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Spectrum of Sm^{2+}:SrClF

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The fluorescence spectrum of Sm^{2+} in SrClF is investigated. One hundred and two lines corresponding to the Stark components of the $^5D_J \rightarrow {}^7F_J$ transitions within the $4f^6$ ground configuration are identified on the basis of temperature dependence and polarization measurements. As a result, the symmetry assignment and energy of thirty-seven Stark levels belonging to the ^7F_J and ^5D_J multiplets of the $4f^6$ configuration are deduced. The experimental data (energy and symmetry of the levels) relative to the splittings of the ^7F_J multiplets are reproduced (with a deviation within the experimental precision) by an effective Hamiltonian. The resulting fitted crystal-field parameters are interpreted in the framework of the angular overlap model.

I. INTRODUCTION

The alkaline-earth halofluorides MXF are suitable hosts in which divalent rare-earth ions (R^{2+}) can be embedded.[1] The R^{2+} ions enter the MXF lattice at M^{2+} sites. No charge compensating defects are needed and the symmetry of the R^{2+} site is C_{4v} as in the undoped material. Samarium has been stabilized in the divalent state in all the MXF compounds ($M =$ Ca, Sr, Ba; $X =$ Cl, Br) and the Sm^{2+} fluorescence in these hosts has been proved to be more efficient than in the fluorides.[2,3] The fluorescent emission originates from transitions between the ^5D_J and ^7F_J multiplets of the $4f^6$ Sm^{2+} ground configuration, the intensity of the fluorescence being enhanced in the MXF crystals since the symmetry of the Sm^{2+} sites lacks a center of inversion and allows induced electric dipole $^5D_J \rightarrow {}^7F_J$ transitions to occur. The ^5D_J emitting levels can be efficiently populated by exciting the Sm^{2+} centers into the $4f^55d$ states thanks to the intense parity-allowed $4f^6 \rightarrow 4f^55d$ transitions in the visible and ultraviolet region, the $4f^55d$ and ^5D_J states being connected by fast nonradiative processes.

The BaClF and SrClF hosts offer the peculiarity that three ^5D_J levels ($^5D_0$, $^5D_1$, and $^5D_2$) are available for the fluorescent emission at low temperature while only one ($^5D_0$) or two ($^5D_0$ and $^5D_1$) emitting levels are efficient in all the other Sm^{2+}-doped materials known at this time.[4] Therefore, numerous intense sharp lines corresponding to the $^5D_J \rightarrow {}^7F_J$ transitions are observed in the Sm^{2+}:MClF ($M =$ Sr, Ba) low-temperature emission spectrum, under ultraviolet excitation, from which reliable energy-level diagrams for the ^7F_J and ^5D_J multiplets can be deduced.

Several papers have been devoted to the Sm^{2+}:BaClF system.[1-11] Recently, we have reported investigations on the Sm^{2+}:BaClF optical spectrum.[12] To the best of our knowledge, only preliminary studies have been performed on the Sm^{2+}:SrClF system.[1-3] We report here the first detailed work on the Sm^{2+}:SrClF energy levels with the aim of extending the collection of data available for further theoretical calculations.

II. CRYSTALLOGRAPHY

SrClF has a PbFCl structure and crystallizes in the tetragonal space group D_{4h}^7.[1-3] The Sm^{2+} ions enter the SrClF lattice substitutionally at Sr^{2+} sites with C_{4v} symmetry. The coordination polyhedron consists of four fluorines (series 1) located in a plane perpendicular to the c axis, four chlorines (series 2) in a plane parallel to the F plane, and one chlorine (series 3) on the c axis above the Cl plane.

A recent refinement of the structure has been performed[13] and accurate atomic position parameters are available for ligand-field analysis. From the data of Ref. 13, the spherical coordinates R (Å), Θ (deg), and Φ (deg) for each series of ligands are the following: (series 1) $R_1 = 2.4943$, $\Theta_1 = 124.2007$, and $\Phi_1 = 0, 90, 180, 270$; (series 2) $R_2 = 3.1118$, $\Theta_2 = 69.6404$, and $\Phi_2 = 45, 135, 225, 315$; and (series 3) $R_3 = 3.0712$, $\Theta_3 = 0$, and $\Phi_3 =$ undetermined.

III. EXPERIMENTAL

A. Materials

The Sm^{2+}:SrClF sample used in the present study is a single crystal of approximate dimensions $9 \times 3 \times 1$ mm^3, the larger faces being perpendicular to the crystallographic axis. It was grown according to the Czochralski technique in the laboratory of Professor Bill at Geneva. The nominal Sm^{2+} concentration was 0.1% per mole.

B. Measurements

Nonpolarized fluorescence spectra were recorded at several temperatures between 1.6 and 300 K, the crystal being oriented with the c axis parallel to the direction of the ultraviolet exciting beam produced by a high-pressure mercury lamp equipped with a Wood filter. The fluorescence was analyzed throughout a Monospek 1000 Hilger and Watts scanning monochromator (reciprocal linear dispersion: 8 Å/mm in first order) and detected by a 9658-R EMI photomultiplier. A VJ 44 Sovirel filter was placed before the entrance slit of the monochromator in order to eliminate the diffused excitation light from the fluorescence and the width of the entrance and output slits was set at 50μ. Polarized fluorescence spectra were also recorded. The polarization of a line was measured by the ratio $(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where $I_{\parallel}(I_{\perp})$ is the intensity of this line when the polarization direction of the analyzer is parallel (perpendicular) to the crystallographic axis. No correction was made to account for experimental depolarization.

C. Results

The Sm^{2+}:SrClF low-temperature emission spectrum under uv excitation turns out to be very similar to that of the Sm^{2+}:BaClF system.[12] Eighteen groups of lines are observed which are attributed to the $^5D_2 \rightarrow {}^7F_J$ ($J = 0$ to 6), $^5D_1 \rightarrow {}^7F_J$ ($J = 0$ to 5), and $^5D_0 \rightarrow {}^7F_J$ ($J = 0$ to 4) transitions. The $^5D_1 \rightarrow {}^7F_6$, $^5D_0 \rightarrow {}^7F_5$, and $^5D_0 \rightarrow {}^7F_6$ groups which are located further in the infrared cannot be observed with our equipment. The intensity of the different groups depends strongly on the temperature. All the groups are present at very low temperature, but the $^5D_2 \rightarrow {}^7F_J$ lines are no longer visible at temperatures higher than 90 K. On the other hand, the fluorescent emission originates mainly from the $^5D_0$ level at room temperature. Such a thermal dependence has also been observed for the Sm^{2+}:BaClF system.[6–11]

The $^5D_J \rightarrow {}^7F_J$ patterns are in good agreement with the emission spectrum originating from a single type of site of C_{4v} symmetry, if we neglect some weak satellites appearing at the bottom of the most intense lines. These satellites which have the same polarization as the main line are probably due to Sm^{2+} ions at inequivalent sites as is the case of the BaClF host.[12] Weak lines appearing at the short-wavelength side of the $^5D_1 \rightarrow {}^7F_3$ group were proved, by means of selective excitation in the $^5D_1$ level and excitation spectrum measurements, to originate from extra impurity centers. Selective excitation was also used to clarify the spectrum in regions where two groups were observed to overlap, like $^5D_1 \rightarrow {}^7F_1$ and $^5D_2 \rightarrow {}^7F_4$.

The data for the 102 lines observed in the emission spectrum are reported in Table I. The intensity of the lines within each group is evaluated relative to that of the most intense component at 5 K, which is taken to be equal to 1000. A comparison of the intensities of the $^5D_1 \rightarrow {}^7F_J$ lines originating from the E level, on one hand, and from the A_2 level, on the other hand, shows that the former are increased by a factor of 5 to 6 relative to the latter as temperature is varied from 5 to 40 K, in good agreement with the 7-cm^{-1} splitting of the $^5D_1$ multiplet. In the same way, the 40-K intensity ratio for the $^5D_2 \rightarrow {}^7F_J$ components originating from the E and A_1 levels is about 13 times that observed at 5 K. This thermal dependence allows a classification of the lines according to the emitting Stark level. The A_1 and E levels of the ^7F_J multiplets ($J = 0$ to 4) are unambiguously identified on the basis of the polarization of the $^5D_0 \rightarrow {}^7F_J$ lines. $A_1 \rightarrow A_1$ components are observed to be strongly polarized, as expected from group-theory considerations. On the other hand, $A_1 \rightarrow E$ lines are only slightly polarized and the associated transitions probably have both electric and magnetic dipole character, as noticed for the Sm^{2+}:BaClF system.[12] The assignment of the remaining Stark levels of the ^7F term is then derived from the data for the $^5D_1 \rightarrow {}^7F_J$ and $^5D_2 \rightarrow {}^7F_J$ groups. As mentioned in Ref. 12, polarization measurements are not sufficient to differentiate B_1 and B_2 levels. Therefore the notation B_a and B_b is used in Table I where a and b may be either 1 and 2 or 2 and 1, respectively. The experimental energy levels deduced from Table I are listed in Table II with their crystal-field term assignments. It is to be noted that a semiempirical approach was used to assign the Stark levels of the $^7F_6$ multiplet on account of the lack of experimental data. Phenomenological crystal-field parameters were first derived from the ^7F_J ($J \leq 5$) levels and the calculated energy-level diagram was taken into account for the assignment of the observed $^5D_2 \rightarrow {}^7F_6$ lines. Moreover, these calculations have shown that the unobserved low-energy $^5D_2 \rightarrow {}^7F_6$ components are expected to occur in the same spectral range as the strong $A_1 \rightarrow E$ line of the $^5D_0 \rightarrow {}^7F_2$ group. On the other hand, no experimental evidence for the B_b component of the $^5D_2$ level was found. This is probably due to a coincidence with one of the three other

TABLE I. Sm^{2+}:SrClF fluorescence spectrum.

