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Electrostatic crystal-field contributions in rare-earth compounds with consistent multipolar effects. I. Contribution to k-even parameters

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Electrostatic crystal-field parameters (CFP: B_q^k) including the contributions of point charges, consistent dipoles, and quadrupoles induced in a crystalline lattice, are calculated for 15 rare-earth or rare-earth-doped compounds and one actinide compound, i.e., for $LiYF_4:Nd^{3+}$, YOBr and $YOCl:Eu^{3+}$, BaFCl and $SrFCl:Sm^{2+}$, $BaTiO_3:Eu^{3+}$, $NdAlO_3$, $LaAlO_3:Eu^{3+}$, UF_6Cs, Nd_2O_3, Nd_2O_2S, LaF_3 and $LaCl_3:Nd^{3+}$, Y_2O_3 and $KY_3F_{10}:Eu^{3+}$, and $Y_3Al_5O_{12}:Nd^{3+}$. The method for solving the unknown moments is described and the correction formulas to the B_q^k are given. The necessary input data are the crystallographic structure, point charges (valence values), the dipolar and quadrupolar polarizabilities (recently computed *ab initio* values), and the $4f$ (or $5f$) radial integrals $\langle r^k \rangle$. The model disregards overlap and covalency, which are likely to provide important contributions via the $4f$ (or $5f$) electron interaction with the ligands. Yet, so as to estimate quantitatively the agreement between experimental and calculated values, two performance indexes are utilized: a scale factor $S_k(B_{\text{expt}}^k/B_{\text{calc}}^k)$ and a reliability factor measuring the angle between B_{expt}^k and B_{calc}^k. The dipolar and quadrupolar contributions do not significantly change the scale factor which is about a factor of 2 too large when screening is taken into account. The reliability factor is rather worsened by the quadrupolar contribution which is higher than the dipolar. An estimation of the octupolar correction confirms the divergence of the multipolar series which might be ascribed to overestimated high-order polarizabilities.

I. INTRODUCTION

This work presents an *a priori* calculation of lanthanide crystal-field parameters (CFP) B_q^k according to the electrostatic model in rare-earth or rare-earth-doped compounds. The k-even CFP cause the experimentally observed Stark splittings in rare-earth spectra while the k-odd CFP, via configuration admixing, allow electric dipole transitions within the $4f^N$ configurations according to the Judd-Ofelt theory.[1] Therefore, both even and odd CFP may, in principle, be deduced as phenomenological parameters from experimental data, and can be compared with theoretical values.

This paper will deal with the even B_q^k for which numerous experimental values are available. The calculation method will be briefly explained in Sec. II. It consists of evaluating the $4f$-electron extra potential that results from its interaction with monopoles, as well as with static dipoles and quadrupoles, consistently induced in the lattice. A first step in that direction was made by Hutchings and Ray[2] in 1963 but Morrison[3] was the first, in 1976, to evaluate the contribution of consistent induced dipoles. Fields due to self-induced dipoles in ionic lattices were also evaluated by Weenk and Harwig in 1977,[4] while Bijvank and den Hartog[5] stated in 1980 that the zero-field splittings of the $4f^7$ state can be explained by a self-consistent polarizable point-charge model. Recently,[6] we included in the B_q^k calculation the contribution of consistently induced quadrupoles.

The electrostatic calculation of the B_q^k has been criticized because of the poor agreement of its results with experimental values, but it was shown,[7] that at least in the case of rare earths, the results may be greatly improved if (a) ionic charges are modified so as to simulate covalency effects in solids and (b) the $4f$ radial-wave functions are expanded so as to reproduce correctly the experimentally deduced Slater integrals.[8] Presently, we shall not speculate on the two types of modifications we have chosen to report for a number of inorganic compounds unshielded B_q^k, with the use of free-ion Dirac-Fock[9] radial integrals, and including for the first time contributions of consistently induced dipoles and quadrupoles as well as monopoles. However, we must keep in mind that our results (and especially their magnitude) would be changed by taking into account the above-mentioned effects (a) and (b).

The investigated compounds are the following. They are classified according to their space group number, the exceptions being the two perovskite families $BaTiO_3$ and $NdAlO_3$, which arise from slight deformations of the same cubic structure:

Space Group			Site Symmetry
88	Tetragonal	$LiYF_4:Nd^{3+}$	S_4
129	Tetragonal	$YOBr:Eu^{3+}, YOCl:Eu^{3+}$ $BaFCl:Sm^{2+}, SrFCl:Sm^{2+}$	C_{4v}
99	Tetragonal	$BaTiO_3:Eu^{3+}$	C_{4v}
167	Trigonal	$NdAlO_3, LaAlO_3:Eu^{3+}$	D_3
148	Trigonal	UF_6C_s	S_6
164	Trigonal	Nd_2O_3, Nd_2O_2S	C_{3v}
165	Trigonal	$LaF_3:Nd^{3+}$	C_2
176	Hexagonal	$LaCl_3:Nd^{3+}$	C_{3h}
206	Cubic	$Y_2O_3:Eu^{3+}$	C_2
225	Cubic	$KY_3F_{10}:Eu^{3+}$	C_{4v}
230	Cubic	$Y_3Al_5O_{12}:Nd^{3+}$	D_2

II. CALCULATION OF ELECTROSTATIC CRYSTAL-FIELD PARAMETERS

The extra potential energy of a lanthanide $4f$ (or an actinide $5f$) electron interacting with the lattice crystal field is conventionally written as

$$H_{\mathrm{cf}} = \sum_{k,q} B_q^k C_q^k(i) , \tag{1}$$

where $C_q^k(i)$ is a tensor operator $[(4\pi/2k+1)^{1/2}$ times the spherical harmonic $Y_k^q(i)]$ depending on the coordinates of the ith electron. Expression (1) is useful for determining phenomenological (or "experimental") B_q^k from observed energy splittings of intraconfiguration transitions in optical absorption or fluorescence spectra. The matrix elements of (1) are readily computed by Racah's methods[10]; the subsequent matrix diagonalization yields the energy levels so that by trial and error, one finds the phenomenological B_q^k. The relevant k values are limited to even integers lower than 6, but a variable B_0^0 only results in an equal displacement of all the configuration levels so that the interesting k values are limited to 2, 4, and 6.

The mutual potential energy of the $4f$ electron at $\vec{r}_i$ and of the elementary charges $\rho(\vec{r})$ throughout the lattice is written as

$$H_{\mathrm{cf}} = -e \int \frac{\rho(\vec{r})dv}{|\vec{r}_i - \vec{r}|} , \tag{2}$$

which becomes, if $|\vec{r}| > |\vec{r}_i|$,

$$H_{\mathrm{cf}} = -e \sum_{k,q} \left[\frac{4\pi}{2k+1} \right]^{1/2} C_q^k(\vec{r}_i) |\vec{r}_i|^k \times \int \frac{Y_k^{q*}(\vec{r})\rho(\vec{r})dv}{|\vec{r}|^{k+1}} . \tag{3}$$

We consider that the charges are not evenly distributed in the lattice but gathered in clusters J, $\vec{r}_J$ being the center of charge of the Jth cluster (ion). Then $\vec{r} = \vec{r}_J + \vec{r}_{Jl}$ with $|\vec{r}_{Jl}| < |\vec{r}_J|$, and (3) may be expanded to

$$H_{\mathrm{cf}} = -e \sum_{k,q} \left[\frac{4\pi}{2k+1} \right]^{1/2} C_q^k(\vec{r}_i) |\vec{r}_i|^k \times \sum_{J,n} \int \frac{1}{n!} \rho(\vec{r}_{Jl}) \vec{r}_{Jl}^{(n)} \cdot \vec{\nabla}_J^{(n)} \times \left[\frac{Y_q^{k*}(\vec{r}_J)}{|\vec{r}_J|^{k+1}} \right] dv \tag{4}$$

or

$$H_{\mathrm{cf}} = -e \sum_{k,q} \left[\frac{4\pi}{2k+1} \right]^{1/2} C_q^k(\vec{r}_i) |\vec{r}_i|^k \times \sum_{J,n} M_J^{(n)} \cdot \vec{\nabla}_J^{(n)} \left[\frac{Y_q^{k*}(\vec{r}_J)}{|\vec{r}_J|^{k+1}} \right] \tag{5}$$

with

$$\begin{aligned} M_J^{(0)} &= \int \rho(\vec{r}_{Jl}) dv \\ M_J^{(1)} &= \int \rho(\vec{r}_{jl}) \vec{r}_{Jl} dv \\ M_J^{(2)} &= \tfrac{1}{2} \int \rho(\vec{r}_{jl}) \vec{r}_{Jl} \times \vec{r}_{Jl} dv , \end{aligned} \tag{6}$$

where $M_J^{(0)}$, $M_J^{(1)}$, and $M_J^{(2)}$ are the monopolar, dipolar, and quadrupolar moments, respectively, of the Jth cluster.

