PHYSICAL REVIEW B VOLUME 21, NUMBER 8 15 APRIL 1980

# Calculation of electrostatic crystal-field parameters including contributions of induced dipoles: Application to $Nd_2O_3$ and $Nd_2O_2S$

M. Faucher, J. Dexpert-Ghys, and P. Caro

*Eléments de Transition dans les Solides, ER 60210-CNRS-1 Place A. Briand, 92190 Meudon, France*

(Received 25 July 1979)

The method utilized for the calculation of the dipolar contribution to crystal-field parameters (cfp) is outlined and applied to the case of neodymium oxide and neodymium oxysulfide. The slowly converging electric field and electric-field gradients necessary for deriving induced moments are calculated by Ewald's method. The dipole components are then obtained by resolving the linear system linking induced moments and the electric field produced by point charges and dipoles throughout the crystal lattice. The dipole components are introduced in a general correction formula for the cfp. The calculation shows that mainly the second-order parameters are changed by the corrections. The total $B_0^2$ (point charges plus dipoles) exhibits the correct experimental sign for both compounds investigated, whereas the point-charge contribution alone does not: $(B_0^2)_{\text{expt}} = -800\ \text{cm}^{-1}(Nd_2O_3)$, $+194\ \text{cm}^{-1}(Nd_2O_2S)$; $(B_0^2)_{\text{PC}} = -1500\ \text{cm}^{-1}(Nd_2O_3)$, $-653\ \text{cm}^{-1}(Nd_2O_2S)$; $(B_0^2)_{\text{D}} = -478\ \text{cm}^{-1}(Nd_2O_3)$, $+1363\ \text{cm}^{-1}(Nd_2O_2S)$. As usual, the calculated second-order parameters are too large, the fourth- and sixth-order parameters too small (1.4 and 2 times, respectively) when utilizing the theoretical radial integrals $\langle r^k \rangle$.

## I. INTRODUCTION

This paper reports one more attempt to calculate "*ab initio*" crystal-field parameters (cfp) of a rare-earth ion embedded in a crystalline host, utilizing a small number of physical constants. The aim is the evaluation of the static potential at the rare-earth site, supposing the electric forces in the lattice are produced by point charges superposed to multipoles. Hutchings and Ray[1] undertook the first calculation of dipolar and quadrupolar contributions in rare-earth halides. Morrison[2] gave a more complete solution concerning dipolar effects only, showing precisely how the static-induced dipoles could readily be evaluated in a crystal lattice. Basically, our work contains little more physical background than is present in Ref. 2, but we felt it was necessary to work through the question once more to ascertain whether or not the dipolar correction improved the point-charge calculated values of the crystal-field parameters since the answer to this question was not very obvious in the two preceding papers. So we present a comparison between experimental and calculated cfp of two well-known compounds, i.e., neodymium sesquioxide ($Nd_2O_3$) and neodymium oxysulfide ($Nd_2O_2S$) which exhibit the same structure but quite different sets of experimental cfp.[3,4] The point-charge electrostatic model (PCEM) alone is unable to explain the difference between the two sets, namely, the opposite sign of $B_0^2$. We shall see that the consideration of induced dipoles explains the discrepancy fairly well.

The following points need to be emphasized:

(a) The induced dipoles are proportional to the local electric field produced by point charges $\vec{E}_{PC}$ as well as induced dipoles $\vec{E}_D$, a fact which seems to have been disregarded in Ref. 1 but not in Ref. 2. It is well known that the direct calculation of the former $\vec{E}_{PC}$ is made by the means of a very slowly converging lattice sum. We have forced the convergence of $\vec{E}_{PC}$ by utilizing Ewald's method.[5,6]

(b) In this work, the cationic polarizabilities ($Nd^{3+}$) which are not necessarily negligible are not disregarded as in Ref. 2. Indeed, the consideration of induced moments on $Nd^{3+}$, though not very important for the calculation of the dipolar corrections (the $Nd^{3+}$ are only second neighbors of a central $Nd^{3+}$), is necessary because they strongly "react" on their neighborhood and drastically change the induced moments on the $O^{2-}$ anions.

(c) Recent accurate structural data available for $Nd_2O_3$ were utilized. Those concerning $Nd_2O_2S$ are somewhat older.

In Sec. II, we shall give relevant formulas for the computation of PCEM parameters, dipolar corrections, and evaluation of induced moments in the general case. Whenever lengthy, the intermediate mathematics are set in an Appendix. In Sec. III, we treat the special case of $Nd_2O_3$ and $Nd_2O_2S$, and in Sec. IV compare calculated results with experimental values.