Transition	Emission wavelength (Å)	Emission frequency (cm^{-1})	Relative intensity		$\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+I_{\perp}}$	Crystal-field component
			5 K	40 K		
$^5D_2 \rightarrow {}^7F_0$	5635.5	17 739.7	143	1828	−0.07	$E \rightarrow A_1$
	5639.0	17 728.7	1000	1000	0.58	$A_1 \rightarrow A_1$
$^5D_2 \rightarrow {}^7F_1$	5725.2	17 461.6	52	1340	−0.28	$B_a \rightarrow E$
	5726.5	17 457.8	130	1652	−0.17	$E \rightarrow E$
	5730.5	17 445.6	1000	1000	−0.30	$A_1 \rightarrow E$
	5733.0	17 438.0	114	1530	−0.30	$E \rightarrow A_2$
$^5D_2 \rightarrow {}^7F_2$	5900.7	16 942.3	60	957	0.66	$E \rightarrow E$
	5901.2	16 940.9		110		$E \rightarrow B_a$
	5904.7	16 930.8		139		$E \rightarrow B_b$
	5905.0	16930.1	1000	1000	−0.35	$A_1 \rightarrow E$
	5913.0	16 907.2		14	−0.28	$E \rightarrow A_1$
	5917.0	16 895.8	23	26	0.63	$A_1 \rightarrow A_1$
$^5D_2 \rightarrow {}^7F_3$	6143.2	16 273.7		96	−0.17	$B_a \rightarrow E$
	6144.3	16 270.7	103	906	0.33	$E \rightarrow E$
	6146.6	16 264.7		259	−0.28	$B_a \rightarrow E$
	6148.5	16 259.6	1000	1000	−0.17	$A_1 \rightarrow E$ and $E \rightarrow E$
	6151.3	16 252.2	24	196	−0.23	$E \rightarrow B_a$
	6152.6	16 248.8	129	76	−0.15	$A_1 \rightarrow E$
	6155.3	16 241.7	98	801	−0.39	$E \rightarrow A_2$
	6156.7	16 238.0		19	−0.43	$B_a \rightarrow B_b$
	6158.1	16 234.3	37	264	−0.13	$E \rightarrow B_b$
	6159.1	16 231.6	61	48	−0.40	$A_1 \rightarrow A_2$
$^5D_1 \rightarrow {}^7F_0$	6321.5	15 814.6	16	21	−0.10	
	6324.5	15 807.2	1000	1000	−0.08	$E \rightarrow A_1$
	6327.3	15 800.3	163	34	−0.33	$A_2 \rightarrow A_1$
$^5D_1 \rightarrow {}^7F_1$	6437.5	15 529.7	341	2166	0.68	$E \rightarrow E$
	6440.5	15 522.4	1000	1000	−0.15	$A_2 \rightarrow E$
	6445.2	15 511.0	30	166	−0.20	$E \rightarrow A_2$
	6448.2	15 503.8	496	552	0.67	$A_2 \rightarrow A_2$
$^5D_2 \rightarrow {}^7F_4$	6427.5	15 553.9	54	624	−0.23	$E \rightarrow A_1$
	6432.0	15 543.0	1000	1000	0.70	$A_1 \rightarrow A_1$
	6451.4	15 496.2	13	248	−0.24	$B_a \rightarrow E$
	6453.0	15 492.4	12	162	0.56	$E \rightarrow E$
	6457.5	15 481.6	80	919	−0.25	$A_1 \rightarrow E$ and $B_a \rightarrow E$
	6459.0	15 478.0	77	913	0.22	$E \rightarrow E$
	6463.2	15 467.8	95	81	−0.27	$A_1 \rightarrow E$
	6469.2	15 453.5	19	231	−0.26	$E \rightarrow A_1$
	6475.1	15 439.5	108	107	0.66	$A_1 \rightarrow A_1$
	6480.0	15 427.8	6	58	−0.22	$E \rightarrow B_a$

TABLE I (*Continued*).

Transition	Emission wavelength (Å)	Emission frequency (cm^{-1})	Relative intensity		$\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+I_{\perp}}$	Crystal-field component
			5 K	40 K		
$^5D_1 \rightarrow {}^7F_2$	6657.2	15017.1	12	12	−0.03	
	6659.7	15011.4	36	181	0.22	$E \rightarrow E$
	6660.7	15009.2	35	135	0.06	$E \rightarrow B_a$
	6663.0	15004.1	1000	1000	−0.11	$A_2 \rightarrow E$
	6677.0	14972.6	22	112	−0.03	$E \rightarrow A_1$
	6680.2	14965.5	59	54	−0.38	$A_2 \rightarrow A_1$
$^5D_2 \rightarrow {}^7F_5$	6811.5	14677.0	45	1363	0.67	$B_a \rightarrow B_a$
	6812.5	14674.9	82	1156	−0.24	$E \rightarrow B_a$
	6820.0	14658.7	104	1439	0.67	$E \rightarrow E$
	6826.7	14644.3	50			$A_1 \rightarrow E$
	6835.1	14626.3	285	4219	0.28	$E \rightarrow E$
	6840.0	14615.4	9			$A_1 \rightarrow E$
	6845.5	14604.1	50	1004	−0.21	$B_a \rightarrow E$ and $E \rightarrow A_2$
	6847.5	14599.8	72	1105	0.56	$E \rightarrow E$
	6852.7	14588.8	475	439	−0.14	$A_1 \rightarrow E$
	6872.5	14546.7	1000	1000	0.71	$A_1 \rightarrow A_1$
$^5D_0 \rightarrow {}^7F_0$	6902.5	14483.5	15		0.67	
	6904.0	14480.3	34	46	0.67	
	6906.2	14475.6	1000	1000	0.67	$A_1 \rightarrow A_1$
	6907.0	14474.1	34	36	0.65	
	6909.0	14469.9	10	23	0.60	
$^5D_1 \rightarrow {}^7F_3$	6972.2	14338.6	9	39	0.62	$E \rightarrow E$
	6976.0	14330.9	1000	1000	−0.23	$A_2 \rightarrow E$
	6978.0	14326.8	24	118	0.62	$E \rightarrow E$
	6981.5	14319.6	447	445	−0.19	$A_2 \rightarrow E$
	6987.2	14307.8	15	83	−0.08	$E \rightarrow A_2$
	6990.5	14301.2	306	362	0.64	$A_2 \rightarrow A_2$
$^5D_0 \rightarrow {}^7F_1$	7043.0	14194.6	1000	1000	0.06	$A_1 \rightarrow E$
	7052.2	14176.0	164	160	−0.32	$A_1 \rightarrow A_2$
$^5D_2 \rightarrow {}^7F_6$	7271.0	13749.5		339	−0.10	$B_a \rightarrow E$
	7274.0	13743.8	331	2548	0.21	$E \rightarrow E$
	7274.5	13742.9	307	2032		$E \rightarrow A_1$ and $E \rightarrow A_2$
	7277.0	13738.1		339	0.05	$B_a \rightarrow E$
	7279.0	13734.4	1000	1000	−0.08	$A_1 \rightarrow E$
	7279.8	13733.0		669		$A_1 \rightarrow A_1$
	7285.0	13723.0	568	863	0.02	$A_1 \rightarrow E$ and $E \rightarrow E$
	7286.8	13719.8	322	871	0.70	$A_1 \rightarrow A_1$ and $E \rightarrow B_b$
	7290.3	13713.2	195	210	−0.27	$A_1 \rightarrow E$
$^5D_0 \rightarrow {}^7F_2$	7309.5	13677.1	1000	1000	−0.16	$A_1 \rightarrow E$
	7329.9	13638.9	74	75	0.69	$A_1 \rightarrow A_1$

TABLE I (*Continued*).

