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Crystal-field determination for trivalent erbium in yttrium orthoaluminate

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A free-ion-model crystal-field calculation has been performed for $\mathrm{YAlO_3:Er^{3+}}$. A free-ion calculation was done by fitting a free-ion Hamiltonian, which included Coulomb, spin-orbit, configuration, spin-spin, and spin–other-orbit interactions. The coefficients which gave the best least-squares deviation of the calculated centers of gravity from the observed centers of gravity were $E^1 = 6174.1$, $E^2 = 32.836$, $E^3 = 651.69$, $\xi = 2350.5$, $\alpha = 27.825$, $\beta = -722.32$, $\gamma = 3729.4$, $M^0 = 3.525$, $M^2 = [1.974]$, $M^4 = [1.339]$, $P^2 = 2.4779$, $P^4 = -0.0406$, $P^6 = 0.1247$, $T^2 = 157.04$, $T^3 = 42.522$, $T^4 = 62.23$, $T^6 = -259.93$, $T^7 = 402.94$, $T^8 = 66.377$ with an rms deviation of 29.1; where all quantities have units of $\mathrm{cm^{-1}}$. The intermediate-coupled free-ion vectors were then used to fit a C_s (C_{1h}) Hamiltonian to the observed Stark splittings. The crystal-field parameters obtained from a previous calculation on $\mathrm{YAlO_3:Tm^{3+}}$ were used as starting parameters. The parameters which gave the best fit to the observed $\mathrm{YAlO_3:Er^{3+}}$ Stark spectra were $B_0^2 = -183.2$, $\mathrm{Re}B_2^2 = 385.6$, $\mathrm{Im}B_2^2 = 185.2$, $B_0^4 = -816.2$, $\mathrm{Re}B_2^4 = 444.0$, $\mathrm{Im}B_2^4 = 39.7$, $\mathrm{Re}B_4^4 = 637.0$, $\mathrm{Im}B_4^4 = -222.8$, $B_0^6 = -603.8$, $\mathrm{Re}B_2^6 = -42.2$, $\mathrm{Im}B_2^6 = 305.4$, $\mathrm{Re}B_4^6 = 229.7$, $\mathrm{Im}B_4^6 = 523.8$, $\mathrm{Re}B_6^6 = 317.0$, $\mathrm{Im}B_6^6 = 87.0$ with an rms deviation of 6.9; where all units are in $\mathrm{cm^{-1}}$.

I. INTRODUCTION

A free-ion-model crystal-field calculation has been performed for $\mathrm{Er^{3+}}$ in $\mathrm{YAlO_3}$. Donlan and Santiago[1] have published the observed Stark spectra of 22 of the lowest 24 J manifolds of $\mathrm{YAlO_3:Er^{3+}}$ and we have used these data for the crystal-field calculations presented here. $\mathrm{YAlO_3}$ has the gadolinium-orthoferrite structure, belonging to the orthorhombic space group $D_{2h}^{16}(Pbnm)$.[2] Rare-earth ions enter the $\mathrm{YAlO_3}$ lattice substitutionally at the $\mathrm{Y^{3+}}$ sites. These sites have the point-group symmetry C_s ($C_s = C_{1h}$).[3]

In the so-called free-ion-model crystal-field calculations, a free-ion Hamiltonian is fit to the centers of gravity of the J manifolds. The resulting free-ion intermediate-coupled eigenvectors are then used in the crystal-field calculations. Since the $\mathrm{Er^{3+}}$ ion occupies a site of C_s symmetry, the crystal-field calculations require the fitting of at least 14 crystal-field parameters. In any fitting procedure which minimizes the rms deviation of the calculated from the observed levels, several minima are possible depending on the number of coefficients to be fit and the starting values of the coefficients. For this reason we have used as starting parameters the results of a $\mathrm{YAlO_3:Tm^{3+}}$ calculation presented in an earlier paper.[4]

The extensive amount of data presented in Ref. 1 makes it possible to carry out more complete crystal-field calculations than is possible in most of the $\mathrm{Er^{3+}}$ systems previously reported. In addition, it is of interest to compare the results of such calculations with those reported for $\mathrm{YAlO_3:Tm^{3+}}$. If the crystal field is a one-electron potential, the fact that $\mathrm{Er^{3+}}$ and $\mathrm{Tm^{3+}}$ are of similar radius would imply that they should have similar crystal-field coefficients for a common host.