The B_q^k in (1) is then given as

$$B_q^k = -e \langle r_i^k \rangle \left[\frac{4\pi}{2k+1} \right]^{1/2} \times \sum_{Jn} M_J^{(n)} \cdot \vec{\nabla}_J^{(n)} \left[\frac{Y_k^{q*}(\vec{r}_J)}{|\vec{r}_J|^{k+1}} \right] , \tag{7}$$

where r_i^k has been replaced by its expectation value. In (1) the $\langle r_i^k \rangle \cdot C_q^k(i)$ are the $4f$-electron multipolar moments in normal coordinates. We have limited ourselves up to the quadrupolar contribution. The final formulas, once the derivations achieved, are reported in Appendix A.

III. DETERMINATION OF THE INDUCED MOMENTS

The components of $M_J^{(1)}$ and $M_J^{(2)}$ which must enter the expressions (A2) and (A3) of Appendix A have to be calculated in a separate step by expressing the electrostatic equilibrium of charges, induced dipoles and quadrupoles at each ion's site. The dipolar and quadrupolar induced moments, are to first order, proportional to the field and field gradients, respectively,

$$M_{J'}^{(n)} = \alpha_{J'}^{(n)} \cdot \vec{\nabla}_{J'}^{(n-1)}(\vec{\mathrm{E}}_{J'}) \ . \tag{8}$$

A 2^p pole at $\vec{\mathrm{r}}_J$ produces at J' placed at the origin, a 2^n pole given by

$$M_{J'}^{(n)} = (-1)^{n+1} \alpha_{J'}^{(n)} \cdot \vec{\nabla}_J^{(n)} \left[M_J^{(p)} \cdot \vec{\nabla}_J^{(p)} \left[\frac{1}{|\vec{\mathrm{r}}_J|} \right] \right] . \tag{9}$$

Each ion is an isotropic medium so that the polarizability tensor reduces to a scalar $\alpha_{J'}^n$ (see Appendix B for the symmetries of $\alpha_{J'}^{(n)}$ in this case). The equilibrium of the moment $M_{J'}^{(n)}$ with all the multipoles of the crystalline lattice is written as

$$M_{J'}^{(n)} = \sum_{J,p=0,1,2} (-1)^{n+1} \alpha_{J'}^n I^{(2n)} \cdot \vec{\nabla}_J^{(n)} \times \left[M_J^{(p)} \cdot \vec{\nabla}_J^p \left[\frac{1}{|\vec{\mathrm{r}}_J|} \right] \right] . \tag{10}$$

$I^{(2n)}$ is the diagonal unit tensor of rank $2n$. $\alpha_{J'}^0 = 1$ and $I^{(0)} = 1$. Equation (10) is written for each ion's site J', for each of the three dipolar and nine quadrupolar moment components to yield a linear system in the unknown moments components. The latter are determined by resolving consistently the whole system. The rank of the linear system (10) is equal to $12N$, N being the total number of ions in the unit cell. Details on the construction of the system (10), taking into account the symmetry properties of the lattice may be found in Appendix C.

IV. INPUT DATA AND POLARIZABILITIES

In the calculation of induced moments [Eqs. (C1) and (C2)] the point charges were assigned their usual valence values, and the scalar dipolar and quadrupolar polarizabilities were theoretical *ab initio* values deduced by quantum-mechanical calculations in closed-shell ions. The most recent papers on the subject utilize Sternheimer's variational method,[11] but include self-consistency and a modified potential simulating the effect of environment. When an ion is embedded in a solid, the following trend is observed: The cation polarizabilities remain nearly the same, whatever the structure whereas the anion polarizabilities depend significantly on the crystalline environment, more precisely they increase with the ion-ion distances. The trend is enhanced as the polarizability order increases. Following Mahan,[12] the ratios of the dipolar, quadrupolar, and octupolar polarizabilities of Cl^- in vacuum and in LiCl are equal to 1.26, 1.66, and 2.44, respectively. A steady increase of $\alpha^n(\mathrm{Cl}^-)$ along the alkali series is also observed from LiCl (lattice constant $a = 5.13$ Å) to RbCl ($a = 6.58$ Å). The same is to be noted in Table I of Ref. 13: a slight decrease (respectively, a large increase) of α^n when a cation (respectively, an anion) is embedded in a solid. We utilized the results of Schmidt *et al.*[13] except for Ba^{2+}, the polarizabilities of which did not respect the usually observed trend along isoelectronic series (α^2 steadily decreasing as ionization increases). In that case we adopted the values of Mahan.[12] The polarizabilities of lanthanides (Nd^{3+} and La^{3+}) were arbitrarily set equal to those of Ba^{2+}; α^1 and α^2 of U^{5+} were taken equal to those of Xe[12]. $\alpha^3(\mathrm{Cl}^-)$ which was utilized to evaluate the octupolar contribution (see Sec. VI) was $\alpha_0(\mathrm{Cl}^-)$ in KCl computed by Mahan.[12] When a rare earth was introduced as a dopant in a host matrix, Nd^{3+} in $\mathrm{LaCl_3}$, for instance, or Eu^{3+} in $\mathrm{KY_3F_{10}}$, we considered that its polarizabilities were the same as those of the ordinary site occupier. The dipolar and quadrupolar polarizabilities which were utilized are listed in Table I. As pointed out in Appendix B, the α^2 literature value must be divided by 6.

The most recent available crystallographic data were utilized for each compound. In each calculation, the coordinates of the central lanthanide ion was the first of the list of equivalent positions in the *International Tables of X-Ray Crystallography*.[14] The radial integrals $\langle r^k \rangle$ were the Dirac-Fock values of Refs. 9 and 15 (Table II).

In Tables III–XVIII we have listed, for each compound, the monopolar, dipolar, and quadrupolar contributions to the relevant crystal-field parameters. Converged as well as first-neighbor values are listed, and the experimental B_q^k are listed

TABLE I. Dipolar and quadrupolar polarizabilities following Refs. 12 and 13.

	α_{dip}	α_{quad}	Ref.
Li^+	0.0321	0.001	13
O^{2-}	1.349	0.616	13
F^-	0.731	0.105	13
Al^{3+}	0.053	0.002	13
S^{2-}	4.893	3.280	13
Cl^-	2.694	0.922	13
K^+	0.827	0.125	13
Ti^{4+}	0.506	0.070	13
Br^-	3.263	1.042	13
Sr^{2+}	1.039	0.180	13
Y^{3+}	0.87	0.144	13
Cs^+	2.492	0.864	13
Ba^{2+}	2.24	0.372	12
La^{3+}	2.24	0.372	12 (Ba^{2+})
Nd^{3+}	2.24	0.372	12 (Ba^{2+})
U^{5+}	5.19	1.290	12 (Xe)

when available. When a rotation was necessary to display the relevant point site symmetry with respect to the central ion, the Euler angles α,β,γ are quoted [crystal rotation around fixed axes $0z(\gamma)$, $0y(\beta)$, and $0z(\alpha)$].

We note that for most compounds, the results for the first coordination shell is quite different from the convergence values, at least for B_q^2 components. For the B_q^4 and especially the B_q^6 parameters, the disagreement is much less pronounced.

V. CORRELATION TEST BETWEEN EXPERIMENT AND CALCULATION

The "ionic" electrostatic model we have applied is believed to give exact contributions to the crystal-field parameters with regard to the $4f$-electron interaction with distant neighbors. Since the model disregards charge penetration (ligand-ligand, ligand-lanthanide) and covalency contributions, it is certainly uncomplete in what concerns the rare-earth interactions with its nearest neighbors. During the past 15 years, consideration of these effects has given rise to the construction of the following two models:

(a) The first, the *superposition model*, due to Newman,[43] is meant to be an intermediary between experimental results and *ab initio* calculations. It assumes that the crystal field can be built by adding separate contributions of all the ions, each contribution being the product of an intrinsic parameter (varying as a power law of the rare-earth—ligand distance) and an angular dependent function (tesseral harmonic). This model has namely been applied to Eu^{3+}-doped lanthanide compounds.[44,45]

(b) Another model taking a specific account of the rare-earth interaction with its nearest neighbors is the angular overlap model (AOM) due to Jörgensen *et al.*[46] and generalized by Schäffer and Jörgensen.[47] In this model, the small Stark splittings observed in the $4f$ optical spectra are assigned to energy shifts due to covalent bonding with the ligands. As derived by Kibler,[48] the crystal-field parameter B_q^k arising from this mechanism is given by a sum over the ligands of the product of three terms: an angular function (tensor operator), a numerical factor depending on k, l, and the degree of overlap λ ($\lambda=\sigma, \pi, \delta\ldots$),

TABLE II. Radial integrals $\langle 4f\,|\,r^k\,|\,4f\rangle$

a.u.	$\langle r^2\rangle$	$\langle r^4\rangle$	$\langle r^6\rangle$	Ref.
Nd^{3+}	1.114	2.910	15.03	9
Eu^{3+}	0.9175	2.020	9.039	9
U^{5+}	1.833	5.838	29.793	15

TABLE III. Calculated (crystallographic data from Ref. 16) and experimental (phenomenological data from Ref. 17) crystal-field parameters of Nd^{3+} in Nd_2O_3 (C_{3V} symmetry site); $\alpha=30°$, $\beta=0°$, and $\gamma=0°$. ( ) equals seven first-neighbor O^{2-} at 2.300 (three), 2.400 (one), and 2.657 Å (three).

cm^{-1}	B_0^2	B_0^4	B_3^4	B_0^6	B_3^6	B_6^6
PC	−1686 (−2047)	518 (502)	−1438 (−1467)	346 (288)	204 (204)	318 (318)
dip	205 (248)	−12 (−8)	20 (−7)	16 (17)	2 (−3)	−6 (−7)
PC + dip	−1481 (−1438)	505 (494)	−1418 (−1474)	363 (305)	206 (206)	312 (284)
dip	−329 (−351)	11 (11)	35 (10)	−23 (−24)	10 (5)	9 (9)
quad	−1477 (−1419)	−554 (−495)	−323 (−326)	−24 (−19)	127 (127)	−15 (−15)
PC + dip + quad	−3491 (−3817)	−25 (18)	−1726 (−1783)	299 (245)	341 (341)	313 (284)
Expt	−836	634	−1606	752	237	672

and an e_λ parameter describing the antibonding effects of each particular ligand.