## II. CALCULATION OF CRYSTAL-FIELD PARAMETERS: DIPOLAR CORRECTION

### A. Point-charge contribution

The nucleus of an ionized transition metal is at the origin of coordinates $O$ (for instance, the nucleus of $\mathrm{Nd}^{3+}$). The polar coordinates of the $i$ open-shell electrons (i.e., the $4f$ electrons) with respect to $O$ are $r_i, \theta_i, \varphi_i$. If a point charge $+Ce$ is located at $(R, \alpha, \beta)$ or $(X, Y, Z)$ such that $R > r_i$, the potential energy of the point charge and electron is given as a function of spherical harmonics by the classical development

$$W = -Ce^2 \sum_{kq} \frac{4\pi}{2k+1} Y_k^{q*}(\alpha, \beta) Y_k^q(\theta_i, \varphi_i) \frac{r_i^k}{R^{k+1}} = Cef(\theta_i, \varphi_i) g(\vec{R}) . \tag{1}$$

The summation over positive integer values of $k$ is infinite. The integer values of $q$ range from $-k$ to $+k$. If the lattice surrounding the rare-earth ion is approximated as an assembly of point charges $C_j e(R_j, \alpha_j, \beta_j)$, the lattice-electron interaction is obtained by summing Eq. (1) over $j$ and $i$:

$$w_1 = -e^2 \sum_{ijkq} \frac{4\pi}{2k+1} C_j Y_k^{q*}(\alpha_j, \beta_j) Y_k^q(\theta_i, \varphi_i) \frac{r_i^k}{R_j^{k+1}} . \tag{2}$$

$w_1$ is a very crude approximation for the crystal-field potential. Following Wybourne,[7] the development of the true potential is conventionally written as

$$W_p = \sum_{kqi} B_q^k \mathfrak{C}_{qi}^k , \tag{3}$$

with

$$\mathfrak{C}_{qi}^k = \left(\frac{4\pi}{2k+1}\right)^{1/2} Y_k^q(\theta_i, \varphi_i) . \tag{4}$$

Picking up the coefficient of $\mathfrak{C}_{qi}$ in Eq. (2), we obtain the point-charge contribution to the experimental cfp, provided $r_i^k$ is replaced by its expectation value

$$\langle r^k \rangle = \langle P(nl) | r_i^k | P(nl) \rangle ,$$

$P(nl)$ being the radial function, and

$$(B_q^k)_{\mathrm{PC}} = -\left(\frac{4\pi}{2k+1}\right)^{1/2} e^2 \langle r^k \rangle \sum_j \frac{C_j}{R_j^{k+1}} Y_k^{q*}(\alpha_j, \beta_j) . \tag{5}$$

This expression has been utilized[8-10] to yield starting values for the refinement of phenomenological $B_q^k$'s.

### B. Dipolar contribution

If the lattice ions are considered as extended charge distributions, each one of these is equivalent to the superposition of point charges, point dipoles, point quadrupoles, etc. The interaction potential energy between $4f$ electrons and one of these extended distributions is equal to a doubly infinite development. The first term concerning monopoles is $w_1$ [Eq. (2)]. The second term to deal with is $w_2$, interaction of $4f$ electrons with induced dipoles. Let us consider such a dipole at $P(\vec{R})$. The potential energy of the dipole and $4f$ electron is easily derived from (1) by summing up the individual potential energies of two point charges $+Ce$ at $\vec{R} + d\vec{R}/2$ and $-Ce$ at $\vec{R} - d\vec{R}/2$.

$$W' = f(\theta_i, \varphi_i) \vec{M} \cdot \vec{\nabla}[g(\vec{R})] \tag{6}$$

($\vec{M} = Ce\, d\vec{R}$). The total interaction potential $w_2$ between the $4f$ electrons and all the dipoles at $\vec{R}_j$ is given by summing Eq. (6) over $j$ and $i$:

$$w_2 = -e \sum_{ijkq} \frac{4\pi}{2k+1} r_i^k Y_k^q(\theta_i, \varphi_i) \vec{M}_j \cdot \vec{\nabla}\left(\frac{Y_k^{q*}(\alpha_j, \beta_j)}{R_j^{k+1}}\right) . \tag{7}$$

$w_2$ is a first-order correction term to $w_1$ Eq. (2). Picking out the coefficient of $\mathfrak{C}_{qi}^k$ in Eq. (7) and replacing $r_i^k$ by $\langle r^k \rangle$, we obtain the dipolar contribution to the cfp $B_q^k$, that is

$$(B_q^k)_{\mathrm{D}} = -\left(\frac{4\pi}{2k+1}\right)^{1/2} e \langle r^k \rangle \sum_j \vec{M}_j \cdot \vec{\nabla}\left(\frac{Y_k^{q*}(\alpha_j, \beta_j)}{R_j^{k+1}}\right) , \tag{8}$$

and the corrected electrostatic cfp

$$(B_q^k)_{\mathrm{PCD}} = (B_q^k)_{\mathrm{PC}} + (B_q^k)_{\mathrm{D}} . \tag{9}$$

Our purpose is to calculate $(B_q^k)_{\mathrm{PC}}$ and $(B_q^k)_{\mathrm{D}}$ and to compare the values of Eq. (9) with experimental results.

As it stands, Eq. (8) needs some arrangements to be tractable for computing purposes. These are described in Appendix A and the final result (A4) is convenient for computing $(B_q^k)_{\mathrm{D}}$ provided one knows the magnitude and orientation of point dipoles $(M_{jx}, M_{jy}, M_{jz})$ in the lattice of interest.