II. THEORY

A. Free ion

The ground configuration of trivalent rare-earth ions (R^{3+}) is $(\mathrm{Xe})4f^N$. The Hamiltonian of the free ion can be accurately represented by effective operators which include Coulomb, spin-orbit, configuration, spin-spin, orbit-orbit, and spin–other-orbit interactions. In general the effective free-ion Hamiltonian for the incomplete f^N shell can be written

$$H = E^1\epsilon_1 + E^2\epsilon_2 + E^3\epsilon_3 + \xi \sum_i \vec{s}_i \cdot \vec{l}_i + \alpha L(L+L) + \beta G(G_2) + \gamma G(R_7) + H_{ss}(M^0,M^2,M^4) + H_{soo}(M^0,M^2,M^4)$$
$$+ H_{oo}(M^0,M^2,M^4) + H_{ci}(P^2,P^4,P^6) + \sum_{\substack{i=1\\ i\neq 5}}^{8} t_i T^i \ . \tag{1}$$

The first three terms are the electrostatic interaction cast in a form due to Racah.[5] The E^k's are combinations of Slater integrals which are treated as adjustable parameters and the ϵ_k's are angular operators which have been tabulated by Nielson and Koster.[6] The fourth term, $\xi \sum_i \vec{s}_i \cdot \vec{l}_i$, is the spin-orbit interaction with ξ being an adjustable parameter. The next three terms are two-body configuration-interaction terms; α, β, and γ are adjustable parameters and $G(G_2)$ and $G(R_7)$ are eigenvalues of Casimir's operator for the groups G_2 and R_7.[7] The terms H_{ss}, H_{soo}, and H_{oo} stand for spin-spin, spin–other-orbit, and orbit-orbit interactions. They are functions of M^0, M^2, and M^4 which are the so-called Marvin integrals,[8] which are treated as adjustable parameters. The term H_{ci} is the electrostatically correlated spin-orbit interaction.[9,10] The quantities P^2, P^4, and P^6 are essentially radial integrals which are also treated as adjustable parameters. The remaining terms in the Hamiltonian are the effective three-body interactions.[11]

The matrix of the free-ion Hamiltonian in the Russell-Saunders basis can be diagonalized to obtain the intermediate coupled eigenvectors. The diagonalization is carried out several times by iteratively varying the adjustable parameters to minimize the rms deviation

$$\left(\sum_{i=1}^{n} \frac{(E_e^i - E_c^i)^2}{n-p}\right)^{1/2}, \tag{2}$$

where E_e^i is the center of gravity of the ith experimental manifold, E_c^i is the calculated energy, n is the number of experimental centers of gravity used in the fit, and p is the number of parameters varied. The "best-fit" parameters, i.e., those giving the minimum rms deviation for Eq. (2), are then used to generate intermediate coupled eigenvectors for use in the crystal-field calculations.

B. Crystal field

The perturbation Hamiltonian for a crystal field for C_s symmetry involves complex coefficients and can be written as

$$H_{\mathrm{CF}} = \sum_{j=1}^{N} V_j ,$$

$$\begin{aligned} V_j = [&B_0^2 C_0^2 + \mathrm{Re}B_2^2(C_2^2 + C_{-2}^2) + i\,\mathrm{Im}B_2^2(C_2^2 - C_{-2}^2) + B_0^4 C_0^4 + \mathrm{Re}B_2^4(C_2^4 + C_{-2}^4) \\ &+ i\,\mathrm{Im}B_2^4(C_2^4 - C_{-2}^4) + \mathrm{Re}B_4^4(C_4^4 + C_{-4}^4) + i\,\mathrm{Im}B_4^4(C_4^4 - C_{-4}^4) + B_0^6 C_0^6 + \mathrm{Re}B_2^6(C_2^6 + C_{-2}^6) + i\,\mathrm{Im}B_2^6(C_2^6 - C_{-2}^6) \\ &+ \mathrm{Re}B_4^6(C_4^6 + C_{-4}^6) + i\,\mathrm{Im}B_4^6(C_4^6 - C_{-4}^6) + \mathrm{Re}B_6^6(C_6^6 + C_{-6}^6) + i\,\mathrm{Im}B_6^6(C_6^6 - C_{-6}^6)]_j . \end{aligned} \tag{3}$$

The complete specification of the crystal field of $YAlO_3:R^{3+}$ requires the fitting of fifteen B_q^k parameters. Only fourteen of these parameters are independent; thus the number of parameters to be fit could be reduced to fourteen by a suitable axis rotation. We have chosen not to do this, however, for the following reason. In Ref. 4 an approach for obtaining physically correct coefficients for $YAlO_3:Tm^{3+}$ was described. This approach utilized all fifteen parameters for reasons described in Ref. 4. Since we have used the results of the $YAlO_3:Tm^{3+}$ as starting parameters for the $YAlO_3:Er^{3+}$ calculations, we have thus fit all fifteen parameters.