No power law is assigned to e_λ.

This model has been extensively utilized in the past.[39,40,44,45,49] Recently,[32] we tried to combine the electrostatic model with the AOM, leaving to the AOM the part of experimental parameters not taken into account by the electrostatic model (the reverse step might also be advisable). Presently, we shall not make such an attempt. We fully exploit the electrostatic model, well aware that short-range interactions are not fully taken into account. Yet, so as to appreciate the degree of agreement between calculated and experimental values, we utilize performance indexes independent on the particular site symmetries. The best way is to consider the B_q^k as the components of a generalized vector B^k and to compare the lengths and directions of $B_{\rm expt}^k$ and $B_{\rm calc}^k$. Following this line we calculate (a) a scale factor

$$S_k=\frac{|B_{\rm expt}^k|}{|B_{\rm calc}^k|} \qquad (11)$$

with

$$|B^k| = \left[\sum_{q\gtrless 0} B_q^k \cdot B_q^{k*}\right]^{1/2} = (B^k \cdot B^k)^{1/2} . \qquad (12)$$

This length was already utilized by Chang *et al.*[50] to weight the crystal-field strength in various com-

TABLE IV. Calculated (crystallographic data from Ref. 16) and experimental (phenomenological data from Ref. 17) crystal-field parameters of Nd^{3+} in Nd_2O_2S (C_{3V} symmetry site); $\alpha=30°$, $\beta=0°$, and $\gamma=0°$. ( ) equals seven first-neighbor at 2.3615 (three oxygens), 2.3636 (one oxygen), and 2.9645 Å (three sulfurs).

cm^{-1}	B_0^2	B_0^4	B_3^4	B_0^6	B_3^6	B_6^6
PC	24 (−92)	646 (716)	−972 (−1056)	260 (223)	167 (158)	249 (226)
dip	905 (916)	6 (−4)	−14 (−29)	65 (64)	−6 (−8)	−20 (−20)
PC + dip	929 (824)	652 (712)	−986 (−1085)	325 (287)	161 (150)	228 (206)
dip	816 (796)	10 (−3)	−6 (−25)	57 (56)	−4 (−7)	−18 (−17)
quad	−2082 (−2088)	−201 (−193)	−262 (−258)	9 (9)	97 (97)	20 (20)
PC + dip + quad	−1242 (−1268)	455 (520)	−1240 (−1339)	327 (288)	260 (249)	251 (229)
Expt	194	912	−924	512	300	256

TABLE V. Calculated (crystallographic data from Ref. 18) and experimental (phenomenological data from Ref. 19) crystal-field parameters of Nd^{3+} in $NdAlO_3$ (D_3 symmetry site); $\alpha=30°$, $\beta=0°$, and $\gamma=0°$. ( ) equals twelve first neighbor O^{2-} at 2.3896 (three), 2.6586 (six), and 2.9324 Å.

cm^{-1}	B_0^2	B_0^4	B_3^4	B_0^6	B_3^6	B_6^6
PC	−1120	345	285	−505	250	−366
	(−1091)	(554)	(502)	(−398)	(187)	(−299)
dip	−249	27	−17	−9	−7	−18
	(−248)	(28)	(−16)	(−9)	(−7)	(−18)
PC + dip	−1368	372	269	−514	243	−384
	(−1339)	(583)	(486)	(−407)	(180)	(−317)
dip	−940	102	−63	−34	−27	−66
	(−938)	(107)	(−60)	(−34)	(−27)	(−66)
quad	−1011	557	312	378	−334	286
	(−890)	(512)	(267)	(378)	(−334)	(286)
PC + dip + quad	−3071	1004	535	−161	−111	−146
	(−2919)	(1174)	(708)	(−54)	(−174)	(−80)
Expt	−481	481	390	−1700	950	−1080

pounds. Here it will give a quantitative appreciation of the ratio between experimental and calculated field strength.

(b) the angle between the two generalized vectors B_{expt}^k and B_{calc}^k which is a sort of reliability factor,

$$R_k=\arccos\left[\frac{B_{\text{expt}}^k\cdot B_{\text{calc}}^k}{|B_{\text{expt}}^k|\cdot|B_{\text{calc}}^k|}\right]. \tag{13}$$

A perfect agreement would therefore correspond to $S_k=1$ and $R_k=0$. Besides, if S_k is very different from 1 but with R_k displaying low values, we may look for reasons which systematically alter the magnitude of the overall calculated field. R_k depends on the relative orientations of the reference axes of B_{expt}^k and B_{calc}^k. When the axes have a degree of freedom, R_k is not determined unambiguously. This occurs namely for Y_2O_3:Eu^{3+} and LaF_3:Nd^{3+} (C_2 site symmetry). These symmetries involve imaginary as well as real B_q^k components, the relative magnitude of which is very sensitive to small rotations around the polar axis (α). For Y_2O_3:Eu^{3+}, a total R [expression (13) with a sum over k as well] was calculated for several α values. The α value (45°) yielding the smallest R was selected to compute R_k. For LaF_3:Nd^{3+}, R_k was calculated for $\alpha=57.84°$ and 62.57°; $\beta=90°$, that is when the S_2^2 component was cancelled in calculations (b) and (c), respectively. When, for a given k, only one parameter (B_0^2) exists, then the reliability factor is necessarily equal to 0° indicating the signs

TABLE VI. Calculated (crystallographic data from Ref. 20) and experimental (phenomenological data from Ref. 21) crystal-field parameters of Eu^{3+} in $LaAlO_3$ (D_3 symmetry site); $\alpha=30°$, $\beta=0°$, and $\gamma=0°$. ( ) equals twelve first-neighbor O^{2-} at 2.5484 (three), 2.6816 (six), and 2.8166 Å (three).

cm^{-1}	B_0^2	B_0^4	B_3^4	B_0^6	B_3^6	B_6^6
PC	−212	196	217	−265	153	−174
	(−206)	(322)	(361)	(−206)	(117)	(−137)
dip	−46	4	−3	−1	−1	−2
	(−46)	(4)	(−3)	(−1)	(−1)	(−2)
PC + dip	−258	200	214	−266	152	−176
	(−252)	(326)	(359)	(−207)	(116)	(−139)
dip	−173	14	−10	−4	−4	−8
	(−172)	(15)	(−10)	(−4)	(−4)	(−8)
quad	−123	201	195	218	−143	145
	(−104)	(175)	(164)	(218)	(−143)	(145)
PC + dip + quad	−508	412	401	−51	6	−37
	(−482)	(512)	(516)	(8)	(−29)	(1)
Expt	∼−157	∼417	∼398	∼−1635	∼1117	

TABLE VII. Calculated (crystallographic data from Ref. 22) and experimental (phenomenological data from Ref. 23) crystal-field parameters of Nd^{3+} in $Y_3Al_5O_{12}$ (D_2 site symmetry); ( ) equals eight first-neighbor (O^{2-}) at 2.3049 (four) and 2.4343 Å (four).

cm^{-1}	B_0^2	B_2^2	B_0^4	B_2^4	B_4^4	B_0^6	B_2^6	B_4^6	B_6^6
PC	−449 (1578)	177 (318)	−192 (98)	1003 (1076)	−534 (−671)	−391 (−295)	141 (137)	141 (128)	127 (128)
dip	4297 (4116)	−101 (155)	−59 (−54)	−48 (−57)	200 (191)	−12 (−14)	76 (76)	−78 (−79)	−66 (−66)
PC + dip	3847 (5694)	77 (473)	−250 (43)	955 (1018)	−333 (−481)	−403 (−310)	217 (213)	63 (49)	61 (62)
dip	2996 (2830)	−430 (−224)	33 (30)	−11 (−16)	148 (139)	−1 (−2)	59 (59)	−42 (−43)	−27 (−28)
quad	−308 (6)	1338 (1395)	1147 (1103)	−821 (−822)	−248 (−221)	444 (445)	−61 (−61)	81 (81)	−128 (−128)
PC + dip + quad	2238 (4473)	1085 (1489)	988 (1230)	172 (237)	−634 (−753)	52 (147)	139 (135)	180 (165)	−29 (−28)
Expt	514	−129	−363	2005	−950	−1702	763	837	718

agree, or 180° in the opposite case. The scale factors S_k and reliability factors R_k are reported in Tables XIX and XX, respectively. We grouped at the beginning the Nd^{3+}, then the Eu^{3+}, at last the Sm^{2+}-doped compounds and UF_6Cs. The S_k and R_k are calculated in three cases: (a) point charge (PC) only (PCEM), (b) PC plus dipoles (dip), and (c) PC plus dipoles plus quadrupoles (quad). The induced dipolar moments are different in calculations (b) and (c) since they coexist consistently with point charges only in (b), with point charges and quadrupoles in (c).