Transition	Emission wavelength (Å)	Emission frequency (cm^{-1})	Relative intensity 5 K	Relative intensity 40 K	$\frac{I_\parallel - I_\perp}{I_\parallel + I_\perp}$	Crystal-field component
$^5D_1 \rightarrow ^7F_4$	7338.1	13 623.8	911	861	−0.11	$E \rightarrow A_1$
	7372.5	13 560.2		28	0.67	$E \rightarrow E$
	7377.0	13 551.9	353	49	−0.02	$A_2 \rightarrow E$
	7381.5	13 543.6	1000	1000	0.69	$E \rightarrow E$
	7385.2	13 536.8	706	127	−0.06	$A_2 \rightarrow E$
	7386.5	13 534.5	217	44	0.67	$A_2 \rightarrow A_2$
	7393.7	13 521.2	111	94	−0.16	$E \rightarrow A_1$
	7405.5	13 499.8	76	81	−0.06	$E \rightarrow B_a$
$^5D_0 \rightarrow ^7F_3$	7688.4	13 003.0	1000	1000	−0.07	$A_1 \rightarrow E$
	7694.1	12 993.3	430	426	−0.04	$A_1 \rightarrow E$
$^5D_1 \rightarrow ^7F_5$	7846.9	12 740.4	170	1148	−0.09	$E \rightarrow B_a$
	7859.9	12 719.3	957	932	−0.13	$A_2 \rightarrow E$
	7874.0	12 696.5		216	0.00	$E \rightarrow E$
	7879.5	12 687.7	1000	1000	−0.11	$A_2 \rightarrow E$
	7885.2	12 678.4	visible at 70 K		0.27	
	7889.5	12 671.6	visible at 70 K		−0.08	$E \rightarrow A_2$
	7891.5	12 668.4	145	933	0.67	$E \rightarrow E$
	7894.0	12 664.4	667	666	0.60	$A_2 \rightarrow A_2$
	7896.0	12 661.2	742	733	0.00	$A_2 \rightarrow E$
$^5D_0 \rightarrow ^7F_4$	8134.4	12 290.1	1000	1000	0.56	$A_1 \rightarrow A_1$
	8176.5	12 226.8	43	42	0.11	$A_1 \rightarrow E$
	8186.2	12 212.3	555	586	−0.03	$A_1 \rightarrow E$
	8202.0	12 188.8	49	50	0.48	$A_1 \rightarrow A_1$

Stark levels. Generally speaking, the energy-level diagrams for the SrClF and BaClF[12] are very similar. Nevertheless, they differ in the relative positions of the Stark levels. As a striking example, the A_2 and E components of the $^7F_1$ multiplet are inverted while the $^5D_1$ splitting remains unchanged.

IV. THEORY

A. Effective Hamiltonian

The calculation of the energy levels of nl^N ions (especially triply ionized lanthanide ions) embedded in crystalline hosts has reached a high degree of sophistication. In fact, it is now feasible to optimize more and more refined Hamiltonians.[14–21] One frequently employs a Hamiltonian $\mathcal{H}$ which includes, in addition to the conventional (Coulomb, spin-orbit, and one-body crystal-field) interactions, effective (two- and three-body) electrostatic interactions[14] as well as real (spin-other-orbit and spin-spin) magnetic interactions and effective (two-body) magnetic interactions.[15] It is also possible to introduce refined crystal-field Hamiltonians.[16–21] For example, we may mention, on one hand, the two-body correlation crystal-field Hamiltonian[19,20] that describes the combined effects of the Coulomb and crystal-field interactions and, on the other hand, the relativistic crystal-field Hamiltonian[21] that describes the combined effects of the crystal-field and spin-orbit interactions. The matrix of $\mathcal{H}$ is then generally set up on the complete nl^N manifold. Configuration mixing between the nl^N and other manifolds is thus taken into account by the various effective interactions.

The case of the (Eu^{3+}, Sm^{2+}) $4f^6$ configuration in (C_{4v}) tetragonal symmetry deserves special consideration. As a matter of fact, the dimension of the

nf^6 manifold is 3003 and symmetry adaptation yields energy matrices of dimension 398 (A_1), 363(A_2), 379(B_1), 379(B_2), and 742(E) when classified according to the IRC's (irreducible representations classes) of the group C_{4v}. Therefore, it is hardly possible to handle the $4f^6$ configuration in tetragonal symmetry without a perturbation and/or truncation procedure. Fortunately, the crystal-field interaction does not mix the ground term ^7F with the excited terms ^5D, ^5L, ^5G, . . . , of $4f^6$. Moreover, for Sm^{2+}:SrClF (as well as for Sm^{2+}:BaClF), the mixing between the ^7F term and the excited terms (which begin to be located some 15 000 cm^{-1} above $^7F_0$) of $4f^6$ or $4f^55d$ is mainly due to the spin-orbit interaction or the odd crystal-field plus various minor interactions, respectively. Thus, it seems reasonable (as is *a posteriori* justified) to reduce the $4f^6$ manifold to the ^7F submanifold and, if necessary, to consider second-order perturbation mechanisms.

We therefore start with the effective Hamiltonian

$$\mathcal{H} = \sum_{k_1k_2ka_1} D[(k_1k_2)ka_1]\, W^{(k_1k_2)k}_{a_1A_1} \qquad (1)$$

to describe the combined action of spin- and orbit-dependent interactions within the term ^7F. Here, $W^{(k_1k_2)k}_{a_1A_1}$ is a component, transforming as the identity IRC A_1 of the group C_{4v}, of a double tensor[21,22] $W^{(k_1k_2)k}$ of spin rank k_1, orbital rank k_2, and total rank k. (The index a_1 stands for a classification label required when the IRC A_1 of C_{4v} appears several times in the IRC k of SO_3, cf. Appendix A.) Moreover, the parameters $D[(k_1k_2)ka_1]$ describe (as will be seen below) the spin-orbit and crystal-field interactions as well as some effective interactions. The matrix of $\mathcal{H}$, within the term ^7F, in a $SO_3 \supset C_{4v}$ symmetry adapted basis, can be obtained from the general formula

$$\langle nl^N\alpha'S'L'J'a'\Gamma'\gamma'|\mathcal{H}|nl^N\alpha SLJa\Gamma\gamma\rangle = \delta(\Gamma'\Gamma)\delta(\gamma'\gamma)[(2J'+1)(2J+1)]^{1/2}$$
$$\times \sum_{k_1k_2ka_1}(2k+1)^{1/2}\begin{Bmatrix} S' & S & k_1\\ L' & L & k_2\\ J' & J & k\end{Bmatrix}$$
$$\times (l^N\alpha'S'L'||W^{k_1k_2}||l^N\alpha SL)\, f\begin{pmatrix} J' & J & k\\ a'\Gamma & a\Gamma & a_1A_1\end{pmatrix} D[(k_1k_2)ka_1] \qquad (2)$$

valid for any configuration nl^N in any symmetry G. In Eq. (2), { } denotes a 9-j symbol,[22] (|| ||) a reduced matrix element,[23] and $f(\ )$ a $SO_3 \supset G$ or $SU_2 \supset G^*$ symmetry adapted coupling coefficient[24] (cf. Appendix A). The use of a symmetry adapted basis will allow us to systematically introduce the assignments of the symmetry species to the experimental levels in the fitting procedures.

B. Phenomenological parameters

1. *Global parameters*

From Eq. (2), it can be seen, in the general case of a configuration nl^N in symmetry G, that the Hamiltonian $\mathcal{H}$ of Eq. (1) decomposes as

$$\mathcal{H} = \mathcal{H}_{so} + \mathcal{H}_{cf} + \mathcal{H}_{socf} \ . \qquad (3)$$

To be more explicit:

(i) The isotropic spin-orbit interaction $\mathcal{H}_{so}$ is described by

$$D[(11)0] = -\left[\frac{l(l+1)(2l+1)}{2}\right]^{1/2} \zeta_{nl} \ , \qquad (4)$$

where ζ_{nl} denotes the conventional spin-orbit parameter.

(ii) The crystal-field interaction $\mathcal{H}_{cf}$ is described by the parameters

$$D[(0k)ka_1] = (-1)^l\left[\frac{2}{2k+1}\right]^{1/2}(2l+1)\begin{pmatrix} l & k & l\\ 0 & 0 & 0\end{pmatrix}$$
$$\times \sum_{q=-k}^{k} B^k_q \langle kq|ka_1A_1\rangle^* \ , \qquad (5)$$

which are related to the (Wybourne) crystal-field parameters[25] B^k_q through the unitary transformation of matrix elements $\langle kq|ka_1A_1\rangle$ (cf. Appendix A).

