PHYSICAL REVIEW B VOLUME 27, NUMBER 12 15 JUNE 1983

Electrostatic crystal-field contributions in rare-earth compounds with consistent multipolar effects. II. Contribution to k-odd parameters (transition probabilities)

D. Garcia and M. Faucher
Laboratoire des Eléments de Transition dans les Solides, Equipe de Recherche No. 060210 du Centre National de la Recherche Scientifique, 1 Place A. Briand, F-92190 Meudon, France

O. L. Malta
Departamento de Química da Universidade Federal de Pernambuco, Cidade Universitária, 50000 Recife, Pernambuco, Brazil

(Received 20 May 1982; revised manuscript received 12 October 1982)

k-odd electrostatic crystal-field parameters (β_q^k) involved in the Judd-Ofelt theory of electronic transitions within the $4f^n$ configuration are computed including contributions of point charges, consistent dipoles, and quadrupoles induced in a crystalline lattice (calculated and experimental intensity parameters Ω_λ are compared). The coefficients (γ_q^k) involved in the pseudo-multipolar-field theory are also computed for 14 rare-earth or rare-earth—doped compounds (i.e., for $LiYF_4:Nd^{3+}$, YOBr, and $YOCl:Eu^{3+}$; BaFCl and $SrFCl:Sm^{2+}$; $BaTiO_3:Eu^{3+}$, $NdAlO_3$, and $LaAlO_3:Eu^{3+}$; Nd_2O_3, Nd_2O_2S, LaF_3, and $LaCl_3:Nd^{3+}$; Y_2O_3 and $KY_3F_{10}:Eu^{3+}$). The contribution of γ_q^k to transition rates is evaluated for the $^5D_0 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} in Y_2O_3 and compared with the experimental values.

I. INTRODUCTION

In Ref. 1 we presented the calculation of consistent point-charge, dipolar, and quadrupolar contributions to the electrostatic crystal-field parameters (CFP) of rare earths or actinides in crystalline materials. Values of the k-even CFP were listed for 16 rare-earth, rare-earth—doped, and actinide compounds. k-odd CFP are involved in several mechanisms allowing electronic transitions within the $4f^N$ (or $5f^N$) configurations, namely in the framework of the Judd-Ofelt[2,3] and the "pseudomultipolar-field"[4–7] theories. We shall presently give the values of the k-odd CFP for 14 out of the 16 compounds studied in Ref. 1, i.e., $LiYF_4$, YOBr, YOCl, BaFCl, SrFCl, $BaTiO_3$, $NdAlO_3$, $LaAlO_3$, Nd_2O_3, Nd_2O_2S, LaF_3, $LACl_3$, Y_2O_3, and KY_3F_{10}.

The necessary formulas for the computations are basically Eqs. (10), (C1), (C2), (A1), (A2), and (A3) of Ref. 1. The input data are the ionic charges, the dipolar, and quadrupolar polarizabilities, and the crystal structure. All necessary references may be found in Ref. 1.

II. THE β_q^k OF THE JUDD-OFELT THEORY

The k-odd CFP allow an admixture of $4f^N$ with configurations of opposite parity, therefore producing small nonzero matrix elements for the electric dipole operator between the mixed states of the $4f^N$ configuration. The transition probabilities may in principle be calculated by the means of Eqs. (13), (14), and (15) in Ref. 2. The expression for total emission between manifolds J and J' is

$$S_{J\rightarrow J'}=\frac{64\pi^4 e^2}{3h\bar{\lambda}^3}\,\frac{n(n^2+2)^2}{9}\sum_{\lambda=2,4,6}\Omega_\lambda\frac{(\langle SLJ\,|\,U^{(\lambda)}\,|\,S'L'J'\rangle)^2}{2J+1} \tag{1}$$

with

$$\Omega_\lambda=(2\lambda+1)\sum_{k,q}\frac{|\beta_q^k|^2}{2k+1}\Xi^2(k,\lambda)\;, \tag{2}$$

and

$$\Xi(k,\lambda)=14\sum_{n',l'}(2l'+1)(-1)^{1+l'}\begin{Bmatrix}1&\lambda&k\\3&l'&3\end{Bmatrix}\begin{bmatrix}3&1&l'\\0&0&0\end{bmatrix}\begin{bmatrix}l'&k&3\\0&0&0\end{bmatrix}\frac{\langle 4f\,|\,r\,|\,n'l'\rangle\langle 4f\,|\,r^k\,|\,n'l'\rangle}{\Delta_{n'l'}}\;, \tag{3}$$

