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Comparative correlation crystal field analysis of Er^{3+} ($4f^{11}$) in garnet hosts

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Abstract

Comparative correlation crystal field (CCF) analyses of the Er^{3+} ($4f^{11}$) energy level structure in YAG, LuAG, ErAG, ErGG, YSAG and YSGG systems are reported. These analyses are based on the use of a phenomenological Hamiltonian model that includes 20 free-ion parameters and the nine one-electron crystal field parameters plus one two-particle CCF parameter. The present analyses are carried out with a uniform Hamiltonian model and common crystal field levels spanning the lowest 12 multiplets. Comparison between the observed and calculated crystal field levels yields good agreement with rms deviations between 7.7 cm^{-1} (Er:ErGG) and 11.5 cm^{-1} (Er:YAG). The fits are in qualitative agreement with *ab initio* calculations of CCF effects and also with the results of CCF of the Nd^{3+} ion.

1. Introduction

Recently, there has been considerable progress in the parametric crystal field Hamiltonian model which consists of correlation effects for the analysis of crystal field levels of trivalent lanthanides [1–8]. The addition of correlation crystal field (CCF) parameters (two-electron crystal field parameters) to the usual one-electron crystal field parameters greatly improves the fitting errors for the $^2H(2)_{11/2}$ of Nd^{3+} [2,4,8], $^3K_8$ of Ho^{3+} and $^6I_{17/2}$ of Gd^{3+} [1]. Correlation crystal field analysis for Sm^{3+}:SmODA [7] and Np^{3+}:$LaCl_3$ [5] reveals that some CCF parameters have a significant influence on the crystal field level fits.

In the present work, we report on CCF analysis for the Er^{3+} ion in different garnet systems including $Y_3Al_5O_{12}$ (Er:YAG), $Lu_3Al_5O_{12}$ (Er:LuAG), $Er_3Al_5O_{12}$ (Er:ErAG), $Er_3Ga_5O_{12}$ (Er:ErGG), $Y_3Sc_2Ga_3O_{12}$ (Er:YSGG) and $Y_3Sc_2Al_3O_{12}$ (Er:YSAG). The energy level data were analysed in terms of a Hamiltonian model that assumes D_2 site symmetry for the Er^{3+} ions in the garnet matrices. This is the first comparative study of erbium garnet systems in which the energy level analyses were carried out with a uniform Hamiltonian model which includes the CCF effects for 59 common crystal field levels spanning the 12 lowest multiplets of Er^{3+} ion.

2. Correlation crystal field fits

The Hamiltonian model with correlation crystal field effects used in the energy level data fits can be written as [1–10]

$$\hat{H}=\hat{H}_a+\hat{H}_{CF}+\hat{H}_{OCCF} \quad (1)$$

where $\hat{H}_a$ contains the usual isotropic (atomic) parts of H that consists of 20 parameters (F^k ($k=2, 4, 6$), ζ, α, β, γ, T^i ($i=2, 3, 4, 6, 7, 8$), M^j ($j=0, 2, 4$) and P^k) [9–11], $\hat{H}_{CF}$ consists of nine one-electron crystal field parameters (B_{kq}) for the D_2 site symmetry of the rare earth ion in garnets and $\hat{H}_{OCCF}$ contributes the orthogonal correlation effects in the Hamiltonian model.

The correlation effects due to two-body operators on the crystal field splitting are defined as [1–3]

$$H_{OCCF}=\sum_{ikQ} G_{iQ}^{(k)} g_{iQ}^{(k)} \quad (2)$$

The correlation crystal field parametrization has been discussed in refs. 1–3 for the CCF analysis of lanthanides. Quagliano *et al.* [6] found that out of the 43 possible CCF parameters, the $G_{10A}^{(4)}$ parameter was particularly important for the analysis of Er:YSAG and Er:YSGG which is in agreement with the CCF analysis of Nd^{3+} [2] systems. In the present study, we employed only the $G_{10A}^{(4)}$ parameter for the correlation crystal field analysis for Er:garnet systems.

