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Crystal-field analysis of Eu^{3+} doped in cubic yttrium sesquioxide. Application of the electrostatic and angular overlap models

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The phenomenological crystal-field parameters of Eu^{3+} in Y_2O_3 are determined with reference to previous symmetry assignments obtained for the ^7F_J ($J = 1$ to 4) sublevels by laser-induced polarized fluorescence. The crystal-field plus spin-orbit Hamiltonian is diagonalized on the truncated basis containing the lowest ^7F multiplet of the f^6 configuration. The final mean deviation of the experimental and calculated values is equal to 4.8 cm^{-1}. The results are interpreted on the basis of the electrostatic model including point-charge and dipolar contributions. A possible complementary covalency contribution is found by application of the angular overlap model.

I. INTRODUCTION

In a previous work,[1] we investigated the laser-induced fluorescence of Eu^{3+} doped in the C_2 sites of cubic yttrium sesquioxide. In this compound, the rare earth also occupies S_6 sites, but Eu^{3+} substituted in the C_2 site of yttrium is responsible for the quasitotality of the fluorescence spectrum under ultraviolet excitation. The symmetry labels of the ^7F_J ($J = 1-4$) electronic levels of Eu^{3+} ($4f^6$) were identified. Conventional polarization analysis could not be performed since, owing to the cubic symmetry of the matrix, the C_2 axis of the local site could lie with equal chances along the X, Y, or Z crystallographic axes. However, site-selective laser-induced fluorescence displayed partial polarization of the $^5D_0 \rightarrow {}^7F_j$ spectral lines, in agreement with Feofilov's[2] statements. Theoretical polarizations depending on the symmetry of the terminating levels were calculated by summing up the intensities emitted individually by the differently oriented sites. Comparison with experimental results allowed for the assignment of symmetry labels. The present paper reports the following.

(a) A phenomenological crystal-field analysis of Eu^{3+}: determination of *experimental* crystal-field parameters (CFP).

(b) The calculation of *ab initio* electrostatic CFP including point-charge and dipolar contributions. The values are then corrected for shielding and expansion of the $4f$ wave function in the solid and compared to experimental CFP.

(c) A prediction of the CFP of the quasi-invisible, centrosymmetrical S_6 site.

(d) An attempt to apply the angular overlap model (AOM) to experimental results.

II. PHENOMENOLOGICAL CRYSTAL-FIELD ANALYSIS

The crystal-field potential energy[1] is written as

$$V = \sum_{k,q>0} b_q^k(C_{-q}^k + C_q^k) + is_q^k(C_{-q}^k - C_q^k) + \sum_k b_0^k C_0^k$$

for an even-order symmetry axis. The C_2 symmetry implies nine real (b_q^k) and five imaginary (is_q^k) CFP. The matrix elements of V are calculated between the 49 ^7F_J ($J = 0-6$) lower states of the $4f^6$ configuration. Adjustable constants are added to diagonal terms of the spin-orbit interaction to correct for the truncation. Twenty experimental energies (from $^7F_1$ to $^7F_4$, see Ref. 1) were introduced in the refinement process. The energies of the $^7F_5$ and $^7F_6$ levels previously measured by absorption experiments by Chang and Gruber[3] were not utilized for two reasons: Firstly, the symmetry of these experimental levels is unknown, and secondly, some sparse lines originating from the S_6 site could have led to erroneous interpretations.

The starting values of the CFP were electrostatic *ab initio* values multiplied by 0.5, 1.7, and 2.5 for B_q^2, B_q^4, and B_q^6, respectively (see Sec. III and Ref. 4). A diagonalization with the obtained values showed that this choice ensured for electric dipolar (ED) transitions ($^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_4$) a disposition of levels in agreement with the previous experimental assignments.[1] With regard to the polarization of magnetic dipolar (MD) lines, it must be pointed out that there exists a misstatement in Ref. 1 where the active ion was considered as a magnetic rotor instead of an electric rotor. In fact, when the symmetry of the terminating level is A, the polarization of the MD transition must be negative, so that the A level of $^7F_1$ corresponds to the unique negatively polarized central line. This disposition comes out naturally from the diagonalization of the interaction matrix with the choice of (corrected) electrostatic CFP.