(iii) The mixed interaction $\mathcal{H}_{socf}$ is described by means of those parameters $D[(1k_2)ka_1]$ for which k and $1+k_2+k$ are even. The effective interaction $\mathcal{H}_{socf}$ includes, among others, anisotropic spin-orbit contributions as well as spin and orbit contributions correlated via even crystal-field terms.[21] As an example, the parameter $D[(11)2a_1]$ may be thought to describe: (1) anisotropy of the spin-orbit interaction, i.e., the G invariant part of the spin-orbit coupling $\{s^1l^1\}^2$, as well as; (2) the G invariant part of the spin and orbit contribution correlated to the second-order crystal-field term $\{s^1\{u^2l^1\}\}^2$. A similar significance

TABLE II. Sm^{2+}:SrClF experimental energy levels of ^7F_J and ^5D_J multiplets.

Multiplet	Crystal-field term assignment	Energy (cm^{-1})
$^7F_0$	A_1	0
$^7F_1$	E	280.3
	A_2	298.5
$^7F_2$	E	797.3
	B_a	798.5
	B_b	808.5
	A_1	834.3
$^7F_3$	E	1470.0
	E	1480.5
	B_a	1487.5
	A_2	1498.1
	B_b	1505.8
$^7F_4$	A_1	2185.1
	E	2247.9
	E	2262.8
	A_2	2265.8
	A_1	2287.1
	B_a	2309.7
$^7F_5$	B_a	3066.2
	E	3082.1
	E	3112.5
	A_2	3135.7
	E	3139.5
	A_1	3182.0
$^7F_6$	E	3994.9
	A_1	3996.3
	A_2	3996.8
	E	4005.8
	A_1	4008.9
	E	4016.1
	B_b	4019.9
$^5D_0$	A_1	14 475.6
$^5D_1$	A_2	15 800.3
	E	15 807.2
$^5D_2$	A_1	17 728.7
	E	17 739.7
	B_a	17 744.1

may be ascribed to the other parameters $D[(1k_2)ka_1]$. It should be stressed that the introduction of $\mathcal{H}_{\text{socf}}$ does not bring any additional symmetry breaking when compared to the situation where $\mathcal{H} = \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{cf}}$ (cf. Appendix B). It is expected that the effective Hamiltonian $\mathcal{H}_{\text{socf}}$ only weakly modifies (in the right sense) the eigenvalues of $\mathcal{H}_{\text{so}} + \mathcal{H}_{\text{cf}}$.

2. *Additive parameters*

Due to the (formidable) difficulty inherent in *ab initio* calculation of the $D[(k_1k_2)ka_1]$'s, the best thing to do (at least in a preliminary approach) is to consider them as phenomenological (adjustable) parameters and to interpret the fitted values with the aid of microscopic models. In that direction:

(i) Nothing special may be said about $D[(11)0]$.

(ii) The crystal-field parameters $D[(0k)ka_1]$ can be interpreted in the framework of additive models. Each $D[(0k)ka_1]$ is then partitioned as

$$D[(0k)ka_1] = (-1)^l 2(2\pi)^{1/2} \frac{2l+1}{2k+1} \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \sum_J c_{ka_1}(J) \quad , \tag{6}$$

in terms of independent and linearly cumulative contributions $c_{ka_1}(J)$ arising from the ligands and ions around the central metal atom. In the case of the electrostatic model, including both monopolar and dipolar contributions, $c_{ka_1}(J)$ is of the type

$$c_{ka_1}(J) = e^2 g_J Y_{ka_1A_1}(\Theta_J, \Phi_J)^* \left\langle nl \left| \frac{r_<^k}{r_>^{k+1}} \right| nl \right\rangle + e^2 \vec{\mathrm{p}}_J \cdot \left\langle nl \left| \vec{\nabla} \frac{r_<^k}{r_>^{k+1}} Y_{ka_1A_1}(\Theta_J, \Phi_J)^* \right| nl \right\rangle \quad , \tag{7}$$

where $Y_{ka_1A_1}$ denotes a $SO_3 \supset G$ harmonic of order k transforming as A_1 and the other symbols[22,26] have their usual meaning. In the case of the superposition model[27] and the angular overlap model,[28] $c_{ka_1}(J)$ is of the type

$$c_{ka_1}(J) = Y_{ka_1A_1}(\Theta_J, \Phi_J)^* I_k(J) \quad . \tag{8}$$

The parameter I_k may be viewed as being proportional to the intrinsic parameter $\bar{A}_k$ of the superposition model[29]

$$I_k = \left(\frac{2k+1}{4\pi} \right)^{1/2} U_k^0 \bar{A}_k \tag{9}$$

or alternatively as being a linear combination of the (anti) bonding parameter e_λ of the angular overlap model[30]

$$I_k=\frac{2k+1}{2l+1}\left[1\Big/\begin{pmatrix} l & k & l\\ o & o & o\end{pmatrix}\right]\sum_{m''=-l}^{l}(-1)^{m''}\begin{pmatrix} l & k & l\\ -m'' & o & m''\end{pmatrix}e_{m''}\ ,$$
$$e_{m''}=e_{\sigma}(m''=0),\quad e_{\pi}(m''=\pm 1),\quad e_{\delta}(m''=\pm 2),\ \ldots,\ . \tag{10}$$

(iii) It should be also possible to discuss the additional parameters $D[(1k_2)ka_1]$ in the framework of the electrostatic model, superposition model, and angular overlap model. However, it seems that the underlying formalism is still in a state of incomplete development. We shall only mention the possibility of interpreting the $D[(1k_2)ka_1]$'s in the framework of the point-charge electrostatic model using Hartree-Fock-Slater-Dirac relativistic (or spin-unrestricted Hartree-Fock) wave functions. Following Wybourne,[21] we may write in this respect

$$D[(1k_2)ka_1]=\frac{[12\pi(2k_2+1)]^{1/2}}{2k+1}\sum_{jj'}(-1)^{j'+1/2}(2j'+1)(2j+1)\begin{pmatrix} j' & k & j\\ \frac{1}{2} & o & -\frac{1}{2}\end{pmatrix}\begin{Bmatrix} \frac{1}{2} & \frac{1}{2} & k_1\\ l & l & k_2\\ j' & j & k\end{Bmatrix}\sum_J e^2 g_J Y_{ka_1A_1}(\Theta_J,\Phi_J)^{*}\mathcal{R}^k_{j'j}\ , \tag{11}$$

where the radial integral $\mathcal{R}^k_{j'j}$ is given by

$$\mathcal{R}^k_{j'j}=\int_0^{\infty}\frac{r_<^k}{r_>^{k+1}}(F_{j'}F_j+G_{j'}G_j)r^2\,dr \tag{12}$$

in terms of the large (F) and small (G) components of the Dirac equation. Note that, if $r_<\equiv r$ and $r_>\equiv R_J$ (a not too crucial approximation!), then $\mathcal{R}^k_{j'j}$ reduces to $R^k_{j'j}/(R_J)^{k+1}$, where $R^k_{j'j}$ coincides with the corresponding integral discussed by Wybourne.[21] It is perhaps worth mentioning, for subsequent investigations, that relativistic wave functions for transition-metal, lanthanides, and actinides ions are now available in the literature.[31]

C. Symmetry adaptation

The use of a $SO_3\supset C_{4v}$ symmetry adapted basis both for the Hamiltonian and the state vectors *a priori* allows us to break the matrix of dimension 49 associated to the term ^7F into the direct sum of six submatrices of dimension $7(A_1)$, $6(A_2)$, $6(B_1)$, $6(B_2)$, and twice $12(E)$. The main interest, here, in using a $SO_3\supset C_{4v}$ symmetry adapted basis is not so much to reduce the size of the secular equation but rather to permit the symmetry assignments of the experimental levels to be systematically entered in the fitting procedures, in contradistinction with a brute force diagonalization (cf. Appendix B).