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TABLE 1. Hamiltonian parameters derived from parametric fits of calculated to observed energy level data (values in cm^{-1})[a]

Parameter	Er:YAG		Er:LuAG		Er:ErAG		Er:ErGG	
	No CCF	CCF	No CCF	CCF	No CCF	CCF	No CCF	CCF
E_{Avg}	35831	35830	35712	35712	35675	35674	35718	35717
F^2	100436	100456	99590	99613	99501	99528	99739	99751
F^4	72346	72299	71387	71335	71465	71403	71493	71450
F^6	49351	49353	48402	48408	48810	48820	48730	48717
α	28.68	28.68	22.78	22.78	20.07	20.07	21.78	21.78
β	−825	−825	−684	−684	−626	−626	−656	−656
γ	1622	1622	1740	1740	1596	1596	1646	1646
ζ	2354	2354	2355	2355	2357	2357	2356	2356
M^0	5.88	5.88	5.79	5.79	5.91	5.91	6.25	6.25
P^2	760	760	772	772	837	837	873	873
B_{20}	385	400	253	278	413	422	146	80
B_{22}	78	92	62	77	45	67	−57	−48
B_{40}	−140	−173	−104	−130	−59	−107	152	85
B_{42}	−1455	−1369	−1525	−1462	−1545	−1440	−1350	−1314
B_{44}	−872	−778	−920	−764	−889	−762	−1067	−883
B_{60}	−1165	−1138	−1226	−1167	−1111	−1070	−1151	−1122
B_{62}	−253	−332	−234	−341	−295	−383	−165	−234
B_{64}	432	481	440	506	446	506	415	456
B_{66}	−401	−406	−413	−432	−416	−437	−360	−372
$G^{(4)}_{10A}$	–	57	–	41	–	27	–	57
N	59	59	59	59	59	59	59	59
σ	14.4	11.5	13.7	9.9	13.6	8.2	12.8	7.7

[a]T^i values were held fixed to the following values: $T^2=640$; $T^3=40$; $T^4=73$; $T^6=-369$; $T^7=330$; $T^8=564$.

All the empirical energy level data are taken directly from the literature and were used without making any reassignments. The primary sources of these data were: Er:YAG [12]; Er:LuAG [12]; Er:ErAG [13]; Er:ErGG [13]; Er:YSGG [6]; and Er:YSAG [6]. Calculations performed on the six Er:garnet systems were carried out by diagonalizing the total (atomic + crystal field) Hamiltonian (eqn.(1)) within the complete 364 $SLJM_J$ basis set for the $4f^{11}$ configuration. Energy level data fits were carried out without and with the inclusion of the CCF terms in eqn. (1). The data fitting procedures were identical to ref. 2, involving a minimization of

$$\sigma=\left[\frac{\sum(\text{calculated energy}-\text{experimental energy})^2}{\text{number of experimental levels}}\right]^{1/2} \quad (3)$$

3. Results and discussion

Parameter values obtained from the calculated versus observed energy level data fits are presented in Tables 1 and 2 along with the σ values for these fits. Comparison of the crystal field parameters obtained without and with the inclusion of CCF terms in $\hat{H}$ are listed under the (No CCF) and (CCF) columns, respectively for four systems in Table 1 and two systems in Table 2. We note that the B_{kq} crystal field parameters are not significantly different. The values of the B_{kq} parameters

TABLE 2. Hamiltonian parameters derived from parametric fits of calculated to observed energy level data (values in cm^{-1})