An ambiguity appears for the $^5D_0 \rightarrow {}^7F_3$ transition. The two extreme lines are positively polarized. Therefore, either the transition is mainly ED [via a crystal-field (CF) J mixing $^7F_3$-$^7F_2$ by the strong fourth-order CFP] and then the extreme levels have an A symmetry, or the transition is mainly MD (via a CF J mixing $^7F_3$-$^7F_1$) and the extreme levels have a B symmetry. The first hypothesis is in agreement with the disposition of levels resulting from the choice of corrected electrostatic CFP and was therefore retained.

The CFP were then refined by the least-squares method and the final set of parameters is reported in Table I with their estimated standard deviations. The second- and fourth-order parameters are the most reliable. The sixth-order CFP are weaker and less well determined since they only act directly on the $^7F_3$ and $^7F_4$ levels. The final average deviation between calculated and observed levels is equal to 4.8 cm^{-1}. The CFP of Er^{3+} and Tm^{3+} in Y_2O_3 previously refined by Gruber, Krupke, and Poindexter[5] are also reported in Table I for comparison. The main discrepancies between the three sets emphasize the weak point of the refinement, i.e., the imperfect determination of the small parameters, the imaginary components s_q^4 and all the sixth-order CFP. Their action is overwhelmed by that of the much stronger b_q^2 and b_q^4.

TABLE I. Experimental crystal-field parameters (cm^{-1}) of Eu^{3+}, Er^{3+}, and Tm^{3+} in the C_2 sites of Y_2O_3.

Parameter	Eu^{3+} [a]	Er^{3+} [b]	Tm^{3+} [b]
b_0^2	-196 ± 7	-154 ± 38	-164 ± 54
b_2^2	-695 ± 3	-608 ± 17	-519 ± 23
b_0^4	-1264 ± 9	-1216 ± 80	-800 ± 120
b_2^4	-1519 ± 9	-1496 ± 29	-1353 ± 64
s_2^4	-321 ± 12	3 ± 33	149 ± 71
b_4^4	1092 ± 7	773 ± 24	800 ± 46
s_4^4	255 ± 13	18 ± 25	-65 ± 70
b_0^6	267 ± 18	-112 ± 48	48 ± 48
b_2^6	228 ± 9	333 ± 26	130 ± 58
s_2^6	276 ± 13	-25 ± 39	3 ± 34
b_4^6	894 ± 11	212 ± 26	324 ± 67
s_4^6	281 ± 14	-140 ± 29	-450 ± 37
b_6^6	157 ± 9	-14 ± 25	1 ± 39
s_6^6	95 ± 10	56 ± 27	162 ± 56

[a] This work, 20 experimental levels, mean deviation = 4.8 cm^{-1}.

[b] Following Ref. 5.

III. *Ab initio* CRYSTAL-FIELD PARAMETERS

Both point charge (PC) and dipolar (D) contributions were taken into account. These calculations are very sensitive to small changes in atomic positions, so the structure of Y_2O_3 was refined by the neutron diffraction technique at the temperature of the fluorescence experiments (77 K).[6] The final structural data with space group $Ia3$, $Z = 16$, and $a = 10.6073(3)$ Å at 77 K are the following:

$$\mathrm{Y}(1)\quad 8b\quad \tfrac{1}{4}\quad \tfrac{1}{4}\quad \tfrac{1}{4}$$

$$\mathrm{Y}(2)\quad 24d\quad u\quad 0\quad \tfrac{1}{4}\quad u = 0.0323(2)$$

$$\mathrm{O}\quad 48c\quad x\quad y\quad z$$

$$x = 0.3912(3),\ y = 0.1515(3),\ z = 0.3800(3)\ .$$

The point-charge contribution to the CFP is given as usual by a lattice sum over the ions of the lattice (j):

$$B_q^k = -\left[\frac{4\pi}{2k+1}\right]^{1/2} e^2 \langle r^k \rangle \sum_j \frac{C_j}{R_j^{k+1}} Y_k^{q*}(\vec{j})\ . \quad (1)$$

If the distances (R_j,r) are expressed in atomic units (0.5292 Å) and the charges (C_j) as multiples of the electron charge $|e|$, then the B_q^k are given in units of 219 474 cm^{-1}. Charges + 3 and − 2 were assigned to yttrium and oxygen, respectively. The $\langle r^k \rangle$ were the recent values computed by Freeman and Desclaux[7], $\langle r^2 \rangle = 0.917$, $\langle r^4 \rangle = 2.02$, and $\langle r^6 \rangle = 9.04$ a.u. A good convergence of the second-order parameter was obtained by a lattice sum extending at 60 Å from the central ion (involving 60 629 atoms). The results (in cm^{-1}) are gathered in Table II.