©1983 The American Physical Society

TABLE I. k-odd lattice sums $\beta_q^k = B_q^k / \langle r^k \rangle$, $\sigma_q^k = S_q^k / \langle r^k \rangle$ in $(a_0)^{-k} \cdot \mathrm{cm}^{-1}$, and γ_q^k defined by (1) in $(a_0)^{-k} \cdot \text{Å}^3\,\mathrm{cm}^{-1}$ for Nd_2O_3 and Nd_2O_2S.

Compound site symmetry	Contribution	β_0^1	β_0^3	β_3^3	β_0^5	β_3^5	β_0^7	β_3^7	β_6^7
	PC	11940	229	−1014	116.5	60.6	−1.25	0.73	2.84
		(11717)	(536)	(−1160)	(121)	(50.5)	(−1.16)	(0.46)	(2.84)
Nd_2O_3[a]	PC + dip	9251	371	991	118.9	58.1	−1.00	0.84	2.82
		(12616)	(554)	(−1135)	(123)	(47.9)	(−0.91)	(0.57)	(2.82)
(C_{3v})	PC + dip + quad	8774	−506	−1160	121.9	50.8	−6.5	3.41	4.82
		(11063)	(−342)	(−1293)	(125)	(41.7)	(−6.41)	(3.14)	(4.82)
	γ		−185	848	−79.8	−25.3	0.84	−0.09	−1.91
			(−362)	(783)	(−81.9)	(−34)	(0.78)	(−0.30)	(−1.91)
	PC	8079	254	−1203	127	45.6	0.21	0.79	2.73
		(12580)	(349)	(−1327)	(123)	(40.0)	(0.13)	(0.68)	(2.75)
Nd_2O_2S[b]	PC + dip	7944	398	−1112	135	38.4	1.11	1.23	2.71
		(15193)	(420)	(−1243)	(130.8)	(31.9)	(1.05)	(1.09)	(2.73)
(C_{3v})	PC + dip + quad	10204	165	−981	115	35.3	−1.95	1.39	2.95
		(17121)	(185)	(−1111)	(110.8)	(28.9)	(−2.0)	(1.27)	(2.98)
	γ		−497	213	−48.2	−27.6	0.34	−0.18	−0.66
			(−479)	(147)	(−50.9)	(−30.5)	(0.31)	(−0.23)	(−0.65)

[a]( ) equals contributions from seven first neighbors O^{2-} at 2.300 (three), 2.400 (one), and 2.657 Å (three).

[b]( ) equals contributions from seven first neighbors at 2.3615 (three O^{2-}), 2.3636 (one O^{2-}), and 2.9645 Å (three S^{2-}).

TABLE II. k-odd lattice sums β_q^k, σ_q^k, and γ_q^k for $LaCl_3$, $NdAlO_3$, and $LaAlO_3$.