Parameter	Er:YSGG		Er:YSAG	
	No CCF	CCF	No CCF	CCF
E_{Avg}	35660	35660	35653	35652
F^2	99281	99304	99291	99311
F^4	70943	70893	71651	71632
F^6	49267	49281	49913	49901
α	18.80	18.80	17.70	17.70
β	−646	−646	−625	−625
γ	1691	1691	1421	1421
T^2	546	546	554	554
T^3	40	40	40	40
T^4	88	88	84	84
T^6	−349	−349	−361	−361
T^7	359	359	280	280
T^8	415	415	584	584
ζ	2363	2363	2368	2367
M^0	3.70	3.70	3.60	3.60
P^2	458	458	517	517
B_{20}	262	270	312	541
B_{22}	67	51	219	64
B_{40}	−87	−115	−78	−103
B_{42}	−1522	−1419	−1506	−1330
B_{44}	−863	−719	−906	−880
B_{60}	−940	−842	−1218	−1110
B_{62}	−245	−373	−138	−333
B_{64}	404	472	321	426
B_{66}	−360	−442	−332	−356
$G^{(4)}_{10A}$	–	32	–	33
N	58	58	55	55
σ	13.4	10.3	14.1	9.8

TABLE 3. Experimental and calculated (without and with CCF) energies for $^4I_{15/2}$, $^2H(2)_{11/2}$, and $^2G(1)_{9/2}$ levels of Er^{3+}: garnet systems[a]

System	$^4I_{15/2}$			$^2H(2)_{11/2}$			$^2G(1)_{9/2}$		
	Expt.	Δ_B	Δ_G	Expt.	Δ_B	Δ_G	Expt.	Δ_B	Δ_G
Er:YAG	0	4	10	19093	−29	−10	24422	17	3
	22	1	−3	19114	−21	0	24576	−20	−10
	61	0	−4	19151	−15	−1	24591	−25	−13
	79	−2	−3	19310	−8	−22	24765	21	10
	417	2	−1	19347	17	−6	24784	−5	−2
	430	−16	−1	19365	22	3			
	526	24	18						
	573	−11	−8						
σ		11.1	8.1		19.8	10.2		18.9	8.7
Er:LuAG	0	3	10	19098	−28	−11	24419	15	0
	36	7	−1	19118	−20	−3	24576	−23	−14
	56	4	1	19154	−21	−4	24595	−23	−15
	80	1	−1	19349	14	−2	24775	22	7
	440	4	−2	19360	14	−12	24797	−5	0
	459	−11	4	19380	21	1			
	539	24	16						
	582	−13	−10						
σ		10.9	7.7		20.2	7.0		18.9	9.7
Er:ErAG	0	2	11	19091	−34	−11	24417	17	−1
	27	6	0	19113	−25	−1	24573	−24	−12
	58	5	0	19149	−16	0	24589	−29	−14
	79	6	3	19348	17	0	24764	20	6
	423	0	2	19366	25	−2	24785	0	0
	436	−12	0	19371	17	−7			
	530	14	5						
	574	−8	−3						
σ		7.9	4.6		23.2	5.4		20.5	8.7
Er:ErGG	0	16	2	19103	−33	−15	24435	18	−2
	46	12	2	19121	−18	−4	24587	−19	−12
	54	−9	−3	19157	−17	−2	24599	−20	−10
	78	3	4	19350	18	3	24766	26	9
	427	2	−4	19363	21	−2	24781	−9	−2
	440	−3	−2	19369	10	−6			
	495	0	13						
	527	−16	−13						
σ		9.7	7.0		20.7	7.0		19.2	8.2
Er:YSGG	0	−3	8	19106	−26	−9	24436	5	−4
	33	18	6	19122	−20	−5	24581	−27	−23
	41	7	7	19154	−15	−5	24604	−30	−18
	71	6	7	19340	12	0	24751	20	7
	380	−9	−5	19356	15	−5	24772	2	−2
	410	−6	−3	19360	6	−9			
	485	22	5						
	503	−8	1						
σ		11.6	5.7		16.9	6.3		20.3	13.6
Er:YSAG	0	15	8	19107	−26	−10	24427	2	−8
	21	9	10	19126	−15	−1	24575	−20	−16
	60	−1	−4	19155	−33	−11	24608	−12	−4
	86	12	8	19350	11	−5	24760	28	15
	385	3	−7	19368	19	−6	24787	−4	2
	418	−18	5	–	–	–			
	–	–	–						
	555	−8	−14						
σ		11.0	8.6		22.2	7.5		16.4	10.6