In the case where $G\equiv C_{4v}$, it is interesting to classify the $SO_3\supset C_{4v}$ symmetry adapted state vectors and operators according to the group chain $SO_3\supset C_{\infty v}\supset C_{4v}\supset C_{2v}$. Indeed, the introduction of the classification groups $C_{\infty v}$ and C_{2v}, besides the symmetry group C_{4v}, makes it possible to replace the indices a and γ by IRC's of $C_{\infty v}$ and C_{2v}, respectively. By using the abbreviation $|J\Gamma(C_{\infty v})\Gamma(C_{4v})\Gamma(C_{2v})\rangle$ for $|4f^{6\,7}FJ\Gamma(C_{\infty v})\Gamma(C_{4v})\Gamma(C_{2v})\rangle$, the state vectors for each of the aforementioned six submatrices are

$$\begin{aligned}
&7(A_1)\text{ matrix: } |0A_1A_1A_1\rangle,\ |2A_1A_1A_1\rangle,\ |4A_1A_1A_1\rangle,\ |4E_4A_1A_1\rangle,\ |5E_4A_1A_1\rangle,\ |6A_1A_1A_1\rangle,\ |6E_4A_1A_1\rangle\ ,\\
&6(A_2)\text{ matrix: } |1A_2A_2A_2\rangle,\ |3A_2A_2A_2\rangle,\ |4E_4A_2A_2\rangle,\ |5A_2A_2A_2\rangle,\ |5E_4A_2A_2\rangle,\ |6E_4A_2A_2\rangle\ ,\\
&6(B_1)\text{ matrix: } |2E_2B_1A_1\rangle,\ |3E_2B_1A_1\rangle,\ |4E_2B_1A_1\rangle,\ |5E_2B_1A_1\rangle,\ |6E_2B_1A_1\rangle,\ |6E_6B_1A_1\rangle\ ,\\
&6(B_2)\text{ matrix: } |2E_2B_2A_2\rangle,\ |3E_2B_2A_2\rangle,\ |4E_2B_2A_2\rangle,\ |5E_2B_2A_2\rangle,\ |6E_2B_2A_2\rangle,\ |6E_6B_2A_2\rangle\ ,\\
&12(E)\text{ matrix: } |1E_1EB_1\rangle,\ |2E_1EB_1\rangle,\ |3E_1EB_1\rangle,\ |3E_3EB_1\rangle,\ |4E_1EB_1\rangle,\ |4E_3EB_1\rangle,\ |5E_1EB_1\rangle,\ |5E_3EB_1\rangle\ ,\\
&\qquad |5E_5EB_1\rangle,\ |6E_1EB_1\rangle,\ |6E_3EB_1\rangle,\ |6E_5EB_1\rangle\ ,\\
&12(E)\text{ matrix: } |1E_1EB_2\rangle,\ |2E_1EB_2\rangle,\ |3E_1EB_2\rangle,\ |3E_3EB_2\rangle,\ |4E_1EB_2\rangle,\ |4E_3EB_2\rangle,\ |5E_1EB_2\rangle,\ |5E_3EB_2\rangle\ ,\\
&\qquad |5E_5EB_2\rangle,\ |6E_1EB_2\rangle,\ |6E_3EB_2\rangle,\ |6E_5EB_2\rangle\ .
\end{aligned} \tag{13}$$

The two $12(E)$ matrices are responsible for the doublet levels of symmetry E. It is therefore possible to choose the $SO_3 \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$ basis in such a way that the two $12(E)$ matrices be identical. The development of $|J\Gamma(C_{\infty v})\Gamma(C_{4v})\Gamma(C_{2v})\rangle$ in terms of the state vectors $|4f^6\,{}^7FJM\rangle$ may be obtained from Appendix A.

It is easily seen that in our case the total number of parameters $D[(k_1k_2)k\Gamma(C_{\infty v})]$ is fourteen:

(i) One spin-orbit parameter, viz., $D[(11)0A_1]$.

(ii) Five crystal-field parameters, viz., $D[(02)2A_1]$, $D[(04)4A_1]$, $D[(04)4E_4]$, $D[(06)6A_1]$, and $D[(06)6E_4]$. Specialization of Eq. (5) to the case under consideration shows that $D[(0k)k\Gamma(C_{\infty v})]$ is merely proportional to some B_q^k

$$\begin{aligned}
D[(02)2A_1] &= -\tfrac{2}{5}(\tfrac{14}{3})^{1/2}B_0^2 \ ,\\
D[(04)4A_1] &= \tfrac{2}{3}(\tfrac{7}{11})^{1/2}B_0^4 \ ,\\
D[(06)6A_1] &= -\tfrac{10}{13}(\tfrac{14}{33})^{1/2}B_0^6 \ ,\\
D[(04)4E_4] &= \tfrac{2}{3}(\tfrac{14}{11})^{1/2}B_{\pm 4}^4 \ ,\\
D[(06)6E_4] &= -\tfrac{20}{13}(\tfrac{7}{33})^{1/2}B_{\pm 4}^6 \ .
\end{aligned} \tag{14}$$

(iii) Eight additional parameters, viz., $D[(11)2A_1]$, $D[(13)2A_1]$, $D[(13)4A_1]$, $D[(13)4E_4]$, $D[(15)4A_1]$, $D[(15)4E_4]$, $D[(15)6A_1]$, and $D[(15)6E_4]$.

D. Fitting procedures

In view of the number of the experimental data (30 energy levels plus 30 corresponding symmetry assignments) as compared to the number of variables (1 spin-orbit plus 5 crystal-field plus 8 additional parameters) and in order to test the relative importance of the various parameters, we proceed in three steps. All the optimizations in the three steps are made possible by using the program *Minuits* based on the simplex method.[32] (The simplex method, in contrast to the least-squares method, may be used to converge reasonably rapidly towards the exact minimum when no starting point is known.)

Step 1: This step is an adaptation of procedure B described at length in Ref. 12. Only six (hopefully the most significant ones) parameters are retained to be freely varied, viz., the spin-orbit parameter $D[(11)0A_1]$ and the five crystal-field parameters $D[(0k)k\Gamma(C_{\infty v})]$. We choose to fit the levels arising from the term ${}^7F$ by minimizing either the mean linear deviation

$$f=\sum_J \sum_i |\Delta_i(J)|/E \tag{15}$$

or the quadratic deviation

$$\sigma=\left\{\sum_J \sum_i [\Delta_i(J)]^2/E\right\}^{1/2} \ , \tag{16}$$

where $\Delta_i(J)$ is the difference between the observed and calculated positions, expressed with respect to the center of gravity of the multiplet ${}^7F_J$, of the ith Stark level arising from ${}^7F_J$ and where the number E of Stark levels fitted is taken to be equal to 30. The linear (f) and quadratic (σ) optimizations are carried out with and without mixing, via $\mathcal{H}_{\text{cf}}$, the various multiplets ${}^7F_J$. The values of the spin-orbit and crystal-field parameters thus obtained appear in Table III.

From Table III, we note that the introduction of the J-mixing effects does not considerably decrease the linear and quadratic deviations, a situation to be contrasted with the one for Sm^{2+}:BaClF.[12]

In order to examine the reliability of the values of the crystal-field parameters reported in Table III, we also proceeded with a somewhat different fitting procedure based upon an adjustment of the center of

TABLE III. Fitted parameters and corresponding linear and quadratic deviations obtained by means of step 1 (units are cm^{-1}).

	Without J mixing		With J mixing	
	From f optimization	From σ optimization	From f optimization	From σ optimization
$D[(02)2A_1]$	−52.00	−48.73	−47.37	−49.05
$D[(04)4A_1]$	−116.23	−114.32	−116.87	−115.98
$D[(04)4E_4]$	−23.54	−21.81	−16.82	−19.69
$D[(06)6A_1]$	−236.28	−235.05	−239.03	−236.12
$D[(06)6E_4]$	153.22	152.78	155.31	154.39
$D[(11)0A_1]$	−8821.31	−8820.72	−8820.28	−8820.97
f	1.14	1.15	1.13	1.18
σ	1.66	1.62	1.43	1.40

TABLE IV. Fitted parameters and corresponding linear and quadratic deviations obtained by means of step 2 (units are cm^{-1}).

	Without J mixing		With J mixing	
	From f optimization	From σ optimization	From f optimization	From σ optimization
$D[(11)0A_1]$	−8821.25	−8820.28	−8820.42	−8820.10
$D[(11)2A_1]$	−3.92	−3.95	−0.85	0.21
$D[(13)2A_1]$	−3.25	1.22	5.91	5.43
$D[(13)4A_1]$	0.14	−0.18	3.22	4.32
$D[(13)4E_4]$	−7.12	−6.84	−4.06	−4.68
$D[(15)4A_1]$	−8.20	−8.22	−9.49	−8.44
$D[(15)4E_4]$	−1.56	0.28	−7.62	−4.71
$D[(15)6A_1]$	−2.90	−5.55	−5.11	−1.41
$D[(15)6E_4]$	−8.75	−9.23	−8.34	−10.09
f	0.81	0.87	0.63	0.61
σ	1.25	1.17	0.97	0.76

gravity of each ^7F_J, a procedure (described as procedure A in Ref. 12) which amounts to associate a fictitious spin-orbit parameter to each ^7F_J.[33] Complete agreement of the results given by the two procedures was achieved so that we may conclude that a physically significant minimum has been reached.

Step 2: Maintaining the five crystal-field parameters $D[(0k)k\Gamma(C_{\infty v})]$ at their values obtained in step 1, we optimize the nine spin- and orbit-dependent parameters $D[(1k_2)k\Gamma(C_{\infty v})]$. To fully parallel step 1, the f and σ optimizations are also conducted in step 2 with and without mixing, via $\mathcal{H}_{\text{cf}}+\mathcal{H}_{\text{socf}}$, the various multiplets ^7F_J. The resulting values for the isotropic spin-orbit parameter and the eight additional parameters are listed in Table IV.