Compound site symmetry	Contribution	β_3^3	σ_3^3	β_3^5	σ_3^5	β_3^7	σ_3^7	σ_6^7
	PC	21.3	153.8	−26.8	−4.2	−0.21	−0.07	
		(148.8)	(17.5)	(−26.8)	(−5.8)	(−0.20)	(−0.07)	
$LaCl_3$[a]	PC + dip	183.8	−159.4	−34.4	−12.6	−0.5	−0.48	
		(275.0)	(−265.6)	(−34.0)	(−14.4)	(−0.3)	(−0.48)	
(C_{3h})	PC + dip + quad	164.4	−30	−43.4	4.0	−0.66	0.32	
		(218.8)	(−144.4)	(−43.5)	(1.3)	(−0.68)	(0.32)	
	γ	−372.5	293.8	71.45	−2.1	0.6	0.02	
		(−399.6)	(53.6)	(73.8)	(−2.5)	(0.6)	(0.01)	
	PC		−842.5		69.8		−0.46	0.32
			(−756.3)		(70.7)		(0.45)	(0.32)
$NdAlO_3$[b]	PC + dip		−945		77.6		−0.59	0.34
			(−849.4)		(78.6)		(−0.59)	(0.34)
(D_3)	PC + dip + quad		−954.4		54.2		−1.7	−2.36
			(−806.9)		(55.5)		(−1.7)	(−2.36)
	γ		571.3		−47.1		0.29	−0.21
			(510)		(−95.4)		(0.31)	(−0.21)
	PC		382.4		−31.71		0.08	−0.16
			(339.8)		(−31.97)		(0.08)	(−0.16)
$LaAlO_3$[c]	PC + dip		423.5		−34.98		0.08	−0.16
			(376.8)		(−35.24)		(0.08)	(−0.16)
(D_3)	PC + dip + quad		349.4		−23.7		0.04	0.701
			(279.4)		(−24.2)		(0.04)	(0.70)
	γ		−258.5		21.4		−0.04	0.12
			(−229.4)		(43.0)		(−0.06)	(0.11)

[a]( ) equals contributions from nine first neighbors Cl^- at 2.9504 (six) and 2.9534 Å (three).

[b]( ) equals contributions from twelve first neighbors O^{2-} at 2.3896 (three), 2.6586 (six), and 2.9324 Å (three).

[c]( ) as for (b) but at 2.5484, 2.6816, and 2.8166 Å.

TABLE III. k-odd lattice sums β_q^k, σ_q^k, and γ_q^k for LaF_3, Y_2O_3, and $LiYF_4$.

Compound site symmetry	Contribution	β_0^1	β_0^3	β_2^3	σ_2^3	β_0^5	β_2^5	σ_2^5
	PC	871	−172	−255	152	−31.6	13.5	−21.3
		(811)	(−100)	(−270)	(121)	(−35.2)	(14.0)	(−22.0)
LaF_3[a]	PC + dip	847	−198	−212	200	−32.9	14.2	−21.9
		(894)	(−131)	(−217)	(164)	(−36.6)	(14.7)	(−22.4)
(C_2)	PC + dip + quad	645	−219	−269	282	−40.5	13.1	−25.8
		(772)	(−157)	(−276)	(249)	(−44.0)	(13.4)	(−26.5)
	γ		88.1	−3.1	−216.3	26.9	10.81	15.0
			(73)	(−7.0)	(−216.0)	(25.8)	(11.0)	(15.6)
	PC	−528	−1360	1026	−149	109.5	15.1	−11
		(6286)	(−1659)	(1190)	(−154)	(103.5)	(13.6)	(−11.1)
Y_2O_3[b]	PC + dip	2041	−1425	936	−163	101.4	9.6	−9.1
		(9629)	(−1708)	(1100)	(−170)	(95.4)	(7.8)	(−9.1)
(C_2)	PC + dip + quad	−4342	−658	2604	147	159	49.1	−23.9
		(4473)	(−956)	(2757)	(188)	(152)	(48.8)	(−22.6)
	γ		1088	−844	72	−67.2	−10.2	7.3
			(1120)	(−803)	(104)	(−69.8)	(−9.2)	(7.5)
	PC			−89.4	−1075		110.8	1.9
				(−218.1)	(140)		(110.3)	(8.9)
$LiYF_4$[c]	PC + dip			−305.6	153.7		126.6	9.8
				(−418.7)	(379.4)		(126.9)	(16.6)
(S_4)	PC + dip + quad			−362.5	163.7		162.3	11
				(−468.7)	(390.0)		(161.9)	(17.6)
	γ			(203.7)	−254.4		−78.7	−4.5
				(156.0)	(−108.0)		(−80.8)	(−4.0)

where e,h,n,λ stand for the electronic charge, Planck's constant, the refractive index of the material, and the transition wavelength, respectively. S,L,J and S',L',J' are the intermediate-coupling labels for the wave function of the initial and final states, respectively, but are in fact linear combinations of such states mixed by spin-orbit or crystal-field interaction. β_q^k are k-odd lattice sums. n',l' are the principal and orbital quantum numbers of the mixing configurations. The $\Delta_{n'l'}$ are the mean energy differences between the $4f^N$ and the $n'l'$ configurations.