### C. Induced dipoles

We want to evaluate the components of the dipoles induced at the ions sites by the crystal field. Adopting the simplifying hypothesis of a scalar polarizability, we have

$$\vec{M}_j = \alpha_j \vec{E}_j . \tag{10}$$

$\vec{E}_j$, electric field at $P(R_j, \alpha_j, \beta_j)$, is produced by point charges but also by induced dipoles, so that a component of Eq. (10) can be written

$$M_{jv} = \alpha_j \left( E_{\mathrm{PC}}(j, v) + \sum_{j', v'} E_{\mathrm{D}}(j, j', v', v) M_{j'v'} \right)$$

or

$$\alpha_j E_{\mathrm{PC}}(j, v) + \sum_{j', v'} [\alpha_j E_{\mathrm{D}}(j, j', v', v) - \delta(j', j; v', v)] M_{j'v'} = 0 . \tag{11}$$

$v$ and $v'$ span over the three components $x, y, z$, and $j, j'$ over the atoms of the unit cell.

$E_D(j, j', v', v)$ is the $v$ component at $j$ produced by a unit dipole at $j'$ pointing along $v'$. The linear system can be resolved for the unknown $M_{jv}$'s.

Whereas $E_{PC}$ in Eq. (11) is created by charges, i.e., scalar quantities distributed in the crystal lattice, $E_D$ is produced by vector components which have to be arranged according to the space-group constraints. There are two ways for handling the problem:

(a) For a very small unit cell enclosing a small number of ions, each one of them can be treated as a different species even though they may be in fact identical atoms occupying "equivalent" crystallographic positions. Then we need not bother with symmetry and we only utilize the translational invariance for a displacement $m\vec{a}+n\vec{b}+l\vec{c}$ in the crystal lattice ($m, n, l$ are integers, and $\vec{a}, \vec{b}, \vec{c}$ the lattice vectors), and build up the linear system (11), the dimension of which will be in this case $3\times N$, $N$ being the total number of atoms in the unit cell.

(b) For a large unit cell with several species $j$, each of them occupying a great number of equivalent positions $p$, the procedure described in (a) is rather clumsy and it is obvious that the transformation properties of the space group must be utilized to find all the transformed dipoles generated by an arbitrary initial one $\vec{M}(j, 1)$. More precisely, transformed atomic coordinates may be written in the tensorial form

$$R(j,p,v)=T(j,p,v)+\sum_{v'} S(j,p,v',v)\,R(j,1,v')\,,$$

where $j$ is the index of the species, $p$ is the atom number, and $v$ and $v'$ span over $x$, $y$, and $z$ coordinates. $S(j,p,v',v)$ is the proportion of the $v'$ component of atom 1 which can be found in the $v$ component of atom $j$. Then, of course, $S(j,1,v',v)=\delta(v',v)$. $T(j,p,v)$ is a possible translation. $R(j,1,v')$ with $v'=x,y,z$ are the positional parameters for atom 1. Then a unit dipole $S(j,1,v',v')=1$, pointing along $v'$ on species $j$ atom 1, will span throughout the unit cell a set of dipoles $S(j,p,v',v)$, given by the same fourth-rank tensor as above. This set in turn is utilized to calculate the total dipolar field created by species $j'$ at $j$ [Eq. (11)]. In this way, the dimension of the linear system [Eq. (11)] is reduced to $3\times s$, $s$ being the total number of species (or "different atoms") in the unit cell.

Both approaches (a) and (b) were utilized. The $Nd_2O_3$ and $Nd_2O_2S$ unit cells are very small and contain only five atoms so that approach (a) could be safely adopted. However, this is a very special case and we preferred to work out the more general path (b) which of course leads to the same numerical results.

The origin being $P$, the electric field due to point charges located at $P'(R_{j'}, \alpha_{j'}\beta_{j'})$ is equal to

$$(\vec{E}_P)_{PC}=-\vec{\nabla}_P\sum_{j'}\frac{q_{j'}e}{R_{j'}}=+\sum_{j'}\vec{\nabla}_{P'}\left(\frac{q_{j'}e}{R_{j'}}\right). \qquad (12)$$

The electric field created in $P$ by point dipoles placed in $P'(R_{j'}, \alpha_{j'}, \beta_{j'})$ is equal to

$$(\vec{E}_P)_D=\sum_{j'}\vec{\nabla}_{P'}[\vec{M}_{j'}\cdot\vec{\nabla}_{P'}(1/R_{j'})]\,. \qquad (13)$$

The lattice sums (13) and especially Eq. (12), converge very slowly. Several efficient accelerating processes have been proposed, namely by Bertaut[11] and de Wette and Schacher.[12] However, we have utilized the older Ewald's method[5,6] which was more familiar to us and did not consume much computer time either. Ewald's method is briefly described in Appendix B where we give the final result for the $z$ component of Eqs. (12) and (13) in Eqs. (B2) and (B6).

## III. APPLICATION TO NEODYMIUM OXIDE AND NEODYMIUM OXYSULFIDE

### A. Experimental crystal-field parameters

The absorption spectrum of $Nd_2O_3$ in powder form was interpreted by Caro *et al.*,[3] who refined one set of cfp for the excited levels measured at 4 K, plus two sets of cfp which fit both the splittings of the ground level at 300 K and the parallel and perpendicular magnetic susceptibility curves up to 300 K. These values are reported in Table I.

The cfp of polycrystalline $Nd_2O_2S$ listed in Table I were determined by Souillat *et al.*[4] It is noteworthy that the sign of $B_0^2$ is different for the two compounds. A positive value of $B_0^2$ was already found by Sovers *et al.*,[13] for $Eu^{3+}$ doped in rare-earth oxysulfides. On the other hand, the magnetic susceptibility curves of $Nd_2O_3$ can only be fitted with a negative value[3] of $B_0^2$.