[a]All values are in cm^{-1}. Δ_B, experimental energies minus calculated values without CCF. Δ_G, experimental energies minus calculated values with CCF. The calculated values are obtained by using the parameters listed in Tables 1 and 2, respectively. In this table, the σ are r.m.s. deviations.

derived from the data fits are consistent for all the data sets except for the case of Er:ErGG where the signs for the B_{22} and B_{40} parameters are changed. Significant influence of the CCF was noticed in the Er:ErGG data set as the σ value was reduced from 12.8 cm^{-1} to 7.7 cm^{-1} for 59 levels. In each Er:garnet system, inclusion of the phenomenological CCF parameter in the fits produced improved σ values and better agreement between the calculated and observed crystal field splittings within some individual multiplet manifolds, particularly the abnormal $^2H(2)_{11/2}$ multiplet and the $^4I_{15/2}$ and $^2G(1)_{9/2}$ multiplets. The empirical data, energy level locations and assignments for the $^4I_{15/2}$, $^2H(2)_{11/2}$ and $^2G(1)_{9/2}$ levels used in the parametric analyses are listed in Table 3. In the case of the Er:ErAG data set, the σ value for $^2H(2)_{11/2}$ multiplet has been reduced from 23.2 cm^{-1} to 5.4 cm^{-1}.

The predicted ratio from *ab initio* [15] calculations for $G^{(4)}_{10A}/B^{(4)}_0$ is -0.50 which is consistent with our results of -0.33 (Er:YAG), -0.32 (Er:LuAG), -0.25 (Er:ErAG), -0.28 (Er:YSGG) and -0.32 (Er:YSAG). These results are in agreement with CCF analysis of other lanthanides [1–8].

The strength (S) of the crystal field defined by Chang *et al.* [14] has been calculated for the Er^{3+} ion in different garnet systems. The order of the magnitude of S without and with CCF is as follows:

(1) Strength parameter (in cm^{-1}) without CCF: ErAG (550) > LuAG (548) > YSAG (540) > YAG(530) > ErGG (522) = YSGG (522);
(2) Strength parameter (in cm^{-1}) with CCF: LuAG (521) > ErAG (519) > YSAG (512) > YAG (506) > ErGG (490) = YSGG (490).

Focussing on the magnitude of the S values, we note that the crystal field strength experienced by the Er ion in different garnets follows a similar trend either without or with CCF effects. However, the magnitudes of the S values are reduced relatively when the CCF parameter is introduced in the fit. Er:ErAG and Er:LuAG systems exhibit more or less similar crystal field strength which is slightly stronger when compared to the remaining four garnets.

4. Conclusions

The CCF effects have been studied for the common crystal field levels of six Er:garnet systems. Inclusion of the phenomenological correlation crystal field (CCF) terms in the 4f electron Hamiltonian results in improved calculated versus experimental fits for the Er:garnet systems. The effects of the CCF operators are shown to be a small perturbation on the standard one-particle B_{kq} formalism.

The CCF effects for the Er^{3+} ion resolves not only the anomalous $^2H(2)_{11/2}$ multiplet fitting but also improves the fit for the ground state multiplet $^4I_{15/2}$ where the latter multiplet fit is essential to calculate the exact ground state wave functions for the evaluation of magnetic properties.

The crystal field strength parameter (S), when evaluated, was found to differ quantitatively for the Er^{3+} ion in different garnet environments and the S value was also found to be dependent on the exact Hamiltonian model.

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