Expression (1) was mostly utilized to derive the Ω_λ as "intensity parameters" from experimental data.[4–7,9] Attempts to derive *a priori* values of the Ω_λ have been more or less successful.[5,8] Various reasons, besides the inaccuracy of the lattice sums β_q^k may explain the discrepancy between the experimental and calculated values, firstly, the uncertainties of the matrix elements $|U^\lambda|^2$ utilized to calculate the experimental Ω_λ's, and secondly, the approximations made in the evaluation of the radial integrals included in the expression of $\Xi(k,\lambda)$.

In Tables I–IV the lattice sums β_q^k, σ_q^k are listed (real and imaginary parts, respectively) which are to be utilized in (2). The β_q^k,σ_q^k ($a_0^{-k}\cdot\mathrm{cm}^{-1}$) include converged and first neighbors, point charge, dipolar, and quadrupolar contributions. *They were calculated by Eqs. (A1), (A2), and (A3) of Ref. 1, in which* $\langle r^k\rangle$ *was omitted;* therefore they are quantities dependent only upon the host. Three cases were considered: point-charge—only contribution (PC), contribution from dipoles in equilibrium with point charges (PC + dip), and contribution of consistent point charges, dipoles, and quadrupoles (PC + dip + quad). When the separate contributions are examined [they are not listed for the sake of clarity (separate contributions—point charge, dipolar, and quadrupolar—are available on request) since only the total β_q^k (σ_q^k) are useful], the divergence of the multipole series is apparent. This point is made still more evident by the examination of the octupolar term (which was evaluated without regard to consistency) for the k-even B_q^k in BaFCl:Sm^{2+} (see Ref. 1). It suggests that the following points should be considered:

(a) The multipolar polarizabilities are possibly overestimated, when free-ion values are utilized.

(b) The assumption that characterizes the electrostatic model, in which the existence of chemical

TABLE III. (*Continued.*)

β_4^5	σ_4^5	β_0^7	β_2^7	σ_2^7	β_4^7	σ_4^7	β_6^7	σ_6^7
-36.4	1.8	-1.07	-0.23	-0.77	$+0.21$	-0.045	-0.93	-0.84
(-38.7)	(5.0)	(-1.11)	(-0.20)	(-0.75)	(-0.18)	(-0.020)	(-0.91)	(-0.84)
-38.5	6.5	-0.93	-0.27	-0.77	$+0.25$	-0.068	-1.23	-0.84
(-40.8)	(9.5)	(-0.95)	(-0.27)	(-0.75)	(0.23)	(-0.068)	(-1.23)	(-0.84)
-46.5	16.8	-1.3	-0.41	-1.05	0.46	-0.16	-1.61	-0.73
(-47.6)	(20.3)	(-1.3)	(-0.39)	(-1.00)	(0.43)	(-0.14)	(-1.59)	(-0.73)
-23.7	-17.4	0.84	0.55	0.07	0.09	0.09	-0.86	-0.29
(-22.6)	(-17.3)	(0.81)	(0.56)	(0.06)	(0.11)	(0.08)	(-0.85)	(-0.30)
75.3	43	-0.12	1.28	0.62	-4.33	0.54	2.19	0.17
(66.4)	(42)	(0.20)	(1.24)	(0.58)	(-4.41)	(0.41)	(2.14)	(0.12)
85.3	40.8	0.12	1.07	0.58	-3.71	0.62	1.98	-0.12
(76.5)	(39.8)	(0.41)	(1.03)	(0.54)	(-3.79)	(0.50)	(1.94)	(-0.16)
3.5	60.7	-3.3	-8.82	0.21	-11.05	2.43	8.7	4.74
(-7.0)	(59.9)	(-3.0)	(-8.82)	(0.21)	(-8.70)	(2.34)	(8.7)	(4.74)
-41.8	26.4	-0.21	-0.87	-0.37	3.00	-0.25	-1.44	-0.04
(-44.9)	(-28.3)	(-0.13)	(-0.84)	(-0.39)	(2.98)	(-0.28)	(-1.46)	(-0.08)
			-0.07	0.16			3.00	0.16
			(-0.07)	(0.07)			(-2.93)	(0.18)
			0.55	0.34			-4.11	1.02
			(0.55)	(0.25)			(-4.05)	(1.05)
			0.16	0.02			-6.3	0.93
			(0.16)	(0.07)			(-6.2)	(0.95)
			0.02	-0.07			2.14	0.29
			(0.05)	(-0.06)			(2.12)	(-0.34)