Step 3: The 14 parameters $D[(k_1k_2)k\Gamma(C_{\infty v})]$ are allowed to freely vary starting from the zero value, except $D[(11)0A_1]$ which is varied from the

TABLE V. Fitted parameters and corresponding linear and quadratic deviations obtained by means of step 3 (units are cm^{-1}).

	With J mixing	
	From f optimization	From σ optimization
$D[(02)2A_1]$, B_0^2	−51.69, 59.82	−52.16, 60.37
$D[(04)4A_1]$, B_0^4	−116.76, −219.55	−116.57, −219.20
$D[(04)4E_4]$, B_4^4	−20.76, −27.61	−22.47, −29.88
$D[(06)6A_1]$, B_0^6	−236.82, 472.66	−233.72, 466.48
$D[(06)6E_4]$, B_4^6	154.58, −218.16	153.30, −216.35
$D[(11)0A_1]$, ζ	−8819.93, 1360.94	−8818.59, 1360.74
$D[(11)2A_1]$	0.53	0.41
$D[(13)2A_1]$	2.49	4.12
$D[(13)4A_1]$	7.01	6.01
$D[(13)4E_4]$	−8.87	−4.98
$D[(15)4A_1]$	−12.09	−9.15
$D[(15)4E_4]$	−6.66	−6.01
$D[(15)6A_1]$	−3.81	−0.39
$D[(15)6E_4]$	−9.51	−10.14
f	0.49	0.57
σ	0.84	0.69

value reached in step 2. In step 3, the f and σ optimizations are conducted only in the case of J mixing. The results are set out in Table V. For the purpose of comparison, the values of ζ, cf. Eq. (4), and of B_q^k, cf. Eq. (14), also appear in Table V.

As a final result, the theoretical Stark levels arising from the term ^7F and calculated from the parameters (relative to the f optimization) of Table V are listed, together with the corresponding experimental levels, in Table VI.

TABLE VI. Sm^{2+}:SrClF observed and calculated Stark splittings of the ^7F_J multiplets (units are cm^{-1}).

Multiplet	Crystal-field labeling	Observed	Calculated
$^7F_1$	A_2	12.13	12.26
	E	−6.07	−6.13
$^7F_2$	A_1	27.12	25.86
	B_1	1.32	2.56
	B_2	−8.68	−8.43
	E	−9.88	−10.00
$^7F_3$	A_2	13.47	16.41
	B_1	21.17	21.17
	B_2	2.87	2.86
	E	−14.63	−15.83
	E	−4.13	−4.39
$^7F_4$	A_1	−73.54	−73.53
	A_1	28.46	28.25
	A_2	7.16	7.17
	B_1		90.57
	B_2	51.06	51.06
	E	−10.74	−10.64
	E	4.16	4.16
$^7F_5$	A_1	65.10	66.22
	A_2	18.80	18.84
	A_2		70.05
	B_1		−4.96
	B_2	−50.70	−50.70
	E	−34.80	−34.80
	E	−4.40	−5.61
	E	22.60	23.23
$^7F_6$	A_1	−9.25	−8.77
	A_1	3.35	4.75
	A_2	−8.75	−8.76
	B_1	14.35	12.67
	B_1		54.73
	B_2		−0.70
	B_2		54.48
	E	−10.65	−10.65
	E	0.25	0.17
	E	10.55	10.54

We now briefly comment on the various results in this section. First, the (Racah) quadratic error

$$\sigma(P)=\left\{\sum_J\sum_i[\Delta_i(J)]^2/(E-P)\right\}^{1/2}, \qquad (17)$$

where P notes the number of parameters freely varied, is decreased from $\sigma(6)\sim1.60$ to $\sigma(14)\sim1.05$ cm^{-1} when passing from step 1 to step 3. Second, the value $\zeta\sim1360$ cm^{-1} of the spin-orbit parameter in Table V compares with the value of Ref. 34. Third, the parameters in Table V (surprisingly) turn out to be roughly the superposition of the corresponding parameters in Tables III and IV, a fact which reflects the goodness of the various fits. Although no marked correlation between the fourteen parameters was detected, there is some evidence from Table V, by comparing the σ optimization and the f optimization, to indicate that the nine spin- and orbit-dependent parameters are less well stabilized than the five crystal-field parameters. In this vein, it is instructive to look at the extreme values for each of the parameters appearing in Tables III, IV, and V in the case of J mixing. The latter values define a reasonable reliability coefficient for each parameter $D[(k_1k_2)k\Gamma(C_{\infty v})]$. Note that simultaneous change of the sign of the parameters $D[(k_1k_2)kE_4]$ in Table V leads to an equally well acceptable set of parameters because the mathematical spectrum of $\mathcal{H}$ within the $4f^6$ manifold exhibits remarkable symmetries[35,36] (cf. Appendix B).

E. Parameter analysis

The crystal-field parameters in Table V are sufficiently well defined to warrant an analysis along the lines discussed in Sect. IV B 2.

As a first preliminary step, *ab initio* crystal-field parameters were calculated from the electrostatic model involving both point-charge and induced-dipole contributions, cf. Eqs. (6) and (7).[37] When substituted in the energy matrices, the resulting crystal-field parameters yield a mean linear deviation $f\sim14$ cm^{-1} which is considerably far from the fitted value $f\sim1.2$ cm^{-1} of Table III. This clearly shows the difficulty of describing the experimental spectrum of Sm^{2+}:SrClF on the basis of point and dipolar electrostatic contributions only. More surprisingly, it is to be noted that the electrostatic model ratios[37] $B_0^4/B_4^4\sim-4.2$ and $B_0^6/B_4^6\sim0.9$ are markedly different from the fitted values (cf. Table V) $B_0^4/B_4^4\sim\pm7.6$ and $B_0^6/B_4^6\sim\mp2.2$, respectively.

As a second preliminary step, we tried to interpret the fitted crystal-field parameters of Table V in the framework of the Ξ^2 model (i.e., the angular overlap model restricted to the σ effects). By combining Eqs. (6) and (8) with $I_k(J) = (2k+1)e_\sigma(J)/7$ (cf. Appendix C), we are left with two linear systems: a 3-3 system connecting $D[(02)2A_1]$, $D[(04)4A_1]$, $D[(06)6A_1]$ with $e_\sigma(1)$, $e_\sigma(2)$, $e_\sigma(3)$ and a 2-2 system connecting $D[(04)4E_4]$, $D[(06)6E_4]$ with $e_\sigma(1)$, $e_\sigma(2)$. [J in $e_\sigma(J)$ refers to the three series of ligands, cf. Sec. II.] The resolution of the latter two systems gave inconsistent values for the $e_\sigma(J)$'s, a fact which shows the impossibility of describing the metal-ligand bonding in Sm^{2+}:SrClF with the Ξ^2 model.

The next step should be to introduce π, δ, and φ effects in addition to the σ effects.[38,39] For the sake of simplification, we could imagine introducing equally weak π, δ, and φ contributions. According to result 2 of Appendix C, this approach would be equivalent to the Ξ^2 approach. We therefore establish (a physically reasonable) hierarchy between the σ, π, δ, and φ effects by assuming

$$e_\sigma(J) > e_\pi(J) = t_J e_\sigma(J) > e_\delta(J) = e_\varphi(J) = 0 \ .$$

Then, the combination of Eqs. (6), (8), and (10) leads to the following 5-6 linear system:

$$\begin{aligned}
D[(02)2A_1] &= -8(\tfrac{2}{21})^{1/2}[C_0^2(1)e_\sigma(1)(1+\tfrac{3}{2}t_1)+C_0^2(2)e_\sigma(2)(1+\tfrac{3}{2}t_2)]-2(\tfrac{2}{21})^{1/2}e_\sigma(3)(1+\tfrac{3}{2}t_3) \ ,\\
D[(04)4A_1] &= 24(\tfrac{1}{77})^{1/2}[C_0^4(1)e_\sigma(1)(1+\tfrac{1}{3}t_1)+C_0^4(2)e_\sigma(2)(1+\tfrac{1}{3}t_2)]+6(\tfrac{1}{77})^{1/2}e_\sigma(3)(1+\tfrac{1}{3}t_3) \ ,\\
D[(06)6A_1] &= -40(\tfrac{2}{231})^{1/2}[C_0^6(1)e_\sigma(1)(1-\tfrac{3}{2}t_1)+C_0^6(2)e_\sigma(2)(1-\tfrac{3}{2}t_2)]-10(\tfrac{2}{231})^{1/2}e_\sigma(3)(1-\tfrac{3}{2}t_3) \ , \qquad (18)\\
D[(04)4E_4] &= 12(\tfrac{2}{77})^{1/2}\{[C_4^4(1)+C_{-4}^4(1)]e_\sigma(1)(1+\tfrac{1}{3}t_1)+[C_4^4(2)+C_{-4}^4(2)]e_\sigma(2)(1+\tfrac{1}{3}t_2)\} \ ,\\
D[(06)6E_4] &= -40(\tfrac{1}{231})^{1/2}\{[C_4^6(1)+C_{-4}^6(1)]e_\sigma(1)(1-\tfrac{3}{2}t_1)+[C_4^6(2)+C_{-4}^6(2)]e_\sigma(2)(1-\tfrac{3}{2}t_2)\} \ .
\end{aligned}$$