III. RESULTS AND DISCUSSION

A. Free-ion calculations

The results of the free-ion calculation are given in Tables I and II. The computer programs for these calculations have been verified by reproducing other calculations which appear in the literature. It will be noted from Table II that the inclusion of the spin-spin, spin–other-orbit, orbit-orbit, electrostatically correlated configuration interaction, and three-body interactions account for considerable improvement in the calculation, namely, a decrease in the rms error from 70.8 to 29.1 cm^{-1}. We also observe a significant change in the E^1 parameter and an order of magnitude change in the configuration interaction parameter γ.

While the additional parameters improved the calculation, the calculation was more sensitive to some parameters than others. In addition to the usual parameters E^1, E^2, E^3, ξ, α, β, and γ, the calculation was most sensitive to T^3 and T^4. The calculations were not insensitive to T^8 as observed by Carnall *et al.*[12] for $LaF_3:Er^{3+}$ and $ErCl_3 \cdot 6H_2O$. It will be noted in Table II that the Marvin integrals M^2 and M^4 were fixed by their Hartree-Fock ratios M^2/M^0 and M^4/M^0.[10] This was done in order to reduce the number of independent parameters and to avoid the problem of obtaining unphysical values for M^2 and M^4 as has been the experience of some investigators.

The value obtained for γ is somewhat surprising and interesting. Most previous calculations for

TABLE I. Comparison of calculated and experimental centers of gravity of $YAlO_3$: Er^{3+}.

Free-ion manifold[a]	Experimental center of gravity, E_e(cm^{-1})	Calculated center of gravity, E_c(cm^{-1})	$E_e - E_c$ (cm^{-1})
$^4I_{15/2}$	256.5	230.0	26.5
$^4I_{13/2}$	6725.9	6740.5	−14.6
$^4I_{11/2}$	10 338.1	10 346.3	−8.2
$^4I_{9/2}$	12 568.5	12 563.7	4.8
$^4F_{9/2}$	15 371.4	15 400.0	−28.6
$^4S_{3/2}$	18 446.4	18 443.6	2.8
$^2H_{11/2}$	19 214.8	19 213.0	1.8
$^4F_{7/2}$	20 584.4	20 582.9	1.5
$^4F_{5/2}$	22 227.4	22 202.5	24.9
$^4F_{3/2}$	22 526.4	22 535.5	−9.1
$^2G_{9/2}$	24 626.8	24 621.4	5.4
$^4G_{11/2}$	26 411.8	26 423.5	−11.7
$^4G_{9/2}$	27 471.7	27 461.3	10.4
$^2K_{15/2}$	27 724.8	27 750.5	−25.7
$^2G_{7/2}$	27 894.6	27 897.2	−2.6
$^2P_{3/2}$	31 517.1	31 522.4	−5.3
$^2K_{13/2}$	33 068.5	33 043.5	25.0
$^2P_{1/2}$		33 054.5	
$^4G_{5/2}$		33 195.8	
$^4G_{7/2}$	33 988.7	33 991.5	−2.8
$^2D_{5/2}$	34 780.2	34 783.6	−3.4
$^2H_{9/2}$	36 491.9	36 485.0	6.9
$^4D_{5/2}$	38 423.0	38 419.8	3.2
$^4D_{7/2}$	39 058.5	39 059.8	−1.3
			rms = 29.1

[a] Only those multiplets for which have been observed experimentally (Ref. 1) are presented.