TABLE II. Experimental and calculated crystal-field parameters of Eu^{3+} in the C_2 site of Y_2O_3.

b_q^k	PC[a]	Dipole[b]	PC + dipole (ES)	rotated (ES′)	ES′$(1-\sigma_k)^{c}$ $\times \langle r'^k\rangle/\langle r^k\rangle$	Expt.
b_0^2	−308	−336	−644	−644	−256	−196
b_2^2	−876	−319	−1195	−1206	−480	−695
s_2^2	282	−120	161	0	0	0
b_0^4	−770	−64	−834	−834	−1209	−1264
b_2^4	−1015	57	−958	−951	−1378	−1519
s_2^4	0	7	7	−119	−172	−321
b_4^4	813	30	843	758	1099	1092
s_4^4	240	−32	208	422	611	255
b_0^6	89	39	128	128	305	267
b_2^6	−5	19	14	13	32	228
s_2^6	5	0	5	6	14	276
b_4^6	271	17	288	274	654	894
s_4^6	16	2	18	93	222	281
b_6^6	37	−6	31	22	52	157
s_6^6	25	−8	17	27	66	95

[a] Point charges only; see Sec. III.

[b] Contribution of induced dipoles; see Sec. III.

[c] Total electrostatic parameter (ES′) corrected for shielding and for the expansion of the radial wave function (see Sec. III). The radial integrals of Freeman and Watson (Ref. 19) $\langle r^2\rangle$, $\langle r^4\rangle$, and $\langle r^6\rangle$ were previously (Ref. 4) multiplied by 1.4, 2, and 2.6 so that the new values of Freeman and Desclaux (Ref. 7) are multiplied by 1.267, 1.683 and 2.157.

The dipolar contributions to the B_q^k are given by the following expression identical to (A4) in Ref. 4:

$$(B_q^k)_D = e\langle r^k\rangle[4\pi(k+1)(2k+1)]^{1/2}\sum_{j\mu}(-1)^{k+q+\mu+1}\begin{bmatrix} k & 1 & k+1 \\ q & \mu & -q-\mu \end{bmatrix} M_{j\mu}Y_{k+1}^{q+\mu *}(\vec{j})\Big/R_j^{k+2}\ , \tag{2}$$

where $M_{j\mu}$ is a spherical component of the dipolar moment on j, such that

$$M_{j\pm 1} = \mp\frac{1}{\sqrt{2}}(M_{jx} \pm iM_{jy}),\ M_{j0} = M_{jz}\ ,$$

and

$$\begin{bmatrix} k & 1 & k+1 \\ q & \mu & -q-\mu \end{bmatrix}$$

is a $3j$ symbol. The dipolar moments $\vec{M}_j$ are calculated in a consistent way by

$$M_{jv} = \alpha_j\left[E_{PC}(j,v) + \sum_{j'v'} E_D(jj'v'v)M_{j'v'}\right]\ , \tag{3}$$

where v and $v' = x, y$, or z. The monopolar field is given by

$$\vec{E}_{PC}(j) = \sum_{j'} \vec{\nabla}_{j'}\frac{(q_{j'}e)}{R_{j'}}\ , \tag{4}$$

and the dipolar field by

$$\vec{E}_D(j) = \sum_{j'} \vec{\nabla}_{j'}\left[\vec{M}_{j'}\cdot\vec{\nabla}_{j'}\left[\frac{1}{R_{j'}}\right]\right]\ . \tag{5}$$

Ewald's method is utilized to make $\vec{E}_{PC}$ and $\vec{E}_D$ quickly converging.

The yttrium atom in the S_6 ($8b$) centrosymmetrical site cannot carry any dipolar moment since the electric field vanishes in this site. Assuming scalar polarizabilities, we are left with two unknown polarizability values: $\alpha_{O^{2-}}$ (48*c*) and $\alpha_{Y^{3+}}$ (24*d*). There exists some uncertainty concerning the good choice, and the reported experimental data are rather scarce. Since the determinations of dipolar polarizabilities of gaseous ions by Pauling,[8] it is admitted that in a crystal, α is increased for a cation, the reverse being true for an anion. This explained, for example, the difference between Pauling results and those obtained by Tessman, Kahn, and Shockley[9] (TKS) from experimental refraction data and utilizing the additivity assumption. However, the values for O^{2-} obtained by TKS range from 0.9 to 3.2 following the compound (SnO_2 and Cu_2O, respectively). This illustrates the existence of a substantial environmental effect but does not help in choosing a particular value, so we adopted, rather arbitrarily, the dipole polarizabilities calculated *ab initio* by Schmidt *et al.*[10] by a procedure including self-consistency effects. For ions in a crystal $\alpha_{O^{2-}} = 1.349$ Å^3 and $\alpha_{Y^{3+}} = 0.87$ Å^3. The dipolar contributions utilizing these values are reported in Table II; The total electrostatic CFP are also listed with a nonzero s_2^2 component. A ϕ rotation around the C_2 axis (such that $\tan 2\phi = -s_2^2/b_2^2$) was then applied to cancel s_2^2, and the resulting values are also collected in Table II.