[a]( ) equals contributions from eleven first neighbors F^- at 2.4214 (two), 2.4364 (two), 2.4665 (two), 2.4818 (two), 2.6376 (two), and 2.9992 Å (two).

[b]( ) equals contributions from six first neighbors O^{2-} at 2.2435 (two), 2.2677 (two), and 2.3371 Å (two).

[c]( ) equals contributions from eight first neighbors F^- at 2.2459 (four) and 2.2933 Å (four).

bonds is completely ignored, is not sufficient to provide a satisfactory description of crystal-field effects.

It may be useful to utilize some of the conclusions of the comparison between experimental and calculated values of the k-even B_q^k given in Ref. 1. The reliability factor was rather improved when the point charge plus dipolar contributions only are considered (which can be fairly well understood if the quadrupolar contribution is much too large). Therefore we shall utilize here the values (PC + dip).

A priori calculations of Ω_2 and Ω_4 were performed for the Eu^{3+} emission in Y_2O_3, KY_3F_{10}, and LaF_3 (as well as the Pr^{3+} emission in $LaAlO_3$). The β_q^k (σ_q^k) values (PC + dip) of Tables II–IV were utilized. The values of $\Xi(k,\lambda)$ were those of Ref. 5. The mixing configurations are the $5d$ and all the $n'g$. The results are listed in Table V with the experimental results of Refs. 5, 8, and 9. The discrepancy between the experimental and calculated values is serious. Contrary to what happens with k-even crystal-field parameters, no empirical correlation can be deduced between experimental and calculated Ω parameters. More meaningful is perhaps a comparison between the experimental and calculated values for the "sublevel" energy parameters $B_{\lambda kq}$ determined in Refs. 7 and 9. They are defined as

$$B_{\lambda kq}=\beta_q^k \Xi(k,\lambda) . \tag{4}$$

Unfortunately, experimental determinations of the $B_{\lambda kq}$ are very scarce and we listed in Table VI the results for $KY_3F_{10}:Eu^{3+}$ and $LaAlO_3:Pr^{3+}$.[7,9] The only striking fact, perhaps a mere coincidence, is the moderate agreement between experimental and calculated B_{45q} parameters. A systematic comparison over a whole set of compounds such as those presently investigated would probably be quite useful since it might at least provide some empirical scale factors such as those which allow us to predict, from the electrostatic model, the k-even "splitting" parameters for rare-earth elements in ionic solids.

III. THE PSEUDO-MULTIPOLAR FIELD

So as to explain the hypersensitivity of certain $f \rightarrow f$ transitions, which was not taken into account

TABLE IV. k-odd lattice sums β_q^k, σ_q^k, and γ_q^k for $BaTiO_3$, BaFCl, SrFCl, YOCl, YOBr, and KY_3F_{10}.