(C_q^k stands for the spherical harmonic Y_{kq} in the Racah normalization.[22]) The system (18), with the values (relative to the f optimization) of Table V for the D's and the values deduced from Sec. II for the C's, has been solved by freely varying the percentage parameters t_J from 0% to 100%. (Note that the case $t_J = 0$ corresponds to the first preliminary step.) No acceptable solution has been found assuming either $t_1 = t_2 = t_3$ or $t_1 \neq t_2 = t_3$. Acceptable solutions have been obtained for $t_1 \sim 75\%$, $t_2 \sim 9\%$, and $t_3 \sim 35\%$. More precisely, it has been found that the experimental levels reported in Table VI can be reproduced, with a mean linear deviation $f \sim 1.2\ \mathrm{cm}^{-1}$, by taking $e_\sigma(1) = 236$, $e_\sigma(2) = 191$, $e_\sigma(3) = 252$, $e_\pi(1) = 178$, $e_\pi(2) = 17$, and $e_\pi(3) = 88\ \mathrm{cm}^{-1}$. It is probably premature speculating on these results about the Sm^{2+}-ligand bonding in SrClF. We only note that such a bonding involves important π effects in addition to the σ effects.

V. MISCELLANEOUS COMMENTS

(i) The five crystal-field parameters, the spin-orbit parameter, and the eight additional parameters constitute the minimal set of parameters required to treat in a symmetric way the spin- and orbit-dependent parts of the effective Hamiltonian acting within the term ^7F. The various fits of the parameters show an excellent agreement between theory and experiment. The results of the fitting procedures allow us to ascribe a good confidence level for the crystal-field parameters B_q^k: from the extreme values reported in Tables III, IV, and V, we may reasonably take $B_0^2 = 58 \pm 4$, $B_0^4 = -217 \pm 3$, $B_4^4 = -27 \pm 5$, $B_0^6 = 472 \pm 6$, and $B_4^6 = -217 \pm 3\ (\mathrm{cm}^{-1})$. The accuracy of the additional parameters $D[(1k_2)k\Gamma(C_{\infty v})]$ is not so good. The magnitudes of these additional parameters are small and give, in a certain sense, a further measure of the accuracy of the crystal-field parameters. Although the quadratic error turns out to be decreased when introducing the additional parameters, they should not be taken too seriously. Some further information would be of interest to test the significance of the latter parameters. In this connection, it would be useful to look at Zeeman experiments to see if the introduction of the additional parameters would give better theoretical g splitting factors.

(ii) The analysis of the crystal-field parameters in the framework of the angular overlap model leads to a conclusion roughly similar to the one reached for the Sm^{2+}:BaClF system[12]: the Sm^{2+}-ligand bonding includes a noticeable amount of π effects especially for the four fluorines in the plane perpendicular to the c axis. It is felt that the values of the parameters e_λ obtained in Ref. 12 and in the present study might be of interest for exploring, on the basis of investigations of various compounds or series, the chemical bond for rare-earth ions in crystals. In that direction, it should be noted that the analysis of the crystal-field parameters in the framework of the superposition model should be useful too.

The analysis of the additional parameters should be also possible in the framework of linear models. We think however that values of these parameters for other compounds are needed to conduct such an analysis in a comparative way. The physical significance of the additional parameters is still not clear although several mechanisms could be invoked to justify the introduction of double tensors: relativistic crystal-field,[21] spin-polarization effects,[19,20] and charge transfer.[20]

(iii) We close by going back to the introduction where it was mentioned that the spectra for Sm^{2+}:BaClF and Sm^{2+}:SrClF exhibit the same characteristics. This is reflected by the values of the parameters B_q^k which are comparable for the two systems with the exception of B_0^2: B_0^2 (Sm^{2+}:BaClF) $= -93$ cm^{-1} and B_0^2 (Sm^{2+}:SrClF) $= 58$ cm^{-1}. Indeed, the latter values describe the following experimental situation: defining $F = {}^7F_1(E) - {}^7F_1(A_2)$, from Table II we get $F = -18.2$ cm^{-1} for Sm^{2+}:SrClF while from Ref. 12 we have $F = 27$ cm^{-1} for Sm^{2+}:BaClF. We further note that by defining $D = {}^5D_1(E) - {}^5D_1(A_2)$, we obtain from the experimental data in Ref. 12 and in this work $D = 6.9$ cm^{-1} for Sm^{2+}:SrClF and $D = 8$ cm^{-1} for Sm^{2+}:BaClF. So that, the ratio $R = D/F$ assumes the values R (Sm^{2+}:BaClF) $= 0.296$ and R (Sm^{2+}:SrClF) $= -0.379$. The experimental value of R for Sm^{2+}:BaClF is in excellent agreement with the theoretical value $R = 0.298$ derived in Ref. 22. Surprisingly enough, such an agreement does not hold for Sm^{2+}:SrClF. Furthermore, in order to fit the rule[20] $R = \frac{11}{45} + 79c_2/90$, it would be necessary to take $c_2(Sm^{2+}$:SrClF$) = -0.71$, a value which seems to be out of the range of reasonable values. We do not see any physical reason why the experimental values of R are so different for the two considered compounds. We simply note, on the basis of ionic radii data, that Sm^{2+} matches better the cationic sublattice in SrClF than in BaClF.

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APPENDIX A: ON THE SYMMETRY ADAPTED COUPLING COEFFICIENTS

The f symbol for the chain $SO_3 \supset G$ or $SU_2 \supset G^*$ is defined through[24]

$$f\begin{pmatrix} J_1 & J_2 & J_3 \\ \mu_1 & \mu_2 & \mu_3 \end{pmatrix} = \sum_{M_1 M_2 M_3} (-1)^{J_2+J_3-M_1} \langle J_1 -M_1 | J_1 \mu_1 \rangle^* \langle J_2 M_2 | J_2 \mu_2 \rangle \langle J_3 M_3 | J_3 \mu_3 \rangle \begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix} . \qquad \text{(A1)}$$

In Eq. (A1)

$$\begin{pmatrix} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{pmatrix}$$

denotes a Wigner 3-*jm* symbol and $\langle J_i M_i | J_i \mu_i \rangle$ $(i = 1, 2, 3)$ an element of the transformation to pass from the $\{JM\}$ scheme to the $\{J\mu\}$ scheme. The (crystal-field) quantum number μ in $\langle JM | J\mu \rangle$ stands for a three-index label $a\Gamma\gamma$, where Γ is an IRC of the point symmetry group G (respectively, double group G^*) occurring in the IRC J of the special orthogonal group SO_3 (respectively, special unitary group SU_2), γ is a multiplicity index to be used when the dimension of Γ is greater than 1, and a is a (branching) multiplicity index to be used when the frequency of Γ in J is greater than 1. Note that when μ_3 in Eq. (A1) involves the identity IRC A_1 of G, we have the particular selection rule

$$f\begin{pmatrix} J' & J & k \\ a'\Gamma'\gamma' & a\Gamma\gamma & a_1 A_1 \end{pmatrix} = \delta(\Gamma'\Gamma)\delta(\gamma'\gamma) f\begin{pmatrix} J' & J & k \\ a'\Gamma & a\Gamma & a_1 A_1 \end{pmatrix}$$

where

$$f\begin{pmatrix} J' & J & k \\ a'\Gamma & a\Gamma & a_1 A_1 \end{pmatrix}$$

is independent of γ, a result used in Eq. (2).