They must be corrected for the shielding of the electric field by the distorted outer $5s^2$, $5p^6$ closed shells. As for Eu^{3+} in Gd_2O_3 (Ref. 11) we set $\sigma_2 = 0.686$ (Ref. 12), $\sigma_4 = 0.139$, and $\sigma_6 = -0.109$ (small antishielding). These values of σ_4 and σ_6 have been computed for Nd^{3+}.[13] In fact, the shielding factors which can be found in the literature are different according to the calculation technique and the chosen type of wave function. For instance, Leavitt *et al.*,[14] adopting the results of Sternheimer,[15–17] assumed a linear variation of σ_2 across the rare-earth series from 0.545 (Tm^{3+}) to 0.666 for Pr^{3+}, σ_4 and σ_6 constant and equal to 0.09 and -0.04, respectively. Another point is still more crucial. As was pointed out previously,[18,4] the origin of the discrepancy between experimental and electrostatic CFP could be the utilization of inadequate free-ion radial integrals. In the case of Nd^{3+} in Nd_2O_3, we had, in view of the lowering of Slaters integrals F^2, F^4, and F^6 with respect to the free-ion values, crudely estimated that $\langle r^2 \rangle$, $\langle r^4 \rangle$, and $\langle r^6 \rangle$ from Freeman and Watson[19] should be multiplied by 1.4, 2, and 2.6, respectively. The same correction factors were applied here. The final electrostatic CFP corrected for shielding and for the expansion of the radial wave function are listed Table II, together with the experimental parameters; the agreement is fairly good for the second- and fourth-order parameters (real components). It is less satisfactory for the s_q^4 and the sixth-order CFP, but we have already pointed out that their experimental determination was markedly less precise. In addition, the diagonalization of a larger interaction matrix involving higher states (5*D*, 5*F*, and 3*F*) would likely change the aspect of the lower ^7F manifold, and following that, substantially modify experimental CFP. At this stage it would be unrealistic to seek a better agreement. Utilizing the same *ab initio* method, we have calculated the corrected electrostatic CFP of the invisible S_6 site. They are reported in Table III.

IV. ANGULAR OVERLAP MODEL (AOM)

The ionic model requires corrected radial integrals in order to match experimental and calculated values. Other authors look for a different interpretation of the host-dependent lifting of degeneracy of energy levels. Jörgensen, Pappalardo, and Schmidtke,[20] in 1963, put forth the hypothesis that the observed crystal-field splittings of a central ion with a partially filled l shell could find their origin in weak covalent bonding with the ligands. σ overlap was first considered (Ξ^2 model). Schäffer and Jörgensen[21] generalized the model to π and δ antibonding and Kibler[22] stressed the *phenomenological* link between the PCEM and the AOM. Practical-

TABLE III. Predicted crystal-field parameters for Eu^{3+} in the S_6 site of Y_2O_3.

b_q^k	PC	Dipole	PC + dipole (ES)	Predicted parameters $ES(1-\sigma_k) \times \langle r'^k \rangle / \langle r^k \rangle$
b_0^2	-2348	-635	-2983	-1187
b_0^4	-920	77	-843	-1222
b_3^4	-1573	-25	-1598	-2316
s_3^4	271	-87	184	267
b_0^6	303	4	307	734
b_3^6	124	27	151	361
s_3^6	-16	2	-14	-33
b_6^6	218	19	237	567
s_6^6	-40	16	-24	-57

ly, the Ξ^2 model was applied by Linares and Louat[23] to some lanthanum compounds. Then σ as well as π effects were investigated in BaClF and SrClF:Sm^{2+} (Refs. 24 and 25) and in LMO_4 compounds.[26] In the AOM as well as the PCEM, the experimental CFP are given by similar expressions,

$$B_q^k = \sum_j I_k(j) C_q^k(\vec{j}) \ , \tag{6}$$

with

$$C_q^k(\vec{j}) = \left[\frac{4\pi}{2k+1}\right]^{1/2} Y_k^{q*}(\vec{j}) \ . \tag{7}$$