Compound site symmetry	Contribution	β_0^1	β_0^3	β_0^5	β_4^5	β_0^7	β_4^7
	PC	+ 2003	−130.4	−6.29	7.05	0.49	0.04
		(859)	(−30.6)	(−8.05)	(9.82)	(0.45)	(0.04)
$BaTiO_3$[a]	PC + dip	−2870	144.1	−16.61	12.08	0.87	−0.62
		(−6398)	(350.2)	(−18.88)	(16.86)	(0.82)	(−0.58)
(C_{4v})	PC + dip + quad	−2911	−16.9	2.52	−5.54	−0.16	−0.33
		(−7434)	(239.9)	(−0.25)	(0.5)	(−0.29)	(−0.33)
	γ		14.5	5.54	−6.8	−0.29	−0.04
			(20.8)	(5.40)	(−6.6)	(−0.31)	(−0.03)
	PC	−3855	382.3	9.28	−30.64	−0.66	−0.31
		(−6150)	(489.6)	(12.51)	(−29.34)	(−0.64)	(−0.31)
BaFCl[b]	PC + dip	−3482	353.1	9.17	−30.64	−0.67	−0.30
		(−6413)	(483.8)	(12.41)	(−29.45)	(−0.61)	(−0.30)
(C_{4v})	PC + dip + quad	−3457	337.5	9.28	−30.85	−0.68	−0.31
		(−6426)	(465.6)	(12.41)	(−29.56)	(−0.66)	(−0.31)
	γ		−157.8	−26.32	31.5	0.41	0
			(−215.8)	(−28.20)	(33.8)	(0.36)	(0)
	PC	−3813	456.8	12.84	−43.8	−1.04	−0.61
		(−6863)	(597.4)	(17.26)	(−41.9)	(−1.04)	(−0.55)
SrFCl[c]	PC + dip	−4113	422.9	12.51	−44.1	−1.09	−0.59
		(−7478)	(580.2)	(17.15)	(−42.2)	(−1.09)	(−0.53)
(C_{4v})	PC + dip + quad	−4012	395.3	12.19	−44.6	−1.13	−0.58
		(−4385)	(550.0)	(16.61)	(−42.7)	(−1.13)	(−0.52)
	γ		−46.4	−34.6	46.5	0.67	0.06
			(−216.1)	(−37.4)	(48.3)	(0.59)	(0.09)
	PC	−19192	1761	−12.33	−138.9	−3.46	−1.36
		(−48874)	(2205)	(−15.10)	(−120.6)	(−3.75)	(−1.28)
YOCl[d]	PC + dip	−17701	1667	−11.58	−139.7	−3.46	−1.32
		(−48874)	(2205)	(−15.10)	(−120.6)	(3.75)	(−1.28)
(C_{4v})	PC + dip + quad	−18687	1638	0.50	−137.7	−4.78	−2.51
		(−50021)	(2230)	(−1.26)	(−117.5)	(−5.03)	(−2.43)
	γ		−988	−18.9	108.0	2.18	0.45
			(1486.8)	(10.1)	(81.2)	(2.54)	(0.86)
	PC	−20659	1488	13.09	−105.2	−3.54	−2.84
		(−51393)	(1753)	(21.39)	(−95.13)	(−4.39)	(−3.39)
YOBr[e]	PC + dip	−21511	1243	17.12	−110.0	−3.54	−2.76
		(−51393)	(1753)	(21.39)	(−95.13)	(−4.39)	(−3.39)
(C_{4v})	PC + dip + quad	−18165	1336	−24.67	−126.9	−2.23	−0.50
		(−51393)	(1860)	(−18.37)	(−110.3)	(−2.20)	(−0.41)
	γ		692.6	−19.1	87.1	2.02	1.9
			(−1192.6)	(−14.4)	(62.8)	(2.53)	(1.8)
	PC	−2478	657	−43.3	−116.3	−0.66	−2.89
		(4045)	(636)	(−48.8)	(−116.3)	(−0.58)	(−2.76)
KY_3F_{10}[f]	PC + dip	−3353	757	−37.8	−118.6	−1.81	−4.2
		(3080)	(734)	(−43.0)	(−118.8)	(−1.73)	(−4.12)
(C_{4v})	PC + dip + quad	−4548	1200	−81.3	−204.4	−2.18	−3.05
		(1026)	(1185)	(−86.3)	(−204.6)	(−2.14)	(−2.93)
	γ		476.7	34.2	83.1	0.41	1.98
			(−456.6)	(35.6)	(85.0)	(0.43)	(2.02)

[a] ( ) equals contributions from twelve first neighbors O^{2-} at 2.7957 (four), 2.8263 (four), and 2.8817 Å (four).