Returning to the general case, it is worth noting that the indices a and γ often can be characterized (at least partially) by IRC's of groups G_a^* and G_γ^*, respectively, such that $SU_2 \supset G_a^* \supset G^* \supset G_\gamma^*$. In this connection, the group chain $SO_3 \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$ allows us to completely characterize the label μ by the triplet $\Gamma(C_{\infty v})\Gamma(C_{4v})\Gamma(C_{2v})$. The matrix elements $\langle JM|J\Gamma(C_{\infty v})\Gamma(C_{4v})\Gamma(C_{2v})\rangle$ relevant to this work are obtainable from

$$|JA_1A_1A_1\rangle = |J0\rangle, \quad J=0,2,4,6 \ ,$$

$$|JA_2A_2A_2\rangle = |J0\rangle, \quad J=1,3,5 \ ,$$

$$\left.\begin{aligned} |JE_\lambda A_1A_1\rangle &= \frac{1}{\sqrt{2}}(|J\lambda\rangle + (-1)^J|J-\lambda\rangle) \\ |JE_\lambda A_2A_2\rangle &= \frac{1}{\sqrt{2}}(|J\lambda\rangle - (-1)^J|J-\lambda\rangle) \end{aligned}\right\} \lambda=4 \ ,$$

$$\left.\begin{aligned} |JE_\lambda B_1A_1\rangle &= \frac{1}{\sqrt{2}}(|J\lambda\rangle + (-1)^J|J-\lambda\rangle) \\ |JE_\lambda B_2A_2\rangle &= \frac{1}{\sqrt{2}}(|J\lambda\rangle - (-1)^J|J-\lambda\rangle) \end{aligned}\right\} \lambda=2,6 \ , \tag{A2}$$

$$\left.\begin{aligned} |JE_\lambda EB_1\rangle &= \frac{(-1)^{(\lambda+1)/2}}{\sqrt{2}} \\ &\quad \times(|J\lambda\rangle - (-1)^J|J-\lambda\rangle) \\ |JE_\lambda EB_2\rangle &= \frac{1}{\sqrt{2}} \\ &\quad \times(|J\lambda\rangle + (-1)^J|J-\lambda\rangle) \end{aligned}\right\} \lambda=1,3,5 \ .$$

The coefficients f relative to the chain $SO_3 \supset C_{\infty v} \supset C_{4v} \supset C_{2v}$ can be calculated by combining Eqs. (A1) and (A2). This leads to closed-form expressions, the numerical values of which are easily computer generated.

APPENDIX B: ON THE PSEUDOSYMMETRIES OF CERTAIN OPERATORS

We begin with the operator

$$\mathcal{H} = \sum_{ka_1} D[ka_1] T^k_{a_1A_1}$$

defined on a space $\mathcal{E}$ and invariant under a group G. (In the main body of this paper $T \equiv W^{(k_1k_2)}$.) Let us suppose there exists (at least) one symmetry operation $R_0 \in G_0 \supset G$ such that $\mathcal{E}$ be stable under R_0 and $T^k_{a_1A_1}$ transforms as

$$P_{R_0} T^k_{a_1A_1} (P_{R_0})^{-1} = \epsilon(ka_1,R_0) T^k_{a_1A_1} \ ,$$

where ϵ stands for some *(a priori* complex) number. [Note that if R_0 is allowed to be any element of G_0, then $\epsilon(ka_1,R_0)$ is nothing but the character of R_0 in some one-dimensional IRC Γ_0 of G_0.] We have the result[36]:

Result. The change of $D[ka_1]$ into $\epsilon(ka_1, R_0)D[ka_1]$ does not change the eigenvalues spectrum of $\mathcal{H}$ within $\mathcal{E}$. Further, if there exists a pair of IRC's Γ and Γ' of G such that the Γ and Γ' subspaces of $\mathcal{E}$ are interchanged under R_0, then the change of $D[ka_1]$ into $\epsilon(ka_1, R_0)D[ka_1]$ interchanges the eigenvalues belonging to Γ and Γ'.

We continue with the Hamiltonian $\mathcal{H}$, cf. Eqs. (1) and (3), considered in the present work. In the case where $G \equiv C_{4v}$ and $R_0 \equiv C_8$ (and thus belongs to $G_0 \equiv C_{8v}$), it is seen from the elements $\langle kq|k\Gamma(C_{\infty v})\Gamma(C_{4v})\Gamma(C_{2v})\rangle$ obtainable from Appendix A that

$$\epsilon(kA_1, R_0)=1, \quad k=0,\ 2,\ 4,\ 6 \ ,$$

$$\epsilon(kE_4, R_0)=-1, \quad k=4,\ 6 \ .$$

Furthermore, it can be verified from Appendix A that R_0 yields invariant the various $\Gamma(C_{4v})$ subspaces of the $\mathcal{E} \equiv {}^7F$ manifold except for $\Gamma(C_{4v})=B_1$ and B_2. In fact, P_{R_0} changes the ray $|JE_\lambda B_1A_1\rangle$ into the ray $|JE_\lambda B_2A_2\rangle$ and vice versa. Consequently, simultaneous change of signs of $D[(04)4E_4]$, $D[(06)6E_4]$, $D[(13)4E_4]$, $D[(15)4E_4]$, and $D[(15)6E_4]$ leads to the same eigenvalues spectrum of $\mathcal{H}$ within the ${}^7F$ manifold (and even within the $4f^6$ manifold) but with an interchange of the eigenvalues belonging to B_1 and B_2. Consequently, we have two minima when optimizing the 14-parameter Hamiltonian $\mathcal{H}$ within the subspace ${}^7F$ without symmmetry adaptation. Indeed, we have only one minimum in our approach since we experimentally separate the energy levels corresponding to the symmetry species B_a and B_b and we separately optimize five spectra corresponding to the $7(A_1)$, $6(A_2)$, $6(B_1)$, $6(B_2)$, and $12(E)$ submatrices. This further emphasizes the interest using a (prediagonalized) symmetry adapted basis.

In all honesty, the results of this appendix are a mathematical transcription and generalization of the remark[35] according to which "if the signs of $A_4^4(\sim B_4^4)$ and $A_6^4(\sim B_4^6)$ are changed simultaneously, the calculated spectrum (of f^2 in D_{2d}) remains unchanged."

APPENDIX C: ON THE ANGULAR OVERLAP MODEL

We derive here a result (result 2), concerning the *formal* connection between the angular overlap model and the point-charge electrostatic model, which should have its natural place in Ref. 30. For the purpose of comparison, we begin with a known result (result 1).

Result 1. Assuming $e_{m''} = \delta(m''o)e_\sigma$, Eq. (10) reduces to

$$I_k = \frac{2k+1}{2l+1} e_\sigma = (2k+1) I_0 \ .$$

Result 1 was discussed in Ref. 30 and tells under what condition the Ξ^2 model (a particular case of the angular overlap model) is *phenomenologically* a particular case of the point-charge electrostatic model.

Result 2. Assuming $e_{\pm m''} = e \neq e_\sigma$, for any $m'' \neq 0$, we have

$$I_k = \frac{2k+1}{2l+1}(e_\sigma - e), \quad k \neq 0 \ ,$$

$$I_o = \frac{1}{2l+1}(e_\sigma + 2le) \ .$$

To prove result 2, it is sufficient to introduce $e_\pi = e_\delta = e_\varphi = \cdots = e$ into Eq. (10) and then to use the so-called barycenter sum rule

$$\sum_m (-1)^{j-m} \begin{pmatrix} j & k & j \\ -m & q & m \end{pmatrix} = \delta(ko)\delta(qo)(2j+1)^{1/2} \ .$$

Result 2 leads to

$$I_k(J)/I_{k'}(J) = (2k+1)/(2k'+1), \quad k,k' \neq 0 \ ,$$

which also follows from result 1. In other words, the angular overlap model restricted to the case where the π, δ, φ, . . . , bonding and antibonding effects bring equal contributions (in the sense that $e_\pi = e_\delta = e_\varphi = \cdots = e \neq e_\sigma$) is *phenomenologically* equivalent to the Ξ^2 model. Note that such a *phenomenological* equivalence can also be proved to directly follow from the definition[28] of the angular overlap model in terms of $SO_3 \supset SO_2$ rotation matrices.

Most of the angular overlap model calculations have been confined, up to a recent past, to the σ effects. The trend now evolves towards simultaneous consideration of the σ, π, δ, . . . , effects.[12,38,39] The π, δ, φ, . . . , effects are generally assumed to be less important than the σ effects. The physical interest of result 2 may be seen as follows: in the situation where the π, δ, φ, . . . , effects (are supposed to) bring nearly equal contributions, it is sufficient in a *phenomenological* approach to only retain the σ effects.

To close Appendix C, it is perhaps worthwhile to give a word of comment on what we mean by *phenomenological* equivalence between the angular overlap model and the point-charge electrostatic model. Of course, the *ab initio* angular overlap model and point-charge electrostatic model are two inequivalent models: the point-charge electrostatic model comes out from the ionic model whereas the angular overlap model can be derived from a weakly covalent model. Nevertheless, if (and only if) the angular overlap model and point-charge electrostatic model parameters are considered as semiempirical adjustable (rather than *ab initio)* parameters, then the point-charge electrostatic model and the angular overlap model constitute two equivalent (in the sense equally acceptable) parametrizations.

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