Er^{3+} have found γ to be in the range 1000–1500 cm^{-1}.[12,13] Recent calculations by Crosswhite *et al.*[14,15] on other lanthanide ions have found γ to be around 1500 cm^{-1}. The fact that we obtain a value of γ two to three times this is not readily explainable. Carnall *et al.*[12,13] did not include all of the interactions in their free-ion Hamiltonian as have been included here; however, it is unlikely that this is the explanation for the large value of γ because these additional interactions have been included by Crosswhite *et al.*[14,15] The only differences between our free-ion calculations and those of Crosswhite *et al.* are (i) the orbit-orbit interaction has been included explicity in our calculation whereas Crosswhite *et al.* have implicitly included the orbit-orbit interaction in the two-body configuration-interaction terms. This will have some effect on the values obtained for α, β, and γ as well as the Marvin integrals, but it would be very surprising if it could account for such a large difference in the value of γ. (ii) Crosswhite *et al.* fixed P^4 and P^6 by their Hartree-Fock ratios whereas we have allowed them to vary freely. In addition, the values of the P^k's obtained by Crosswhite *et al.* are two orders of magnitude larger than ours, (iii) Crosswhite *et al.* used $LaCl_3$ data for their calculations and simultaneously fit the free ion and crystal-field parameters whereas we have fit the free ion and $YAlO_3$ crystal field separately using the free-ion crystal-field model. It is well known that free-ion calculations done in this manner do not properly account for center-of-

TABLE II. Comparison of free-ion parameters for this work and Ref. 1 and 12. [The brackets on M^2 and M^4 indicate that they are held at their Hartree-Fock ratios (Ref. 10).]

Coefficient	Er^{3+} free ion Ref. 12 (cm^{-1})	$YAlO_3:Er^{3+}$ Ref. 1 (cm^{-1})	$YAlO_3:Er^{3+}$ This work (cm^{-1})
E^1	6636	6786.3	6174.0
E^2	32.910	32.415	32.836
E^3	652.06	643.27	651.69
ξ	2383.1	2380.7	2350.5
α	22.549	21.721	27.825
β	−814.58	−683.43	−722.32
γ	1553.9	389.03	3729.4
M^0			3.524
M^2			[1.974]
M^4			[1.339]
P^2			2.4779
P^4			−0.0406
P^6			0.1247
T^2	[0]		157.04
T^3	75		42.522
T^4	155		62.23
T^6	−162		−259.93
T^7	358		402.94
T^8	[0]		66.377
rms deviation	53	70.8	29.1

gravity shifts caused by J mixing, however, such effects should be insignificant because J mixing is expected to be small in Er^{3+}.[16] In addition, if this were responsible for such large differences in γ, it would have to raise serious questions about the validity of the free-ion model crystal-field approximation.

B. Crystal-field calculations

We have completed a crystal-field calculation which fits 15 C_s parameters to 46 twofold-degenerate Stark splittings in $YAlO_3:Er^{3+}$. Tables III and IV display the results of the crystal-field calculations. The ${}^4F_{3/2}$ state was given zero weight in the fitting procedure because it appeared to be relatively insensitive to the parameter fit. It was thus decided weight it zero in order that it not have a distorting effect on the fitting procedure. The calculations do an excellent job of describing the crystal field of $YAlO_3:Er^{3+}$ with the exception of the ${}^4F_{3/2}$ manifold. Why this particular manifold is so insensitive to the calculation is not clear.

Table III shows the observed and calculated Stark splittings for the lowest twelve manifolds. This calculation involved diagonalizing a 59×59 matrix and fitting the crystal-field coefficients by minimizing the rms deviation given by Eq. (2), where E_e^i is splitting of the ith observed Stark level from its manifold center of gravity and E_c^i is the splitting of the ith calculated Stark level from its manifold center of gravity. Although Donlan and Santiago[1] presented Stark data for 22 J manifolds (104 twofold-degenerate Stark levels), we have arbitrarily terminated the basis at 59 Stark levels because of the time involved in diagonalizing such large matrices. This will undoubtedly introduce some error into the calculations for the higher-lying states because of J mixing from close levels which have not been included in the basis.

The rms error of 6.9 cm^{-1} which we obtained for this calculation compares favorably with other calculations for Er^{3+} which fit a similar number of crystal-field parameters to a low-symmetry crystal field.[16-18] Harrop[17] has fit 15 monoclinic parameters for $ErCl\cdot 6H_2O$ and Stedman and Newman[16] have fit 14 monoclinic parameters to 38 Stark levels of $LaF_3:Er^{3+}$ obtaining a rms error of 4.1 cm^{-1} in a crystal-field calculation which did not include J mixing. Recently Karayianis *et al.*,[18] using the data of Ref. 1, fit 14 C_s parameters to 33 Stark levels of $YAlO_3:Er^{3+}$ obtaining a rms error of 7.46 cm^{-1}. The coefficients obtained by Karayianis *et al.* are for the most part different than those listed in Table IV. This difference is attributable to two facts: (i) although the C_s crystal field is independent of the orientation of the x-y axis, our calculation refers to a specific orientation of the x-y axis, namely the crystallographic axis.[4] Since Karayianis *et al.* fit only 14 C_s parameters, their calculation refers to a

TABLE III. Comparison of observed and calculated Stark splittings from the center of gravity of the 12 lowest J manifolds of $YAlO_3:Er^{3+}$.