### B. Crystal structures

The crystal structure of $A$-$Nd_2O_3$ had first been investigated by Zachariasen,[14,15] and then solved by Pauling[16] and Koehler *et al.*[17] Muller-Buschbaum *et al.*[18] brought in some controversy by suggesting a different space group for isomorphic $La_2O_3$, but a recent neutron-diffraction refinement reported by Boucherle *et al.*,[19] ascertained Pauling's model for $Nd_2O_3$ and provided very precise positional parameters. The definite structural data for $Nd_2O_3$ (Space group $P\bar{3}m1$) are:

TABLE I. Experimental and calculated crystal-field parameters for $Nd_2O_3$ and $Nd_2O_2S$.

| | $Nd_2O_3$ | | | | | | | | $Nd_2O_2S$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $(cm^{-1})$ | PCEM [a] | ID [a] | PCEM + ID Total $(ES)$ | $ES(1-\sigma_k)$ [d] | $ES(1-\sigma_k)$ [e] $\langle r'k \rangle$ | Experimental Set 1 [b] | Set 2 [c] | Set 3 [c] | PCEM [a] | ID [a] | PCEM + ID Total $(ES)$ | $ES(1-\sigma_k)$ [d] | $ES(1-\sigma_k)$ [e] $\langle r'k \rangle$ | Expt. [f] |
| $B_0^2$ | −1500 | −478 | −1978 | −411 | −575 | −836 | −645 | −818 | −653 | 1363 | 710 | 148 | 207 | 194 |
| $B_0^4$ | 420 | 18 | 438 | 377 | 754 | 634 | 992 | 1196 | 746 | −6 | 740 | 637 | 1274 | 912 |
| $B_3^4$ | 1193 | 22 | 1215 | 1046 | 2092 | 1606 | 1141 | 1338 | 685 | −83 | 602 | 518 | 1037 | 924 |
| $B_0^6$ | 287 | −32 | 255 | 227 | 590 | 752 | 585 | 557 | 143 | 114 | 257 | 229 | 595 | 512 |
| $B_3^6$ | −170 | 9 | −161 | −143 | −372 | −237 | −311 | −246 | −147 | 9 | −138 | −123 | −320 | −300 |
| $B_6^6$ | 263 | 13 | 276 | 246 | 640 | 672 | 962 | 846 | 241 | −32 | 209 | 186 | 484 | 256 |

[a] Point charge and dipolar contributions; see Secs. III C and III D. The utilized structural parameters are those of Refs. 19 and 22 for $Nd_2O_3$ and $Nd_2O_2S$, respectively.

[b] cfp fitting the excited levels at 4.2 K (Ref. 3).

[c] cfp fitting the splitting of the ground level at 300 K as well as the variation of the magnetic susceptibility up to 300 K (Ref. 3).

[d] Calculated cfp (PCEM + ID) corrected for the screening factor $\sigma_k$; see Sec. IV.

[e] Calculated cfp corrected for $\sigma_k$ and for "expanded" radial functions, i.e., multiplied by 1.4, 2, and 2.6 for $k=2$, 4, 6, respectively. See Sec. IV.

[f] Following Ref. 4.

| | | | site symmetry |
|---|---|---|---|
| | (2$d$) | Nd(1) $\frac{1}{3}$ $\frac{2}{3}$ $u$ | $u=0.2462$ $C_{3v}$ |
| atomic positions | | Nd(2) $\frac{2}{3}$ $\frac{1}{3}$ $-u$ | |
| (hexagonal | (2$d$) | O(1) $\frac{1}{3}$ $\frac{2}{3}$ $v$ | $v=0.6466$ $C_{3v}$ |
| coordinates) | | O(2) $\frac{2}{3}$ $\frac{1}{3}$ $-v$ | |
| | (1$a$) | O(3) 0 0 0 | $D_{3d}$ |

We have refined the parameters of the hexagonal unit cell utilizing powder x-ray-diffraction data and have obtained $a=3.823$ Å and $c=5.988$ Å, which are very close to the values reported by Roth *et al.*[20] In $Nd_2O_3$, an $Nd^{3+}$ ion is coordinated to seven $O^{2-}$. Four of them belong to the $(NdO)_n^{n+}$ layer (three lie at the apices of an equilateral triangle with $R=2.3$ Å, and one on the ternary axis at a slightly larger distance $R=2.398$ Å). The three remaining interlayer oxygens are on the other side with respect to the ternary axis, farther away ($R=2.654$ Å), and placed on the apices of an identical triangle twisted with respect to the first one (60°). Table II lists the polar coordinates as well as the distances of the nearest and next-nearest neighbors of an $Nd^{3+}$ ion.

The crystal structure of $Nd_2O_2S$ is basically the same as that of the oxide, the interlayer oxygens being replaced by sulfur. The lattice parameters of monothio-oxides are given by Eick.[21] For $Nd_2O_2S$, $a=3.946$ Å and $c=6.79$ Å. A structure determination of $Ce_2O_2S$ based on powder x-ray-diffraction data, was first performed by Zachariasen.[22] More recently, Morosin *et al.*,[23] refined the structure of an $La_2O_2S$ single crystal. However, we have utilized the former results since they apply to a compound which is closer to the one under investigation. The space group and the atomic positions are formally the same as above but with $u=0.29$ and $v=0.64$ (for $La_2O_2S$,[23] $a=4.049$ Å, $c=6.939$ Å, $u=0.2793$, $v=0.6287$). The distances from $Nd^{3+}$ to neighbors and next-nearest neighbors are listed in Table II.