We shall comment on the scale factor values later and will also discuss the shielding of the crystal field at the 4*f*-electron site, and the convergence of the multipolar series.

The reliability factors R_k are not systematically worse (larger) either in doped or in concentrated compounds. Besides, they are rather improved by the dipolar contribution and worsened when the total contribution PC plus dip plus quad is included.

In Ref. 8 were reported *ab initio* B_q^k of Nd_2O_3 including dipolar effects only. The differences (~20%) which are stated with actual results (Table III) arise from the fact that the radial integrals were those from Freeman and Watson,[51] and the oxygen polarizability was deduced from refractive index measurements.

R_4, which is rather satisfactory for (PC + dip), is worsened when the total contribution is considered. The same thing occurs for Nd_2O_2S for which the B_0^2 sign is even reversed by the quadrupolar contribution (Table IV). This is rather exceptional since for all the other compounds (except $SrFCl:Sm^{2+}$) this sign is correctly predicted.

For $LaAlO_3:Eu^{3+}$ (Table VI), no S_k and R_k are reported since the experimental B_q^k of Ref. 21 are directly issued from PCEM-corrected values and not from a refinement. However, it is easy to see from Table V that it behaves in the same way as isomorphic $NdAlO_3$:B_0^2 high with respect to the experimental value, R_4 and especially R_6 worsened by the quadrupolar contribution, S_6 high (8.7 for $NdAlO_3$). The same is to be stated for the garnet $Y_3Al_5O_{12}$: Nd^{3+} ($S_6=7.77$) (Table VII). For this compound there exists six sets[23] of equivalent experimental parameters (owing to the D_2 symmetry); we chose the set for which the disagreement between experimental and calculated values was the smallest and yet the R values are among the worst of all the series. This behavior may be assigned to the presence of the aluminium cation. In point charge lattice sums on $Y_3Al_5O_{12}$, Wortman *et al.*[52] took the Al and O charges as equal to 1.92 and −1.55, respectively, in an attempt to modify the purely ionic description of the AlO_4 and AlO_6 radicals. We can also infer that the experimental parameters apply to a site different from the one investigated. Indeed the metastability of $Y_3Al_5O_{12}$[53] has been emphasized and the presence as a dopant of the large Nd ion could indeed *locally* disturb the crystal structure.

For $LaF_3:Nd^{3+}$ (Table VIII), the R_2 and R_6 values are rather unsatisfactory even when PC plus dipolar contributions only are considered, but for $LaCl_3:Nd^{3+}$ (Table IX) and $LiYF_4:Nd^{3+}$ (Table X), the values are small and rather improved by the total (PC + dip + quad) contributions. We have not reported any experimental CFP for $BaTiO_3:Eu^{3+}$ (Table XI), the structure of which is

TABLE VIII. Calculated (crystallographic data from Ref. 24) and experimental (phenomenological data from Ref. 25) crystal-field parameters of Nd^{3+} in LaF_3 (C_2 symmetry site); PC + dip: $\alpha = 57.84°$, $\beta = 90°$, and $\gamma = 0$, and PC + dip + quad: $\alpha = 62.57°$, $\beta = 90°$, and $\gamma = 0$. ( ) equals eleven first-neighbor F^- at 2.4214 (two), 2.4364 (one), 2.4665 (two), 2.4818 (two), 2.6376 (two), and 2.9992 Å (two).

cm^{-1}	B_0^2	B_2^2	S_2^2	B_0^4	B_2^4	S_2^4	B_4^4	S_4^4	B_0^6	B_2^6	S_2^6	B_4^6	S_4^6	B_6^6	S_6^6
PC	−265	4	9	258	114	130	−23	181	109	−59	−155	−40	−63	110	−69
	(136)	(−44)	(665)	(296)	(135)	(163)	(−61)	(240)	(99)	(−51)	(−140)	(−43)	(−61)	(101)	(−71)
dip	−111	209	−9	−6	21	12	28	45	1	−6	0	−7	7	−10	−11
	(−164)	(281)	(−28)	(−6)	(20)	(12)	(27)	(43)	(1)	(−6)	(0)	(−7)	(7)	(−10)	(−11)
PC+dip	−376	213	0	252	135	142	5	226	110	−65	−155	−48	−56	101	−79
	(−28)	(237)	(637)	(290)	(155)	(176)	(−33)	(282)	(101)	(−57)	(−139)	(−51)	(−55)	(92)	(−82)
PC	−265	5	8	258	134	109	37	179	109	−84	−143	−59	−46	65	−113
	(136)	(66)	(663)	(296)	(160)	(139)	(20)	(246)	(99)	(−73)	(−129)	(−61)	(−44)	(56)	(−111)
dip	−171	187	−70	−4	24	9	47	31	0	−6	2	−6	7	−14	−7
	(−216)	(248)	(105)	(−3)	(24)	(10)	(46)	(29)	(0)	(−6)	(2)	(−6)	(7)	(−14)	(−8)
quad	24	−6	62	94	30	59	−46	92	30	−11	−8	−4	−17	26	−28
	(18)	(−17)	(73)	(91)	(29)	(57)	(−43)	(87)	(30)	(−11)	(−8)	(−4)	(−17)	(26)	(−28)
PC+dip+quad	−411	186	0	348	188	177	38	301	139	−100	−149	−68	−56	76	−148
	(−62)	(297)	(631)	(383)	(212)	(205)	(24)	(363)	(130)	(−90)	(−135)	(−71)	(−53)	(67)	(−146)
Expt	−190	−78	0	717	355	119	427	389	492	−946	−30	−82	−497	−454	−624

a slight tetragonal deformation of the cubic *Pm* 3*m* perovskite structure. Only uncomplete spectroscopic results are available[54] and it is not quite sure that the small europium ion substitutes itself to baryum without perturbing locally the structure so that the $BaTiO_3$:Eu^{3+} fluorescence spectrum which was investigated might correspond to a site completely different from the expected one.

For Y_2O_3:Eu^{3+} (Table XII), the (PC + dip) CFP yield slightly lower R values than the PC-only parameters. For YOCl: Eu^{3+} (Table XIII), the total contribution rather worsens the R values, but for isomorphic YOBr:Eu^{3+}, the induced moments improve R_4 and R_6 and yield a correct B_0^2 sign (Table XIV). KY_3F_{10}:Eu^{3+} (Table XV), as well as $NdAlO_3$, yield the best reliability factors with point-charge-only CFP. In the Sm^{2+}-doped compounds, the contribution of induced moments is weak and only change significantly B_0^2 for SrFCl:Sm^{2+} (Tables XVI and XVII). The LnOX and Ba (or Sr) FCl compounds display the same structure, yet the induced quadrupolar moment M_{zz} on F^- is small (0.001 e Å^2) in BaFCl, while M_{zz} on O^{2-} (equivalent site) equals 0.03 e Å^2 in YOCl and −0.09 e Å^2 in YOBr, responsible in the latter for the main part of the strong quadrupolar correction. The compound UF_6Cs (Table XVIII) behaves in a satisfying way. The multipolar contributions, all of the same sign, contribute nicely in raising the calculated CFP towards the experimental value.

Putting aside the garnet and LaF_3:Nd^{3+}, the mean R_4 and R_6 values are equal to 8° and 20.2°, respectively, for point-charge-only contributions, to 7.8° and 22.4° for (PC + dip), 12.4° and 28.3° for (PC + dip + quad). The reliability factors on a whole are rather more satisfactory when point-charge-only or (PC + dip) CFP are considered. One explanation might be the following: phenomenological refinement, in some cases, utilize as a starting point corrected (radial-expansion-shielding) point-charge parameters. The relative arrangement of experimental and calculated levels do not much change during the refinement even if an uncorrect assignment was ascribed at first so that it is not surprising if the final B_q^k are not very different from the starting values and consequently, their ratios quite similar to the PCEM ratios.