[b] ( ) equals contributions from nine first neighbors at 2.649 (four F^-), 3.195 (one Cl^-), and 3.286 Å (four Cl^-).

[c] ( ) as for (b), but at 2.4943, 3.0712, and 3.112 Å.

[d] ( ) equals contributions from four first neighbors O^{2-} at 2.278 Å.

[e] ( ) as for (d), but at 2.347 Å.

[f] ( ) equals contributions from eight first neighbors F^- at 2.1957 (four) and 2.3312 Å (four).

TABLE V. Theoretical and experimental intensity parameters Ω_2 and Ω_4 in units of 10^{-20} cm^2.

Compound		Ω_2	Ω_4
Y_2O_3:Eu^{3+}	Calc.[a]	5.00	8.00
	Expt.[b]	6.31	0.66
KY_3F_{10}:Eu^{3+}	Calc.[a]	3.64	1.65
	Expt.[c]	0.906	0.92
LaF_3:Eu^{3+}	Calc.[d]	0.444	0.651
	Calc.[a]	0.404	0.498
	Expt.[e]	1.19	1.16
$LaAlO_3$:Eu^{3+}	Calc.[a]	1.09	2.77
	Expt.[f]	0.018	0.65

[a] Calculated with the β_q^k of Tables II–IV.
[b] Reference 5.
[c] Reference 9.
[d] Reference 8.
[e] Reference 10.
[f] Reference 7.

by the former theory, Jørgensen and Judd[11] proposed a mechanism allowing *directly* intraconfigurational transitions. The oscillating dipoles induced on the ligands by the incident electromagnetic field produce an extra oscillating field interacting with the 4f electron, therefore efficient in producing transitions. Mason *et al.*[12] and more recently Judd[13] and Malta[14] discussed the phenomenon. The interaction energy of the 4f electron with the oscillating dipoles is equal to

$$W=-e\sum_{k,q,q',q''}(-1)^{k+q+q''}[4\pi(k+1)(2k+1)]^{1/2}\times\frac{r_j^k}{R_\mu^{k+2}}\begin{pmatrix}k & 1 & k+1\\ q & q'' & -q'\end{pmatrix}\times P_{q''}^{(1)}[Y_{q'}^{k+1}(\Omega_\mu)]^*C_q^{(k)}(j)\ , \qquad (5)$$

where $k=2,4,6$; q, q', and q'' run from $-k$ to $+k$; j and μ stand for the 4f electron and the ligand, respectively.

An oscillating dipole is given as a function of the radiation field by

$$\vec{P}(\mu)=\alpha_\mu\vec{E}(\mu)\ , \qquad (6)$$

where α_μ is the dipolar polarizability of the ion. In the long-wavelength approximation, $\vec{E}(\mu)$ for a given polarization has the following expression:

$$\vec{E}(\mu)x=E_0e^{-i\omega t}\vec{e}_M\ , \qquad (7)$$

where $\vec{e}_M$ $(M=0,\pm1)$ is a unit spherical vector.

TABLE VI. Theoretical and experimental "sublevel" energy parameters $B_{\lambda kq}=\beta_q^k\Xi(k,\lambda)$ in units of 10^{-11} cm.

KY_3F_{10}:Eu^{3+}	B_{210}	B_{230}	B_{430}	B_{450}	B_{454}
Calc.[a]	13.6	8.93	9.13	1.84	5.79
Expt.[b]	−1.85	10.9	−1.45	2.95	7.10
$LaAlO_3$:Eu^{3+}	B_{233}	B_{433}	B_{453}		
Calc.[a]	8.73	9.93	3.78		
Expt.[c]	1.1	−3.5	4.5		

[a] Calculated with the β_q^k from Tables II–IV.
[b] Reference 9.
[c] Reference 7.