In the PCEM, the sum over j is extended to the whole lattice, and by identification of (6) with (1), we see that the radial parameter is given by

$$I_k(j) = -\frac{\langle r^k \rangle e^2 C_j}{R_j^{k+1}} \ .$$

In the AOM the sum is restricted to the ligands. The dependence of I_k on the antibonding monoelectronic energies e_k is given by Kibler[22] as

$$I_2(j) = \tfrac{10}{14} e_\sigma(j),\ I_4(j) = \tfrac{9}{7} e_\sigma(j),\ I_6(j) = \tfrac{13}{7} e_\sigma(j) \ , \tag{8}$$

in the case of σ bonding, and

$$I_2(j) = \tfrac{15}{14} e_\pi(j),\ I_4(j) = \tfrac{3}{7} e_\pi(j),\ I_6(j) = \tfrac{39}{14} e_\pi(j) \ , \tag{9}$$

in the case of π bonding. Note that Kibler's e_σ is equal to $2l+1$ times Jörgensen's σ^* ($l=3$ for f orbitals).

To attempt an interpretation of our results in the framework of the AOM, several approximations were made.

(a) Three pairs of different ligands surround Eu^{3+} substituted to Y^{3+} in Y$_2$O$_3$. Rigorously, we should consider a different I_k value for each sort of ligand. For instance, one pair could be strongly σ bonded to the central ion, and another pair not at all. It seemed to us that this process could be safely applied when the experimental CFP are precisely determined, which is not presently the case. Moreover, the distances from the central ion are not very different (2.244, 2.268, and 2.337 Å) so that we ascribed (as in Ref. 23) the same I_k value to the six ligands, but with a $(R_m/R_J)^6$ dependence law, R_m being the mean distance. Equation (6) then becomes

$$B_q^k = I_k \sum_j \left[\frac{R_m}{R_j}\right]^6 C_q^k(j) \ . \tag{10}$$

(b) Considering the mediocre determination of the imaginary components of the CFP, we found it better to utilize the moduli $[(b_q^k)^2 + (s_q^k)^2]^{1/2}$. Table IV lists the I_k values obtained from the nine experimental B_q^k. Only one I_k value originating from B_2^6 is completely out of range; we shall not take it into account.

Following (8) we must have

$$I_2/I_4 = \tfrac{5}{9},\ I_4/I_6 = \tfrac{9}{13},\ I_2/I_6 = \tfrac{5}{13} \tag{11}$$

for σ bonding. From Table IV we see that none of the relations is obeyed. For π bonding,

$$I_2/I_4 = \tfrac{5}{2},\ I_4/I_6 = \tfrac{2}{13},\ I_2/I_6 = \tfrac{5}{13} \ . \tag{12}$$

The first relation is verified but the second is not. The experimental B_q^6 are about 10 times too small. Moreover, it is not possible to find a convenient combination of σ and π bonding since in both cases, the theoretical ratio I_2/I_6 displays the same value.

This crude approach demonstrates that crystal-field effects in the present case cannot be totally analyzed by the AOM. On the other hand, if we accept the free-ion radial integrals, they cannot be totally predicted by the electrostatic model either. We shall make the assumption that the two models give additive contributions. We have listed in Table IV the differences ΔB_q^k between experimental B_q^k and the total shielded electrostatic parameters (with uncorrected radial integrals, of course). We deduced from (10) the resulting radial parameters ΔI_k.

If the ΔB_q^k are due to covalency, the ΔI_k must display the definite ratios (11) or (12). The ΔI_2 values are inconsistent. The ratio $\Delta I_4/\Delta I_6$ is not *too* far from $\frac{9}{13}$ and could reveal appreciable σ effects. The resulting ΔI_2 due to covalency would then be of the order of $363 \times \frac{5}{13} \sim 140$ or $344 \times \frac{5}{9} \sim 190$ which is 10% of the experimental I_2.

To summarize, covalency contributions (with $e_\sigma \sim 200$ cm^{-1} or $\sigma^* \sim 30$) added to the shielded electrostatic CFP yield values close to the experimental ones. The σ-effect contribution to B_q^2, B_q^4, and B_q^6 would represent 10%, 40%, and 70%, respectively. The value which has been found for σ^* (30 cm^{-1}) is a typical value for the triply ionized elements of the $4f$ group as shown by Jörgensen.[27]

V. CONCLUSION

We discuss the following.

