračunavanja, uključujući optimizaciju parametara, izvršena su personalnim kompjuterom. Za slijedećih pet spojeva navedene su tabele parametara kristalnog polja i standardnih devijacija, pri čemu su optički podaci izvađeni iz literature:

$Er(C_2H_5SO_4)_3 \cdot 9H_2O$, $Er(III) : LuPO_4$, $Er(III) : HfSiO_4$, $Er(III) : LaCl_3$ i $Er(III) : Y_2O_3$.