Multiplet	Empirical label	Obs. splitting (cm^{-1})	Calc. splitting (cm^{-1})	Δ (cm^{-1})
$^4I_{15/2}$	*Z*1	−256.5	−256.0	0.5
	2	−205.8	−210.7	−4.9
	3	−85.9	−84.1	1.8
	4	−38.9	−42.0	−3.1
	5	9.4	11.1	1.7
	6	131.4	135.0	3.6
	7	186.5	183.7	−2.8
	8	259.8	263.0	3.2
$^4I_{13/2}$	*Y*1	−123.7	−127.5	−3.8
	2	−85.1	−85.0	0.1
	3	−57.0	−56.0	1.0
	4	−11.1	−13.2	−2.1
	5	47.1	44.5	−2.6
	6	88.1	88.2	0.1
	7	141.8	149.0	7.2
$^4I_{11/2}$	*A*1	−56.3	−55.3	1.0
	2	−45.4	−50.8	−5.4
	3	−15.8	−18.9	−3.1
	4	8.8	12.6	3.8
	5	43.7	38.5	−5.2
	6	64.9	74.0	9.1
$^4I_{9/2}$	*B*1	−175.2	−169.9	5.3
	2	−122.9	−121.4	1.5
	3	55.0	45.6	−9.4
	4	79.5	83.8	4.3
	5	163.6	161.9	−1.7
$^4F_{9/2}$	*D*1	−108.7	−105.6	3.1
	2	−27.9	−34.1	−6.2
	3	2.2	6.7	4.5
	4	24.9	26.1	1.2
	5	109.3	106.7	−2.6
$^4S_{3/2}$	*E*1	−40.3	−36.1	4.2
	2	40.3	36.1	−4.2
$^2H_{11/2}$	*F*1	−96.1	−85.0	11.1
	2	−52.6	−52.9	−0.3
	3	−25.1	−14.5	10.6
	4	25.2	16.4	−8.8
	5	60.3	60.8	0.5
	6	88.4	75.2	−13.2
$^4F_{7/2}$	*G*1	−102.9	−96.4	6.5
	2	−30.0	−32.1	−2.1
	3	32.3	30.7	−1.6
	4	100.6	97.8	−2.8
$^4F_{5/2}$	*H*1	−31.6	−24.8	6.8
	2	−0.4	−9.1	−8.7
	3	31.9	33.9	2.0
$^4F_{3/2}$	*I*1	−10.0	−48.3	···
	2	−10.0	48.3	···
$^2G_{9/2}$	*K*1	−148.0	−147.4	0.6
	2	−100.9	−96.5	4.4
	3	39.1	37.4	−1.7
	4	71.1	72.2	1.1
	5	138.7	134.4	−4.3

TABLE III. (*Continued*)

Multiplet	Empirical label	Obs. splitting (cm^{-1})	Calc. splitting (cm^{-1})	Δ (cm^{-1})
$^4G_{11/2}$	$L1$	-104.2	-104.2	0.0
	2	-89.8	-90.7	-0.9
	3	-31.4	-35.6	-4.2
	4	46.7	41.8	-4.9
	5	64.6	78.0	-13.4
	6	114.1	110.7	-3.4
			rms deviation[a] = 6.9	

[a] The rms deviation was obtained from Eq. (2) where n stands for 46 energy differences and p stands for 14 independent B_q^k parameters.

different orientation of the x-y axis thus yielding different values for some of the coefficients. (ii) The fact that the two calculations had quite different starting values for the parameters implies a strong probability that we have obtained different minima. This is substantiated by the fact that the B_0^2 coefficient in the two calculations is different, we obtain $-183.2\ \text{cm}^{-1}$ for B_0^2 whereas Karayianis *et al.* obtained a value of $431\ \text{cm}^{-1}$. Since the $q=0$ coefficients are invariant to a z-axis rotation it would appear that we are indeed describing different minima. It is also of interest to compare the other $q=0$ coefficients in this calculation and those of Karayianis *et al.* For B_0^4 we obtained $-816.2\ \text{cm}^{-1}$ as compared to $-839\ \text{cm}^{-1}$ for their calculation, and for B_0^6 we obtained $-603.8\ \text{cm}^{-1}$ while their calculation yielded $-724\ \text{cm}^{-1}$.