### C. Point-charge contribution

The only even nonvanishing cfp in a $C_{3v}$ site symmetry are $B_0^2$, $B_0^4$, $B_3^4$, $B_0^6$, $B_3^6$, and $B_6^6$. Their expression is given in Appendix C. Point charges $+3e$ and $-2e$ are placed at neodymium and oxygen (or sulfur) sites, respectively. The $\langle r^k \rangle$ values for $Nd^{3+}$ are those reported by Freeman *et al.*[24] A 30° rotation around the ternary axis cancels the imaginary parts of the cfp.

TABLE II. Nearest and next-nearest neighbors of an $Nd^{3+}$ ion [Nd(1)] in $Nd_2O_3$ and $Nd_2O_2S$. Components and contribution of induced moments to the cfp. ($M_Z$ is expressed in $e$Å, $R$ in Å, $\alpha$ and $\beta$ in degrees, and the cfp in $cm^{-1}$.)

| Compound | Atom | $M_Z$ | $R$ | $\alpha$ | $\beta$ | $(B_0^2)_D$ | $(B_0^4)_D$ | $(B_3^4)_D$ | $(B_0^6)_D$ | $(B_3^6)_D$ | $(B_6^6)_D$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $Nd_2O_3$ | O(2) | 0.0784 | 2.299 | 73.8 | –120.0 | –100.0 | 20.0 | 5.0 | –6.0 | 2.0 | 4.0 |
| | | 0.0784 | 2.299 | 73.8 | 120.0 | –100.0 | 20.0 | 5.0 | –6.0 | 2.0 | 4.0 |
| | | 0.0784 | 2.299 | 73.8 | 0.0 | –100.0 | 20.0 | 5.0 | –6.0 | 2.0 | 4.0 |
| | O(1) | –0.0784 | 2.398 | 0.0 | 0.0 | –232.0 | –45.0 | 0.0 | –16.0 | 0.0 | 0.0 |
| | O(3) | 0.0000 | 2.654 | 123.7 | 180.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0000 | 2.654 | 123.7 | 60.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0000 | 2.654 | 123.7 | –60.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | O(1) | –0.0784 | 3.590 | 180.0 | 0.0 | 46.0 | 4.0 | 0.0 | 1.0 | 0.0 | 0.0 |
| | Nd(2) | –0.1406 | 3.683 | 143.2 | –120.0 | 6.0 | –2.0 | 2.0 | –0.0 | 0.0 | 0.0 |
| | | –0.1406 | 3.683 | 143.2 | 120.0 | 6.0 | –2.0 | 2.0 | –0.0 | 0.0 | 0.0 |
| | | –0.1406 | 3.683 | 143.2 | 0.0 | 6.0 | –2.0 | 2.0 | –0.0 | 0.0 | 0.0 |
| | | –0.1406 | 3.756 | 36.0 | 120.0 | –8.0 | 2.0 | 2.0 | 0.0 | 0.0 | –0.0 |
| | | –0.1406 | 3.756 | 36.0 | –120.0 | –8.0 | 2.0 | 2.0 | 0.0 | 0.0 | –0.0 |
| | | –0.1406 | 3.756 | 36.0 | 0.0 | –8.0 | 2.0 | 2.0 | 0.0 | 0.0 | –0.0 |
| | Nd(1) | 0.1406 | 3.823 | 90.0 | 150.0 | 0.0 | 0.0 | 0.0 | 0.0 | –0.0 | 0.0 |
| | | 0.1406 | 3.823 | 90.0 | –30.0 | 0.0 | 0.0 | –0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.1406 | 3.823 | 90.0 | –150.0 | 0.0 | 0.0 | –0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.1406 | 3.823 | 90.0 | 30.0 | 0.0 | 0.0 | 0.0 | 0.0 | –0.0 | 0.0 |
| | | 0.1406 | 3.823 | 90.0 | 90.0 | 0.0 | 0.0 | –0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.1406 | 3.823 | 90.0 | –90.0 | 0.0 | 0.0 | 0.0 | 0.0 | –0.0 | 0.0 |
| $Nd_2O_2S$ | O(2) | –0.2521 | 2.325 | 78.2 | –120.0 | 240.0 | –54.0 | –30.0 | 19.0 | 3.0 | –10.0 |
| | | –0.2521 | 2.325 | 78.2 | 120.0 | 240.0 | –54.0 | –30.0 | 19.0 | 3.0 | –10.0 |
| | | –0.2521 | 2.325 | 78.2 | 0.0 | 240.0 | –54.0 | –30.0 | 19.0 | 3.0 | –10.0 |
| | O(1) | 0.2521 | 2.373 | 0.0 | 0.0 | 776.0 | 154.0 | 0.0 | 56.0 | 0.0 | 0.0 |
| | S | 0.0000 | 3.008 | 130.8 | 180.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0000 | 3.008 | 130.8 | 60.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0000 | 3.008 | 130.8 | –60.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | Nd(2) | –0.1166 | 3.645 | 38.6 | –120.0 | –1.0 | 2.0 | 2.0 | 0.0 | 0.0 | –0.0 |
| | | –0.1166 | 3.645 | 38.6 | 120.0 | –1.0 | 2.0 | 2.0 | 0.0 | 0.0 | –0.0 |
| | | –0.1166 | 3.645 | 38.6 | 0.0 | –1.0 | 2.0 | 2.0 | 0.0 | 0.0 | –0.0 |
| | Nd(1) | 0.1166 | 3.942 | 90.0 | 150.0 | 0.0 | 0.0 | 0.0 | 0.0 | –0.0 | 0.0 |
| | | 0.1166 | 3.942 | 90.0 | –30.0 | 0.0 | 0.0 | –0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.1166 | 3.942 | 90.0 | –150.0 | 0.0 | 0.0 | –0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.1166 | 3.942 | 90.0 | 30.0 | 0.0 | 0.0 | 0.0 | 0.0 | –0.0 | 0.0 |
| | | 0.1166 | 3.942 | 90.0 | 90.0 | 0.0 | 0.0 | –0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.1166 | 3.942 | 90.0 | –90.0 | 0.0 | 0.0 | 0.0 | 0.0 | –0.0 | 0.0 |
| | O(1) | 0.2521 | 4.407 | 180.0 | 0.0 | –65.0 | –4.0 | 0.0 | –0.0 | 0.0 | 0.0 |
| | Nd(2) | –0.1166 | 4.544 | 149.9 | 120.0 | 9.0 | –0.0 | 0.0 | –0.0 | 0.0 | 0.0 |
| | | –0.1166 | 4.544 | 149.9 | –120.0 | 9.0 | –0.0 | 0.0 | –0.0 | 0.0 | 0.0 |
| | | –0.1166 | 4.544 | 149.9 | 0.0 | 9.0 | –0.0 | 0.0 | –0.0 | 0.0 | 0.0 |