The total transition rate for a $J\rightarrow J'$ emission is then given by formula (6) of Ref. 14 and is identical to

$$S_{J,J'}=\frac{64\pi^4\chi}{3(2J+1)\lambda^3}\frac{3\times10^{10}}{219474a_0^3}\times\sum_k\langle J||U^{(k)}||J'\rangle^2(k+1)\langle f||C^{(k)}||f\rangle^2(1-\sigma_k)^2\times\langle r^k\rangle^2|\gamma^{k+1}|^2\ , \qquad (8)$$

where the γ_q^k are the k-odd lattice sums,

$$\gamma_q^k=e^2\left[\frac{4\pi}{2k+1}\right]^{1/2}\sum_\mu\frac{\alpha_\mu}{R_\mu^{k+1}}[Y_q^k(\mu)]^*\ , \qquad (9)$$

with $|\gamma^k|=\sum_q\gamma_q^k\gamma_q^{k*}$ independent of the reference axes. γ_q^k is in units of $(a_0)^{-k}\cdot$Å^{3}cm^{-1}, α_μ in Å^3, λ in Å, and $\langle r^k\rangle$ in $(a_0)^k$ (*with the Bohr radius* $a_0=0.5292$ Å).

In Tables I–IV we have listed the converged sums γ_q^k involved in (8) as well as the first-neighbor contributions. Note that convergence is attained within distances much smaller than the transition wavelength. The calculation simply amounts to replace in the PCEM computation, point charges by α_μ. The γ_q^k are host-only–dependent quantities. Utilizing (8) and the computed values of γ_q^k (Table III) one finds that the contribution to the transition rate due to the pseudomultipolar field in the case of the $^5D_0\rightarrow{}^7F_2$ and the $^5D_0\rightarrow{}^7F_4$ transitions of Eu^{3+} in Y_2O_3 are equal to 234.0 and 17.9 s^{-1}, respectively, while the experimental values containing all types of contribution are equal to 732 and 75 s^{-1}, respectively. The matrix elements of $U^{(k)}$, the shielding factors, and the radial integrals may be found in Refs. 15–18.

[1] M. Faucher and D. Garcia, Phys. Rev. B 26, 5451 (1982).
[2] B. R. Judd, Phys. Rev. 127, 750 (1962).
[3] G. S. Ofelt, J. Chem. Phys. 37, 511 (1962).
[4] J. D. Axe, Jr., J. Chem. Phys. 39, 1154 (1963).
[5] W. F. Krupke, Phys. Rev. 145, 325 (1966).
[6] M. J. Weber, Phys. Rev. 157, 262 (1967).
[7] C. Delsart and N. Pelletier-Allard, J. Phys. C 6, 1277 (1973).
[8] R. P. Leavitt and C. A. Morrison, J. Chem. Phys. 73, 749 (1980).
[9] P. Porcher and P. Caro, J. Chem. Phys. 68, 4176 (1978).
[10] M. J. Weber, in *Optical Properties of Ions in Crystals,* edited by H. M. Crosswhite and H. M. Moos (Wiley Interscience, New York, 1967), p. 467.
[11] C. K. Jørgensen and B. R. Judd, Mol. Phys. 8, 281 (1964).
[12] S. F. Mason, R. D. Peacock, and B. Stewart, Chem. Phys. Lett. 29, 149 (1975).
[13] B. R. Judd, J. Chem. Phys. 70, 4830 (1979).
[14] O. L. Malta, Mol. Phys. 38, 1347 (1979).
[15] W. T. Carnall, H. Crosswhite, and H. M. Crosswhite (unpublished).
[16] R. P. Gupta and S. K. Sen, Phys. Rev. A 7, 850 (1973).
[17] D. Sengupta and J. O. Artman, Phys. Rev. B 1, 2986 (1970).
[18] A. J. Freeman and J. P. Desclaux, J. Magn. Magn. Mater. 12, 11 (1979).