Table IV compares the crystal-field coefficients for $\text{YAlO}_3\text{:Er}^{3+}$ obtained in this paper with those of a previous calculation[4] on $\text{YAlO}_3\text{:Tm}^{3+}$. It is of interest to compare the $\text{YAlO}_3\text{:Tm}^{3+}$ calculations and the $\text{YAlO}_3\text{:Er}^{3+}$ calculations since their electronic configurations differ only by one f electron. As previously stated, for a one-electron potential, one would expect these two calculations to yield similar coefficients in a common host. Failure to do so should indicate that the correlation crystal field[19-21] due to a two-electron potential or even higher-order n electron potentials is not insignificant.[21,22] We see from Table IV that many of the parameters are consistent between $\text{YAlO}_3\text{:Er}^{3+}$ and $\text{YAlO}_3\text{:Tm}^{3+}$ whereas others change more than one would expect on the basis of a one-electron potential.

IV. CONCLUSIONS

The large number of crystal-field coefficients needed to describe the Stark splittings of a rare-earth ion in C_s site symmetry makes it very difficult to derive the "correct" set of coefficients. In a fitting process that starts with an arbitrary set of crystal-field parameters and attempts to minimize the deviation between calculated and experimental energy levels by cyclically varying the parameters, the probability is great that a local minimum rather than the global minimum will be reached. In order to reduce the probability of converging on some local minimum, we have applied two physical constraints. First, in an even electron rare-earth-ion system the Γ_1 and Γ_2 point-group representations of each energy level, as determined experimentally from polarized spectra, can be used to eliminate local minima that fail to reproduce the correct ordering of the representations. This effectively doubles the probability of finding the global minimum. For this reason, we chose an even electron system, Tm^{3+}, to perform our first crystal-field calculation for YAlO_3.[4] Second, by starting the calculation with a physically realistic initial set of param-

TABLE IV. Crystal-field coefficients, C_s symmetry.

Coefficient	$\text{YAlO}_3\text{:Tm}^{3+}$ Ref. 4 (cm^{-1})	$\text{YAlO}_3\text{:Er}^{3+}$ This work (cm^{-1})
B_0^2	-434.9	-183.2
$\text{Re}B_2^2$	420.8	385.6
$\text{Im}B_2^2$	199.4	185.2
B_0^4	-691.6	-816.2
$\text{Re}B_2^4$	444.9	444.0
$\text{Im}B_2^4$	114.2	39.7
$\text{Re}B_4^4$	501.2	637.0
$\text{Im}B_4^4$	-389.2	-222.8
B_0^6	-260.4	-603.8
$\text{Re}B_2^6$	175.6	-42.2
$\text{Im}B_2^6$	229.7	305.4
$\text{Re}B_4^6$	92.7	229.7
$\text{Im}B_4^6$	542.4	523.8
$\text{Re}B_6^6$	410.5	317.0
$\text{Im}B_6^6$	113.4	87.0
rms dev.	30.3	6.9

eters, the probability of converging to the global minimum is further enhanced. Our approach to obtaining physically plausible starting parameters for the $YAlO_3$:Tm^{3+} calculation was to fit a set of cubic crystal-field parameters to a pseudoset of energy levels obtained by combining clusters of Stark levels of a selected group of lines ($^1G_4$). Starting with these "effective cubic field" parameters, we then fit, in succession, sets of tetragonal, orthorhombic, and finally the monoclinic C_s parameters. The physical basis for forcing the final C_s parameters to be descended from hypothetical cubic field ancestors is the fact that the actual $YAlO_3$ lattice is only slightly distorted from the ideal cubic perovskite lattice. Thus we can be reasonably confident that the crystal-field parameters derived in the Tm^{3+} calculation represent, if not the global minimum, at least a nearby local minimum. The fact that this set of parameters, used as a starting set for the $YAlO_3$:Er^{3+} calculation reported here, leads rapidly to a minimum with a satisfyingly low rms error gives us even more confidence.

As a check on the self-consistency of the final Tm^{3+} and Er^{3+} crystal-field parameters, the Er^{3+} parameters were used as a starting set for the Tm^{3+} system. The parameters converged rapidly back to the Tm^{3+} set. This self-consistency, however, does not shed any light on the fact that large changes take place in some of the parameters in going from Tm^{3+} to Er^{3+}. If these changes reflect some property such as the correlation crystal field then efforts to predict regular changes in one electron crystal-field parameters across the entire rare-earth series using simple models are doomed to failure.

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