### D. Dipolar contribution

*(a) Atomic polarizabilities.* Accurate polarizability values are not available for $Nd^{3+}$ and $O^{2-}$ in $Nd_2O_3$. Approximate values of electronic polarizabilities can be derived from the Lorentz expression[25] (strictly valid for isotropic materials only)

$$\alpha = \frac{3v}{4\pi} \frac{(n^2-1)}{n^2+2} ,$$

where $n$ is the refractive index of the material; $n = 1.91$ for $Nd_2O_3$. The volume $v$ of the unit cell enclosing two $Nd^{3+}$ and three $O^{2-}$, is about equal to 76 $Å^3$. The overall polarizability of the unit cell is about 8.5 $Å^3$. Assuming that the polarizability of the cations is smaller than that of the anions, making also the crude additivity assumption for atomic polarizabilities, we finally set $\alpha(O^{2-}) = 2$ $Å^3$, $\alpha(Nd^{3+}) = 1$ $Å^3$. We also set $\alpha(S^{2-}) = 8.6$ $Å^3$,[25] but the choice of this value is, in fact, unimportant since sulfur in $Nd_2O_2S$ (as well as $O_3$ in $Nd_2O_3$) occupies the centrosymmetric $D_{3d}$ site and must therefore not contribute to the static electric field.

*(b) Induced dipoles.* The site symmetries where the electric field is calculated are $C_{3v}$ for Nd(1),

TABLE III. Coefficients of the linear system Eq. (11) and components of the point-charge electric field for $Nd_2O_3$ and $Nd_2O_2S$. $J$ or $J'=1$, 2, 3 stands for Nd (2$d$), 0 (2$d$), and 0 or S (1a), respectively; $v$ or $v'=1$, 2, 3, stands for $x$, $y$, $z$. The solutions of Eq. (11) (induced dipoles) are (in units of $e$Å)

$Nd_2O_3$
$\vec{M}_1(\mathrm{Nd}(1)\colon\ \frac{1}{3},\frac{2}{3},0.2462) = (0,0,0.1406)$
$\vec{M}_2(\mathrm{O}(2)\colon\ \frac{2}{3},\frac{1}{3},-0.6466) = (0,0,0.0784)$
$\vec{M}_3(\mathrm{O}(3)\colon\ 0,0,0) = (0,0,0)$

and

$Nd_2O_2S$
$\vec{M}_1(\mathrm{Nd}(1)\colon\ \frac{1}{3},\frac{2}{3},0.29) = (0,0,0.1166)$
$\vec{M}_2(\mathrm{O}(2)\colon\ \frac{2}{3},\frac{1}{3},-0.64) = (0,0,-0.2521)$
$\vec{M}_3(\mathrm{S}\colon\ 0,0,0) = (0,0,0)$