VI. SHIELDING AND SCALE FACTORS

We state from Table XIX that for each rare earth, the scale factors are grouped around mean values which depend on whether the transition ion

TABLE IX. Calculated (crystallographic data from Ref. 26) and experimental (phenomenological data from Ref. 27) crystal-field parameters of Nd^{3+} in $LaCl_3$ (C_{3h} site symmetry); PC + dip: $\alpha=-10.350°$, $\beta=0°$, and $\gamma=0°$, and PC + dip + quad: $\alpha=-4.854°$, $\beta=0°$, and $\gamma=0°$. ( ) equals nine first-neighbor Cl^- at 2.9504 (six) and 2.9534 Å (three).

cm^{-1}	B_0^2	B_0^4	B_0^6	B_6^6
PC	−768	−182	−61	32
	(636)	(−127)	(−49)	(31)
dip	1468	−3	−41	16
	(1329)	(−3)	(−41)	(16)
PC + dip	700	−184	−101	47
	(1965)	(−129)	(−89)	(46)
PC	−768	−182	−61	35
	(636)	(−127)	(−49)	(33)
dip	1305	0	−37	5
	(1172)	(0)	(−37)	(6)
quad	235	6	−9	27
	(202)	(8)	(−9)	(25)
PC + dip + quad	772	−176	−107	67
	(2010)	(−118)	(−95)	(64)
Expt	163	−336	−713	462

enters the compound as a dopant or a constituent (at least for Nd^{3+}). For europium-doped compounds, the mean S_k values are 0.66, 1.58, and 3.68 (for $k=2,4$, and 6, respectively) when point-charge-only parameters are calculated, 0.66, 1.54, and 3.69 for (PC + dip), and 0.70, 1.32, and 2.52 when the three contributions are summed up. The screening of the crystal field must also be taken into account. It has been evaluated as reducing the crystal field by a $(1-\sigma_k)$ factor [$\sigma_2=0.686$ (Ref. 55), $\sigma_4=0.139$, and $\sigma_6=-0.109$ (Ref. 56)]. The mean ratios of experimental and screened calculated B_q^k are 2.1, 1.83, and 3.32 for point-charge-only parameters, and 2.2, 1.53, and 2.27 when the three contributions are included. The calculated parameters are too low but they are increased by adding multipolar contributions. So as to estimate the relative strengths of the three multipolar contributions, we calculated a

TABLE X. Calculated (crystallographic data from Ref. 28) and experimental (phenomenological data from Ref. 29) crystal-field parameters for Nd^{3+} in $LiYF_4$ (S_4 site symmetry); PC + dip: $\alpha=32.905°$, $\beta=0°$, and $\gamma=0°$, and PC + dip + quad: $\alpha=33.704°$, $\beta=0°$, and $\gamma=0°$. ( ) equals eight first-neighbor F^- at 2.2459 (four) and 2.2933 Å (four).

cm^{-1}	B_0^2	B_0^4	B_4^4	S_4^4	B_0^6	B_4^6	S_4^6
PC	335	−443	776	61	−5	239	60
	(1716)	(−616)	(818)	(39)	(−22)	(219)	(38)
dip	537	−131	96	−61	23	50	33
	(540)	(−125)	(100)	(−49)	(23)	(50)	(33)
PC + dip	872	−574	871	0	18	289	93
	(2256)	(−741)	(919)	(−9)	(0)	(269)	(71)
PC	335	−443	778	18	−5	242	46
	(1716)	(−616)	(819)	(−6)	(−22)	(221)	(26)
dip	496	−107	84	−66	19	44	26
	(505)	(−102)	(89)	(−55)	(19)	(45)	(26)
quad	3	−264	218	48	−40	68	−68
	(−130)	(−256)	(209)	(49)	(−40)	(68)	(−68)
PC + dip + quad	834	−814	1079	0	−26	354	4
	(2091)	(−974)	(1117)	(−13)	(−44)	(333)	(−16)
Expt	401	−1008	1230	0	30	1074	0

TABLE XI. Calculated (crystallographic data from Ref. 30) crystal-field parameters of Eu^{3+} in $BaTiO_3$ (C_{4V} site symmetry); $\alpha=0°$, $\beta=0°$, and $\gamma=0°$, and ( ) equals twelve first-neighbor $B^2_0 B^4_0 B^4_4 B^6_0 B^6_4$ O^{2-} at 2.7957 (four), 2.2386 (four), and 2.8817 Å (four).

PC	11	−34	−39	−105	195
	(82)	(−344)	(−219)	(−78)	(142)
dip	198	−26	11	5	−6
	(182)	(−23)	(10)	(5)	(−6)
PC + dip	209	−60	−28	−100	189
	(264)	(−366)	(−209)	(−73)	(137)
dip	234	−29	12	5	−7
	(209)	(−25)	(11)	(6)	(−6)
quad	941	−480	−18	165	−231
	(826)	(−417)	(−5)	(167)	(−230)
PC + dip + quad	1186	−543	−44	66	−42
	(1117)	(−785)	(−213)	(95)	(−95)

mean $|B^k_{\mathrm{PC}}|$, $|B^k_{\mathrm{dip}}|$, and $|B^k_{\mathrm{quad}}|$ for all the compounds listed in Tables III–XVIII. We found

$$|B^2_{\mathrm{dip}}|/|B^2_{\mathrm{PC}}|=1{,}4\ ,\quad |B^2_{\mathrm{quad}}|/|B^2_{\mathrm{PC}}|=1{,}4\ ,$$

$$|B^4_{\mathrm{dip}}|/|B^4_{\mathrm{PC}}|=0{,}15\ ,\quad |B^4_{\mathrm{quad}}|/|B^4_{\mathrm{PC}}|=0{,}54\ ,$$

$$|B^6_{\mathrm{dip}}|/|B^6_{\mathrm{PC}}|=0{,}15\ ,\quad |B^6_{\mathrm{quad}}|/|B^6_{\mathrm{PC}}|=0{,}63\ .$$

With our choice of polarizability values, in the second-order parameters the mean dipolar contribution is equal to the quadrupolar one, whereas in the fourth- and sixth-order parameters, the mean quadrupolar contribution is 3.6 and 4.2 times larger than the dipolar one, respectively. These values cast some doubt about the convergence of the multipolar series, in particular the quadrupolar contribution is larger than the dipolar one in B^4 and B^6. Therefore we attempted the evaluation of the following multipolar contribution, i.e., the octupolar term in the case of BaFCl:Sm^{2+}. The octupolar moments were not calculated in a consistent way but were assumed proportional to the second derivatives of the field created by point charges, dipoles, and quadrupoles only. The scalar polarizabilities were those computed by Mahan[12] (considering that his definition of the moment $M^{(3)}_{zzz}$ is 30 times larger than ours, we divided his value of the octupolar polarizabilities by 30). The obtained octupolar corrections were the following: $(\Delta B^2_0)_O=-89$ cm^{-1}, $(\Delta B^4_0)_O=101$ cm^{-1}, $(\Delta B^4_4)_O=-23$ cm^{-1}, $(\Delta B^6_0)_O=31$ cm^{-1}, and $(\Delta B^6_4)_O=5$ cm^{-1}. These values are larger than the dipolar and quadrupolar contributions (Table XVI) and a consistent treatment would not change the trend. The only explanation for the divergence of the multipolar series is the overestimation of high-order polarizabilities. We tried an evaluation of this overestimation in an empirical way. A multipole M was placed at a nearest-ligand site $(R_J\theta_J\phi_J)$, and we calculated the mean contribution $\langle B^k\rangle_M$ to the $4f$-electron energy when θ_J,ϕ_J varied all over the sphere of radius R_J. We have

$$|B^k|_M=\left[\int_{\theta,\phi}\sum_q |B^k_q|^2\sin\theta\,d\theta\,d\phi\right]^{1/2}, \tag{14}$$

and we obtain

$$|B^k|_{\mathrm{PC}}=e\frac{\langle r^k\rangle}{R_J^{k+1}}q\ , \tag{15}$$

$$|B^k|_{\mathrm{dip}}=e\frac{\langle r^k\rangle}{R_J^{k+2}}\left[\frac{(k+1)(2k+1)}{3}\right]^{1/2}|M_{\mathrm{dip}}|\ , \tag{16}$$

and more generally for higher-order multipoles,

$$|B^k|_n=\left[\frac{[2(k+n)]!}{2^n(2k)!}\frac{1}{2n+1}\right]^{1/2}\frac{e\langle r^k\rangle}{R_J^{k+n+1}}|M_n|\ , \tag{17}$$

with

$$|M_{\mathrm{dip}}|=(M_x^2+M_y^2+M_z^2)^{1/2}\ , \tag{18}$$

$$|M_{\mathrm{quad}}|=(M_{xx}^2+M_{yy}^2+M_{zz}^2+2M_{xy}^2+2M_{yz}^2+2M_{xz}^2)^{1/2}\ . \tag{19}$$

The necessary convergence condition is

$$\frac{|B^k|_{n+1}}{|B^k|_n}=\left[\frac{2n+1}{2n+3}(k+n+1)[2(k+n)+1]\right]^{1/2}\frac{|M_{n+1}|}{|M_n|}\ ,\quad \frac{1}{R_J}<1\ ,\quad n\geq 0 \tag{20}$$

TABLE XII. Calculated (crystallographic data from Ref. 31) and experimental (phenomenological data from Ref. 32) crystal-field parameters of Eu^{3+} in Y_2O_3 (C_2 symmetry site); $\alpha=45°$, $\beta=90°$, and $\gamma=0°$. ( ) equals six first-neighbor O^{2-} at 2.2435 (two), 2.2677 (two), and 2.3371 Å (two).