(a) In the present work, a refinement of the phenomenological crystal-field parameters of Eu^{3+} in Y$_2$O$_3$ was carried out; it was based on the experi-

TABLE IV. Radial parameters I_k and evaluation of the covalent contribution to crystal-field parameters.

B_q^k	B_0^2	$\lvert B_2^2\rvert$	B_0^4	$\lvert B_2^4\rvert$	$\lvert B_4^4\rvert$	B_0^6	$\lvert B_2^6\rvert$	$\lvert B_4^6\rvert$	$\lvert B_6^6\rvert$
Expt.	-196	-695	-1264	-1552	1121	267	358	937	184
I_k[a]	1508	2200	817	923	736	476	(4773)	553	641
$\bar{I}_k$	1854			825			557		
SES[b]	-202	-379	-718	-825	746	142	15	320	40
ΔB_q^k[c]	6	316	-546	-727	375	125	343	617	144
ΔI_k[d]	-46	1000	353	432	246	223	(4573)	364	502
$\Delta\bar{I}_k$				344			363		

[a] As calculated from (10).
[b] SES: Shielded electrostatic parameter, (PC + dipole) $(1-\sigma_k)$.
[c] ΔB_q^k: Difference between the experimental parameter, Expt., and the shielded electrostatic CFP, SES.
[d] As calculated utilizing ΔB_q^k in (10).

mental observation of the lowest ^7F_J $(J = 1-4)$ levels of the $4f^6$ configuration. The final mean deviation of the experimental and calculated values was equal to 4.8 cm^{-1}, which is not too bad, considering the broad overall splittings of the levels (~ 500 cm^{-1}). The origin of the remaining discrepancies can be found in the truncation of the $4f^6$ configuration and the neglect of multielectron operators[28] in the crystal-field Hamiltonian which is utilized here.

(b) The electrostatic CFP, including point-charge and dipolar effects, were calculated utilizing recent structural data, usual ionic point charges, and scalar polarizabilities. The discrepancy, which is always stated between experimentally refined F^k and the higher theoretical values deduced from calculated wave functions, gives us some ground to believe that radial integrals $\langle r^k \rangle$, convenient for rare-earth ions in solids, are systematically underestimated. As for Nd_2O_3,[4] corrected values were utilized and in this way, the calculated CFP were quite close to phenomenological parameters. Before the Freeman and Watson's Hartree-Fock (HF) calculation of rare-earth ions' radial wave functions, Ridley[28] and Rajnak[30] deduced $\langle r^k \rangle$ and F^k values from a self-consistent-field calculation without exchange. In fact, their values are not often utilized since in principle the Hartree-Fock calculations give a better representation of free-ion wave functions. However, the F^k from Ridley and Rajnak are closer to experimental values than the Hartree-Fock results, and on the other hand, their $\langle r^k \rangle$ values are 1.3, 1.8, and 2.4 times larger than those of Freeman and Watson, and these are practically the correction factors we need to match the electrostatic CFP with phenomenological parameters.

(c) In a different approach, we supposed that HF radial integrals yield the correct electrostatic CFP, and that the difference with respect to experimental parameters are due to covalency. We found a possible σ overlap mechanism with a σ^* parameter approaching 30 cm^{-1}. A direct estimate of σ^* can be made in the following way: The position of electronic energy levels can be approximately located from x-ray photoemission spectroscopy experiments (XPS). In oxidized europium, the $4f$ levels were observed[31] at $-$ 8 eV ($-$ 64 000 cm^{-1}) from the Fermi level, whereas the position of the oxygen $(2p)$ peaks were located[32] at $-$ 4 eV in La_2O_3. They are not greatly displaced in other compounds (Cr_2O_3 and $LaCrO_3$). Adopting the Wolfsberg-Helmholz approximation as in Ref. 20, we find for an overlap integral as small as 0.04, a *bonding* energy σ equal to 50 cm^{-1} which is the order of magnitude we are anticipating (in this case, the orbital of the ligand has an antibonding energy of 200 cm^{-1}).

Provided the fundamental assumption that the AOM and the electrostatic model give additive contributions, the above approach (c) could be a simple way to interpret crystal-field parameters in compounds where the electrostatic contribution is by no means negligible.

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