| | $E_D$ | | $j=1$ | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | $j'$ | $v'$ | $v=1$ | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | $E_{PC}$ |
| $Nd_2O_3$ | 1 | 1 | +0.0895 | −0.0447 | 0.0 | +0.1951 | −0.0976 | 0.0 | +0.0609 | −0.0305 | 0.0 | 0.0 |
| | 1 | 2 | 0.0 | 0.0775 | 0.0 | 0.0 | +0.1690 | 0.0 | 0.0 | +0.0528 | 0.0 | 0.0 |
| | 1 | 3 | 0.0 | 0.0 | −0.1789 | 0.0 | 0.0 | −0.3903 | 0.0 | 0.0 | +0.0439 | +0.1963 |
| | 2 | 1 | +0.1951 | −0.0976 | 0.0 | +0.0587 | −0.0293 | 0.0 | +0.0228 | −0.0114 | 0.0 | 0.0 |
| | 2 | 2 | 0.0 | +0.1690 | 0.0 | 0.0 | +0.0508 | 0.0 | 0.0 | +0.0197 | 0.0 | 0.0 |
| | 2 | 3 | 0.0 | 0.0 | −0.3903 | 0.0 | 0.0 | −0.1174 | 0.0 | 0.0 | +0.1203 | +0.1033 |
| | 3 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | +0.0987 | −0.0493 | 0.0 | 0.0 |
| | 3 | 2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | +0.0855 | 0.0 | 0.0 |
| | 3 | 3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | −0.0315 | 0.0 |
| $Nd_2O_2S$ | 1 | 1 | +0.0827 | −0.0414 | 0.0 | +0.2016 | −0.1008 | 0.0 | +0.0284 | −0.0142 | 0.0 | 0.0 |
| | 1 | 2 | 0.0 | +0.0717 | 0.0 | 0.0 | +0.1746 | 0.0 | 0.0 | +0.0246 | 0.0 | 0.0 |
| | 1 | 3 | 0.0 | 0.0 | −0.1655 | 0.0 | 0.0 | −0.4032 | 0.0 | 0.0 | +0.0808 | +0.0342 |
| | 2 | 1 | +0.2016 | −0.1008 | 0.0 | +0.0584 | −0.0292 | 0.0 | +0.0134 | −0.0067 | 0.0 | 0.0 |
| | 2 | 2 | 0.0 | +0.1746 | 0.0 | 0.0 | +0.0506 | 0.0 | 0.0 | +0.0116 | 0.0 | 0.0 |
| | 2 | 3 | 0.0 | 0.0 | −0.4032 | 0.0 | 0.0 | −0.1169 | 0.0 | 0.0 | +0.1110 | −0.1085 |
| | 3 | 1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | +0.0900 | −0.0450 | 0.0 | 0.0 |
| | 3 | 2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | +0.0780 | 0.0 | 0.0 |
| | 3 | 3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | −0.0424 | 0.0 |

Nd(2), O(1) and O(2), whereas it is $D_{3d}$ for O(3) (or S). As was stated above, the electric field must vanish at the $D_{3d}$ site while it points along the ternary axis at the neodymium and O[(1) and (2)] sites. The linear system Eq. (11) (dimension =9) was built up. In Table III are reported the values of $E_{PC}(j',v')$ and $E_D(j',j,v,v')$, as well as the solutions of the two systems, i.e., the resulting components of the induced dipoles which are (in units of $e$Å)

$$\mathrm{Nd_2O_3}:\quad \vec{M}(\mathrm{Nd}(1))=(0,0,0.1406)\,;\quad \vec{M}(\mathrm{O}(2))=(0,0,0.078\,46):\quad \vec{M}(\mathrm{O}(3))=(0,0,0)$$

$$\mathrm{Nd_2O_2S}:\quad \vec{M}(\mathrm{Nd}(1))=(0,0,0.1165)\,;\quad \vec{M}(\mathrm{O}(2))=(0,0,-0.2520)\,;\quad \vec{M}(S)=(0,0,0)\,.$$

In both cases,

$$\vec{M}(\mathrm{Nd}(2))=-\vec{M}(\mathrm{Nd}(1)) \text{ and } \vec{M}(\mathrm{O}(1))=-\vec{M}(\mathrm{O}(2))\,.$$

*(c) Dipolar correction to the* $B_q^k$. Since the only nonvanishing component of the induced dipoles is $z$, the expression for their contribution to the electrostatic crystal-field parameter, Eq. (A5), reduces to

$$(B_q^k)_\mathrm{D}=e\langle r^k\rangle\left(\frac{4\pi}{(2k+3)}\right)^{1/2} \times\sum_j M_{jz}[(k-q+1)(k+q+1)]^{1/2}\,\frac{Y_{k+1}^{*q}(\alpha_j\beta_j)}{R_j^{k+2}}\,. \tag{14}$$

The $(B_q^k)_\mathrm{D}$ of interest in the present case are given in Appendix C. The computed dipole corrections after convergence are listed in Table I for $\mathrm{Nd_2O_3}$ and $\mathrm{Nd_2O_2S}$. The total electrostatic parameters (point charge plus dipolar correction) are also reported for a comparison with experimental values. Dipolar corrections for nearest and next-nearest neighbors can be found in Table II for $\mathrm{Nd_2O_3}$ and $\mathrm{Nd_2O_2S}$.