cm^{-1}	B_0^2	B_2^2	S_2^2	B_0^4	B_2^4	S_2^4	B_4^4	S_4^4	B_0^6	B_2^6	S_2^6	B_4^6	S_4^6	B_6^6	S_6^6
PC	−269	−748	363	−770	−1013	3	812	243	90	−5	5	273	16	38	26
	(−786)	(−1696)	(486)	(−917)	(−994)	(8)	(881)	(203)	(78)	(−12)	(6)	(241)	(15)	(32)	(28)
dip	−332	−312	−121	−64	57	6	30	−32	39	19	−1	17	3	−7	−9
	(−306)	(−314)	(−104)	(−63)	(59)	(6)	(31)	(−30)	(39)	(19)	(−1)	(17)	(3)	(−7)	(−9)
PC+dip	−600	−1059	241	−834	−956	9	842	210	129	14	4	290	19	31	17
	(−1092)	(−2010)	(382)	(−980)	(−934)	(14)	(912)	(174)	(117)	(7)	(5)	(259)	(18)	(25)	(19)
dip	−286	−296	−73	−47	46	4	27	−29	30	14	−1	13	3	−5	−7
	(−248)	(−236)	(−97)	(−47)	(44)	(3)	(26)	(−22)	(30)	(14)	(−1)	(13)	(3)	(−5)	(−7)
quad	1036	−5	737	−675	−129	117	−19	−72	−23	−128	−84	167	39	38	90
	(1038)	(−72)	(860)	(−674)	(−133)	(123)	(−29)	(−80)	(−22)	(−127)	(−86)	(164)	(40)	(39)	(90)
PC+dip+quad	482	−1048	1027	−1492	−1096	123	819	142	97	−119	−80	453	58	71	110
	(4)	(−1860)	(1249)	(−1639)	(−1083)	(133)	(878)	(102)	(86)	(−124)	(−81)	(418)	(58)	(66)	(111)
Expt	−196	−695	0	−1264	−1519	−321	1092	255	267	228	276	894	281	157	95

which yields a condition for the ratio of two successive moments. We expect this condition to be more reliable for high values of n and k, that is, when the total CFP is mainly built up with the first-neighbor contribution. From Eq. (20) it may be inferred that for given moments, the ratio of their contribution to the B_q^k are higher, the higher the value of k, and this has been experimentally stated hereabove ($B_{\text{quad}}^4/B_{\text{dip}}^4=3.6$, $B_{\text{quad}}^6/B_{\text{dip}}^6=4.2$, where the B are averaged over the whole series of investigated compounds).

We have listed Table XXI the maximum values for $|M_{n+1}|/|M_n|$ as a function of k and n, in the case of a ligand at 3.2 Å, and compared them with the ratios of the computed moments on Cl^- in BaFCl.

If we suppose that the dipolar polarizabilities are reliable since they can be checked by refractive indexes measurements, then the quadrupolar polarizabilities ought to be 2 times lower and the octupolar polarizability 16 times lower than their literature values, to match the convergence condition. How such discrepancies may occur we cannot say; in recent polarizability calculations, care has been taken to simulate a realistic potential in the solid and indeed the dipolar polarizabilities are well reproduced. Quadrupolar and octupolar polarizabilities are more sensitive to small inaccuracies in the tail of the wave functions. Besides, it is questionable whether high electronic excitations such as those which are usually considered in these computations are physically realistic.

VII. CONCLUSION

We presented the results of an *ab initio* calculation of the even-order crystal-field parameters of lanthanides (and one actinide) in miscellaneous inorganic solid compounds.

The CFP were obtained by considering the interactions of the $4f$- (or $5f$-) electron 2^k poles ($k=2,4,6$) with the 2^n poles in the ion's sites ($n=0$=monopoles, $n=1,2$=consistently induced dipoles and quadrupoles). The multipolar contributions were evaluated for 16 compounds. The conclusions are the following.

(a) The mean ratio of the dipolar contribution to the point-charge contribution is equal to 1.4, 0.15, and 0.15 in B_q^k ($k=2,4$, and 6, respectively) while the ratio of the quadrupolar contribution to the point-charge contribution is equal to 1.4, 0.54, and 0.63, respectively. With the literature values of the multipolar polarizabilities, the multipolar series

TABLE XIII. Calculated (crystallographic data from Ref. 33) and experimental (phenomenological data from Ref. 34) crystal-field parameters of Eu^{3+} in YOCl (C_{4v} site symmetry); $\alpha = 0°$, $\beta = 0°$, and $\gamma = 0°$. ( ) equals four first-neighbor O^{2-} at 2.278 Å.

cm^{-1}	B^2_0	B^4_0	B^4_4	B^6_0	B^6_4
PC	−1290	−618	519	213	226
	(−2046)	(−751)	(677)	(181)	(211)
Dip	164	9	6	−2	2
	(0)	(0)	(0)	(0)	(0)
PC+dip	−1125	−609	525	211	228
	(−2046)	(−751)	(677)	(181)	(211)
dip	129	10	4	−2	2
	(0)	(0)	(0)	(0)	(0)
quad	274	−143	−51	4	19
	(355)	(−105)	(−55)	(4)	(22)
PC+dip+quad	−886	−751	472	215	247
	(−1691)	(−856)	(622)	(186)	(233)
Expt	−813	−712	833	1126	417

diverges. An approximate calculation of the octupolar contribution confirms this assumption. The literature values of $\alpha_{\rm quad}$ and α_0 seem overestimated.

(b) Supposing we ascribe lower polarizability values, therefore obtaining a converging electrostatic series, $B^k_{\rm PC} > B^k_{\rm dip} > B^k_{\rm quad} > B^k_0 \cdots$, then obviously the total contribution will not be very different from the point-charge values (since it is the aim we are seeking for) and therefore, the electrostatic parameters will be too weak as compared to the phenomenological CFP. The ways to remedy the situation are to take an account of charge penetration and covalency,[46,47] to apply a radial-expansion correction,[7,8] and to consider ion-induced multipole contributions.[57] Morrison *et al.* calculated that this process yielded important corrections to the fourth- and sixth-order CFP, but

(a) we wonder what these corrections would become if self-consistency was taken into account,

(b) it seems that in the case where the active ion is a constituent and not a dopant (for instance Nd_2O_3, Nd_2O_2S, or UF_6Cs) the process would be fully taken into account by adopting the correct polarizability values for the transition ion, and then these values would have to be enormous to increase so substantially the fourth- and sixth-order parameters.

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TABLE XIV. Calculated (crystallographic data from Ref. 33) and experimental (phenomenological data from Ref. 35) crystal-field parameters of Eu^{3+} in YOBr (C_{4V} site symmetry); $\alpha = 0°$, $\beta = 0°$, and $\gamma = 0°$. ( ) equals four first-neighbor O^{2-} at 2.347 Å.

cm^{-1}	B^2_0	B^4_0	B^4_4	B^6_0	B^6_4
PC	628	−839	326	129	202
	(−49)	(−801)	(483)	(106)	(195)
dip	−693	16	−38	6	−1
	(0)	(0)	(0)	(0)	(0)
PC+dip	−65	−823	288	134	201
	(−49)	(−801)	(483)	(106)	(195)
dip	−739	14	−40	6	−1
	(0)	(0)	(0)	(0)	(0)
quad	−967	156	156	50	−17
	(−1095)	(178)	(147)	(50)	(−15)
PC+dip+quad	−1078	−669	442	185	184
	(−1144)	(−622)	(630)	(156)	(180)
Expt	−964	−1059	804	897	425

TABLE XV. Calculated (crystallographic data from Ref. 36) and experimental (phenomenological data from Ref. 37) crystal-field parameters of Eu^{3+} in KY_3F_{10} (C_{4V} site symmetry); $\alpha=0°$, $\beta=90°$, and $\gamma=0°$. ( ) equals eight first-neighbor F^- at 2.1957 (four) and 2.3312 Å (four).

cm^{-1}	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6
PC	−1022	−766	241	132	8
	(−77)	(−876)	(240)	(127)	(25)
dip	1367	−133	−7	−17	25
	(1109)	(−132)	(−5)	(−17)	(25)
PC+dip	345	−899	234	115	33
	(1032)	(−1008)	(235)	(110)	(50)
dip	1325	−137	−10	−15	27
	(1065)	(−135)	(−8)	(−14)	(27)
quad	−1295	−242	373	197	111
	(−1350)	(−232)	(370)	(197)	(111)
PC+dip+quad	−991	−1144	604	314	146
	(−362)	(−1243)	(603)	(309)	(163)
Expt	−517	−1379	346	458	−243

APPENDIX A: CONTRIBUTIONS TO THE CFP

The monopolar, dipolar, and quadrupolar contributions to the CFP are given as functions of the Cartesian moment components as

$$(B_q^k)_{\mathrm{PC}}=-e^2\langle r^k\rangle\left[\frac{4\pi}{2k+1}\right]^{1/2}\sum_J\frac{M_J^{(0)}}{r_J^{k+1}}Y_k^{q*}(\vec{\mathrm{r}}_J)\,, \tag{A1}$$

$$\begin{aligned}(B_q^k)_{\mathrm{dip}}=e^2\langle r^k\rangle\left[\frac{4\pi}{2k+3}\right]^{1/2}&\sum_J\{-\tfrac{1}{2}(M_{Jx}^{(1)}+iM_{Jy}^{(1)}[(k+q+1)(k+q+2)]^{1/2}Y_{k+1}^{q+1*}(\vec{\mathrm{r}}_J)\\&+\tfrac{1}{2}(M_{jx}^{(1)}-iM_{Jy}^{(1)})[(k-q+1)(k-q+2)]^{1/2}Y_{k+1}^{q-1*}(\vec{\mathrm{r}}_J)\\&+M_{Jz}^{(1)}[(k-q+1)(k+q+1)]^{1/2}Y_{k+1}^{q*}(\vec{\mathrm{r}}_J)\}/r_J^{k+2}\,,\end{aligned} \tag{A2}$$

$$\begin{aligned}(B_q^k)_{\mathrm{quad}}=&-e^2\langle r^k\rangle\left[\frac{4\pi}{2k+5}\right]^{1/2}\\&\times\sum_J\left\{\frac{(M_{Jxx}^{(2)}-M_{Jyy}^{(2)}+2iM_{Jxy}^{(2)}}{4}[(k+q+1)(k+q+2)(k+q+3)(k+q+4)]^{1/2}Y_{k+2}^{*q+2}(\vec{\mathrm{r}}_J)\right.\\&+\frac{(M_{Jxx}^{(2)}-M_{Jyy}^{(2)}-2iM_{Jxy}^{(2)}}{4}[(k-q+1)(k-q+2)(k-q+3)(k-q+4)]^{1/2}Y_{k+2}^{*q-2}(\vec{\mathrm{r}}_J)\\&-(M_{Jzx}^{(2)}+iM_{Jzy}^{(2)})[(k+q+1)(k+q+2)(k+q+3)(k-q+1)]^{1/2}Y_{k+2}^{*q+1}(\vec{\mathrm{r}}_J)\\&+(M_{Jzx}^{(2)}-iM_{Jzy}^{(2)}[(k-q+1)(k-q+2)(k+q+1)(k-q+3)]^{1/2}Y_{k+2}^{*q-1}(\vec{\mathrm{r}}_J)\\&\left.+\frac{(2M_{Jzz}^{(2)}-M_{Jxx}^{(2)}-M_{Jyy}^{(2)})}{2}[(k-q+1)(k+q+1)(k+q+2)(k-q+2)]^{1/2}Y_{k+2}^{*q}(\vec{\mathrm{r}}_J)\right\}/r_J^{k+3}\,.\end{aligned} \tag{A3}$$

TABLE XVI. Calculated (crystallographic data from Ref. 38) and experimental (phenomenological data from Ref. 39) crystal-field parameters of Sm^{2+} in BaFCl (C_{4V} site symmetry);$\alpha=0°$, $\beta=0°$, and $\gamma=0°$. ( ) equals nine first-neighbors at 2.649 (four fluorine), 3.195 (one chlorine), and 3.286 Å (four chlorine).

cm^{-1}	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6
PC	8	−234	68	128	141
	(−562)	(−283)	(113)	(116)	(126)
dip	−20	5	−2	−2	1
	(−83)	(1)	(−4)	(−2)	(1)
PC+dip	−12	−229	66	126	142
	(−645)	(−282)	(109)	(114)	(127)
dip	−27	6	−3	−2	1
	(−91)	(1)	(−5)	(−3)	(1)
quad	−32	−16	−1	−1	−1
	(−26)	(−15)	(−1)	(−1)	(−1)
PC+dip+quad	−51	−245	64	125	141
	(−679)	(−297)	(107)	(112)	(126)
Expt	−92	−163	67	394	200

The second-order parameters were made rapidly converging[58,59] by Ewald's method. The higher-order CFP as well as the dipolar and quadrupolar corrections were calculated by direct sums within a radius R: 100 000 $1/p$ Å with $p=k+1$, $k+2$, and $k+3$ for monopoles, dipoles, and quadrupoles, respectively.

APPENDIX B: POLARIZABILITY TENSORS, SYMMETRIES, DEFINITIONS AND CONNECTION WITH THE LITERATURE VALUES

Ions are spherically symmetrical species. Therefore the Cartesian components of the dipolar and quadrupolar polarizabilities $\alpha^{(1)}$ and $\alpha^{(2)}$ obey to the following[60]:

(a) $\alpha^{(1)}_{xx}=\alpha^{(1)}_{yy}=\alpha^{(1)}_{zz}=\alpha^1$,

$$\alpha^{(1)}_{xy}=\alpha^{(1)}_{xz}=\cdots=0 \ .$$

The dipolar polarizability tensor reduces to a scalar quantity α^1 with

(b) $M^{(1)}=\alpha^1 E$,

$$\alpha^{(2)}_{xxxx}-\alpha^{(2)}_{xxyy}=\alpha^{(2)}_{zzzz}-\alpha^{(2)}_{zzxx}=\cdots$$

$$=2\alpha^{(2)}_{xyxy}=\cdots=\alpha^2 \ ,$$

$$\alpha^{(2)}_{xyxx}=\alpha^{(2)}_{yzxx}=\cdots=0 \ .$$

TABLE XVII. Calculated (crystallographic data from Ref. 38) and experimental (phenomenological data from Ref. 40) crystal-field parameters of Sm^{2+} in SrFCl (C_{4V} site symmetry); $\alpha=0°$, $\beta=0°$, and $\gamma=0°$, and ( ) equals nine first neighbors at 2.4943 (four fluorines), 3.0712 (one chlorine), and 3.112 Å (four chlorines).

cm^{-1}	B_0^2	B_0^4	B_4^4	B_0^6	B_4^6
PC	105	−368	98	195	215
	(−555)	(−422)	(162)	(173)	(188)
dip	−146	9	−11	−6	4
	(−218)	(3)	(−13)	(−6)	(3)
PC+dip	−41	−359	87	189	219
	(−773)	(−419)	(149)	(167)	(191)
dip	−162	9	−12	−6	4
	(−232)	(3)	(−14)	(−7)	(3)
quad	−61	−27	2	0	−4
	(−54)	(−24)	(2)	(0)	(−4)
PC+dip+quad	−117	−385	88	189	214
	(−841)	(−443)	(150)	(166)	(188)
Expt	60	−219	27	472	218

TABLE XVIII. Calculated (crystallographic data from Ref. 41) and experimental (phenomenological data from Ref. 42) crystal-field parameters for U^{5+} in UF_6 Cs (S_6 site symmetry); $\alpha=-12.347°$, $\beta=0°$, and $\gamma=0°$. ( ) equals six F^- first neighbors at 2.0572 Å.

cm^{-1}	B_0^2	B_0^4	B_3^4	S_3^4	B_0^6	B_3^6	S_3^6	B_6^6	S_6^6
PC	356	−3565	3864	−32	530	527	−3	378	4
	(1331)	(−3506)	(3953)	(−7)	(529)	(519)	(−1)	(370)	(−1)
dip	1180	−4104	4630	−69	861	832	−21	598	−32
	(867)	(−4065)	(4593)	(−142)	(865)	(839)	(−19)	(603)	(−27)
PC+dip	1536	−7669	8494	−101	1392	1360	−24	976	−29
	(2198)	(−7571)	(8546)	(−149)	(1394)	(1358)	(−20)	(974)	(−28)
dip	1797	−3990	4384	−14	756	867	−14	551	−21
	(1568)	(−3956)	(4350)	(−84)	(759)	(872)	(−12)	(557)	(−16)
quad	1660	−3653	4001	70	807	1182	36	677	15
	(1592)	(−3679)	(4001)	(97)	(807)	(1182)	(36)	(677)	(15)
PC+dip+quad	3813	−11208	12250	25	2093	2576	20	1607	−3
	(4491)	(−11141)	(12304)	(5)	(2095)	(2574)	(23)	(1604)	(−3)
Expt	848	−14982			5140				

Let us call elements such α_{xyxy} and α_{xxxx}, α_u and α_v, respectively. The diagonal components of the moments are given by

$$M_{zz}^{(2)}=\alpha_u(\nabla_x E_x+\nabla_y E_y)+\alpha_v \nabla_z E_z \ ,$$

with two similar expressions for $M_{xx}^{(2)}$ and $M_{yy}^{(2)}$. Subtracting $\alpha_u \vec{\nabla}\cdot\vec{E}(=0)$ from the three equations yields

$$M_{zz}^{(2)}=(\alpha_v-\alpha_u)\nabla_z E_z=\alpha^2\nabla_z E_z \ ,$$

and the corresponding expressions for $M_{xx}^{(2)}$ and $M_{zz}^{(2)}$, whereas

$$M_{xy}^{(2)}=\alpha_{xyyx}\nabla_y E_x+\alpha_{xyxy}\nabla_x E_y=\alpha^2\nabla_x E_y \ .$$

The quadrupolar polarizability tensor also reduces to a scalar with $M^{(2)}=\alpha^2\nabla\vec{E}$. The theoretical calculations of electronic polarizabilities which are found in the literature[11,12,13] concern the ratios

$$\alpha_{\rm dip}=M_z^{(1)}/E_z \ ,$$

$$\alpha_{\rm quad}=M_{zz}^{(2)}/\nabla_z E_z \ ,$$

as well as

$$\alpha_0=M_{zzz}^{(3)}/\nabla_z^2 E_z$$

(for the octupolar polarizability), the moments being defined by

$$M_z^{(1)}=\int\rho(\vec{r})z\,dv \ , \quad \left[M_J^{(1)}=\int\rho(\vec{r})z\,dv\right] \ ,$$

$$M_{zz}^{(2)}=\int\rho(\vec{r})(3z^2-r^2)dv \ , \quad \left[M_{zz}^{(2)}=\tfrac{1}{2}\int\rho(\vec{r})z^2dv\right] \ ,$$

$$M_{zzz}^{(3)}=\int\rho(\vec{r})5z^2-3r^2)z\,dv \ , \quad \left[M_{zzz}^{(3)}=\tfrac{1}{6}\int\rho(\vec{r})z^3dv\right] \ .$$

Taking into account the fact that an additional diagonal quadrupolar moment $\int\rho(\vec{r})r^2dv$, or octupolar moment $\int\rho(\vec{r})r^2z\,dv$ does not give any contribution to the potential,[52] we may compare with our definitions of the moments [Eqs. (6) in the main text] and infer that the α^2 and α^3 scalar values of the literature are to be divided by 6 and 30, respectively.

APPENDIX C: CALCULATION OF LATTICE SUMS

The sum over J in Eq. (10) of the main text must run until convergence is attained. It must take into account the translational invariance of the crystalline lattice. So it is split into N summations starting from all the ions of one unit cell. In Cartesian coordinates, this is written as

TABLE XIX. Reliability factors.

		Nd_2O_3	Nd_2O_2S	$NdA1O_3$	$Y_3Al_5O_{12}$ (Nd^{3+})	LaF_3 (Nd^{3+})	$LaCl_3$ (Nd^{3+})	$LiYF_4$ (Nd^{3+})	Y_2O_3 (Eu^{3+})	YOCl (Eu^{3+})	YOBr (Eu^{3+})	KY_3F_{10} (Eu^{3+})	BaFCl (Sm^{2+})	SrFCl (Sm^{2+})
	PC	0	0	0	170	32	180	0	25	0	180	0	180	0
R_2	PC + dip	0	0	0	21	69	0	0	16	0	0	180	0	180
	PC + dip + quad	0	180	0	54	63	0	0	50	0	0	0	0	180
	PC	1	10	1	3	26	0	8	10	9	18	4	8	11
R_4	PC + dip	1	10	3	7	35	0	5	11	8	21	1	8	9
	PC + dip + quad	16	20	12	69	30	0	2	18	17	4	17	10	8
	PC	12	17	6	8	56	3	11	24	29	32	42	22	24
R_6	PC + dip	12	11	7	24	67	9	18	23	29	31	59	22	25
	PC + dip + quad	27	10	62	63	54	1	4	38	31	21	70	22	25

TABLE XX. Scale factors.

		Nd_2O_3	Nd_2O_2S	$NdA1O_3$	$Y_3Al_5O_{12}$ (Nd^{3+})	LaF_3 (Nd^{3+})	$LaCl_3$ (Nd^{3+})	$LiYF_4$ (Nd^{3+})	Y_2O_3 (Eu^{3+})	YOCl (Eu^{3+})	YOBr (Eu^{3+})	KY_3F_{10} (Eu^{3+})	BaFCl (Sm^{2+})	SrFCl (Sm^{2+})
	PC	0.50	8.03	0.43	1.06	0.83	0.21	1.20	0.83	0.63	1.53	0.51	11.99	0.57
S_2	PC + dip	0.56	0.21	0.35	0.14	0.46	0.23	0.46	0.61	0.72	14.92	1.50	7.51	1.48
	PC + dip + quad	0.24	0.16	0.16	0.20	0.45	0.21	0.48	0.47	0.92	0.89	0.52	1.81	0.51
	PC	1.12	1.05	1.38	1.95	2.75	1.85	1.7	1.5	1.44	1.62	1.75	0.74	0.57
S_4	PC + dip	1.14	1.04	1.38	2.17	2.46	1.82	1.5	1.5	1.43	1.69	1.53	0.76	0.59
	PC + dip + quad	0.97	0.88	0.58	2.33	1.82	1.91	1.2	1.2	1.37	1.70	1.02	0.72	0.55
	PC	1.97	1.52	3.29	4.95	5.78	12.26	4.36	3.65	3.31	3.45	4.32	2.05	1.56
S_6	PC + dip	1.96	1.48	3.22	4.88	5.77	7.96	3.54	3.38	3.30	3.44	4.63	2.04	1.56
	PC + dip + quad	1.75	1.25	8.66	7.77	4.91	6.77	3.03	2.07	3.10	3.39	1.52	2.06	1.58

TABLE XXI. Higher limit for the ratio of two successive moments evaluated by Fq. (20) as compared to computed values in the case of BaFCl.

	Higher limit for $\vert M_{n+1}\vert / \vert M_n\vert$				Computed $\vert M_{n+1}\vert / \vert M_n\vert$
n	k	2	4	6	
1		0.78	0.51	0.38	0.59
2		0.56	0.40	0.31	3.2

$$\sum_{J=1,N} \alpha^1(J')M_J^{(0)}\cdot\sum_{\vec{\xi}}\nabla_x\left[\frac{1}{|\vec{\mathrm{R}}_J+\vec{\xi}\,|}\right]+\sum_{\mu}M_{J\mu}^{(1)}\left[-\delta(J,J')\cdot\delta(x,\mu)+\alpha^1(J')\sum_{\vec{\xi}}\nabla^2_{x\mu}\left[\frac{1}{|\vec{\mathrm{R}}_J+\vec{\xi}\,|}\right]\right]$$
$$+\sum_{\mu\nu}M_{J\mu\nu}^{(2)}\alpha^1(J')\sum_{\vec{\xi}}\nabla^3_{x\mu\nu}\left[\frac{1}{|\vec{\mathrm{R}}_J+\vec{\xi}\,|}\right]=0\,, \tag{C1}$$

$$\sum_{J=1,N} \alpha^2(J')M_J^{(0)}\sum_{\vec{\xi}}\nabla^2_{xy}\left[\frac{1}{|\vec{\mathrm{R}}_J+\vec{\xi}\,|}+\sum_{\mu}M_{J\mu}^{(1)}\alpha^2(J')\sum_{\vec{\xi}}\nabla^3_{xy\mu}\left[\frac{1}{|\vec{\mathrm{R}}_J+\vec{\xi}\,|}\right]\right.$$
$$\left.+\sum_{\mu\nu}M_{J\mu\nu}^{(2)}\left[\delta(J,J')\cdot\delta(x,\mu)\cdot\delta(y,\nu)+\alpha^2(J')\sum_{\vec{\xi}}\nabla^4_{xy\mu\nu}\left[\frac{1}{|\vec{\mathrm{R}}_J+\vec{\xi}\,|}\right]\right]\right]=0\,. \tag{C2}$$

where $x,y,\mu,\nu=x$, y, or z, and $\vec{\xi}$ is a lattice translation. These are $3N$ equations (C1) (equilibrium of dipoles in the total field) and $9N$ equations (C2) (equilibrium of quadrupoles in the total field gradient).

The infinite lattice sums

$$\sum_{\vec{\xi}}\nabla^n_{x,y\ldots}\left[\frac{1}{|\vec{\mathrm{R}}_J+\vec{\xi}\,|}\right]$$

for each ion are calculated separately, by Ewald's method[47] for $n\leq 3$ so as to accelerate the convergence, by direct sums for $n=4$ and 5.

The problem is still a little bit more complicated since usually, in a given compound, there are for each species, a number of "equivalent" atoms, the moments of which must be related one to the other by the symmetry operations of the space group. So there are two ways to handle the problem: either to consider each atom in the unit cell as a particular species and resolve system (C1) plus (C2), or to take into account the symmetry transformation of the moments and deduce the equivalent linear system in terms of different crystallographic species. The dimension of the linear system is then greatly reduced.

The transformation matrix R for moments and coordinates may be readily deduced from the general crystallographic positions listed in Ref. 14 for each space group. For a monoclinic lattice angle $(\vec{a},\vec{b})\neq 0$, a Cartesian coordinate of atom J species i is given as a function of the contravariant components of the first one of the set (atom 1, species i) by

$$r_{ijx}=\sum_{K}A(x,K)[iA(i,J,K)$$
$$+\sum_{\alpha}R(i,J,\alpha,K)r_{i1\alpha}]\,, \tag{C3}$$

and α and K range over the three contrevariant components; TA is an eventual translation. $A(x,K)$ is the 3×3 transformation matrix from contravariant to Cartesian coordinates. $A(1,1)=A(3,3)=1$, $A(1,2)=\cos(\vec{a},\vec{b})$, and $A(22)=\sin(\vec{a},\vec{b})$, the other elements being zero. In the same way, the transformed moment components are given by

$$M_{iJx}^{(1)}=\sum_{\alpha K}R(i,J,\alpha,K)A(x,K)M_{i1\alpha}^{1}\,, \tag{C4}$$

$$M_{iJxy}^{(2)}=\sum_{\substack{\alpha K\\ \beta K'}}R(i,J,\alpha,K)R(i,J,\beta,K')$$
$$\times A(x,K)A(y,K')M_{i1\alpha\beta}^{(2)}\,, \tag{C5}$$

Equations (C3), (C4), and (C5) must be utilized in (C1) and (C2) to yield finally a sum over species.

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