## IV. DISCUSSION

If one compares experimental and calculated values of cfp from Table I, we first observe that all the parameters' signs agree. The experimental $B_0^2$ is about one-third the computed value, the experimental $B_0^4$ and $B_3^4$ are 1.4 times the calculated values, and the experimental $B_q^6$ are twice as large. Qualitatively, the same sort of discrepancy[1,26-28] arises every time the results of an electrostatic calculation are compared to experimental results. However, in the present case, the difference is smaller than that stated by Hutchings *et al.*,[1] in the case of $\mathrm{PrCl_3}$ and $\mathrm{PrBr_3}$. Their computed $B_0^2$ was 20 to 30 times the experimental value. The same order of magnitude, however, prevailed for $B_0^4$ while $B_0^6$ and $B_6^6$ were 4 to 10 times smaller. It has been proposed that these discrepancies could be, even for lanthanides, partly accounted for by covalency. This has given rise to the angular-overlap model[29,30] which has been applied to several lanthanide compounds.[31-33] Yet, it has been recognized that rare-earth oxides and oxysulfides are more covalent than halides (see for instance, the nephelauxetic scale of $\mathrm{Nd^{3+}}$ in solids[34] or the values of free-ion parameters of $\mathrm{Nd^{3+}}$ in halides as compared to oxides[35]) and it is surprising to find out that the discrepancy is less important in these compounds.

Let us come back to dipolar corrections. From Table II, we can see that the four nearest oxygens $\mathrm{O_1}$ and $\mathrm{O_2}$, yield corrections which are only 10% larger than the convergence values [for instance 532 $\mathrm{cm^{-1}}$ instead of 478 $\mathrm{cm^{-1}}$ for $(B_0^2)_D$ in $\mathrm{Nd_2O_3}$, 1496 instead of 1363 $\mathrm{cm^{-1}}$ in $\mathrm{Nd_2O_2S}$]. The largest corrections occur on $B_0^2$ and they allow for both compounds a correct prediction of the experimental sign. We must go farther: Sengupta and Artman[36] computed shielding factors for $4f$ electrons in $\mathrm{Nd^{3+}}$. They found $\sigma_2=0.792$, $\sigma_4=0.139$, and $\sigma_6=0.109$. When we apply these shielding factors to our calculated results, they yield corrected $B_q^k(1-\sigma_k)$ which are reported in Table I. They are all smaller than experimental values. But here we must underline as was already done before,[24,37] that the experimental Slater radial integrals $F^k$ (i.e., those fitting experimental spectra) are much smaller than those calculated with Hartree-Fock radial wave functions. Table IV shows the values obtained by Caro et al.,[3] when fitting the absorption spectrum of $\mathrm{Nd^{3+}}$ in $\mathrm{Nd_2O_3}$ compared to the Hartree-Fock $F^k$ for the same ion. The experimental lowering of $F^2$, $F^4$, and $F^6$ is equal to 35, 22, and 22%, respectively. So we tried to guess the right $\langle r^k\rangle$ values by assuming

TABLE IV. Theoretical and experimental $F^k$ $(4f,\,4f)$ parameters for $\mathrm{Nd^{3+}}$ (atomic units).

| | Hartree-Fock [a] | Experimentally fitted [b] | lowering (%) |
|---|---|---|---|
| $F^2$ | 0.498 | 0.323 | 35 |
| $F^4$ | 0.314 | 0.244 | 22 |
| $F^6$ | 0.226 | 0.175 | 22 |

[a] Following Ref. 24.

[b] Following Ref. 3.

that the free ion Hartree-Fock radial wave function yielding a calculated $F^k$ equal to the experimental one, would *also* lead to the true $\langle r^k \rangle$ values. We can see from Ref. 24 that a 20% lowering of the theoretical $F^k$ amounts to a displacement along the rare-earth series, say from $Dy^{3+}$ to $Nd^{3+}$ for instance, or from $Eu^{3+}$ to $Ce^{3+}$, which in both cases comes to multiplying $\langle r^k \rangle$ by 1.4, 2, and 2.6, respectively, for $k=2$, 4, and 6. This is of course an oversimple argument but it finds physical support in the reality of the lanthanide expansion as we follow the indicated path either from $Dy^{3+}$ to $Nd^{3+}$ or from $Eu^{3+}$ to $Ce^{3+}$. Somehow, the choice of such a "displaced" wave function must crudely represent what happens in a solid. Approximate calculations of the real wave function spreading have already been attempted by Burns[37] (without leading to the desired $\langle r^k \rangle$ values, moreover) and are beyond the scope of this work. The computed electrostatic parameters corrected for $\sigma_k$ and the above multiplying factors are reported in Table I along with the experimental parameters, and one can see that the agreement is not too bad.

## V. CONCLUSION

The interpretation of crystal-field parameters from only structural data is important, especially for the fitting of spectra relative to ions in very low symmetry sites or for compounds where rare-earth atoms occupy several different crystallographic positions. In these cases, it is very difficult to derive the crystal-field parameters from the experimental optical data. The interest in deriving crystal-field parameters is essentially in obtaining wave functions for each level. These wave functions are necessary for the understanding of other properties such as ESR spectra, paramagnetic susceptibilities *versus* temperature, and intensities of transitions between Stark levels. The present work is an attempt to make a calculation similar to that[1] carried out for rare-earth halides for two compounds with very different structural properties (they contain two nonequivalent anions) with respect to the chlorides, and which display much larger crystal-field parameters. These two neodymium compounds are known to exhibit a large nephelauxetic effect; that is, their absorption spectra are distinctly displaced towards the red with respect to the chloride ones for instance. This phenomenon corresponds to a lowering[3] of Slater's integrals, especially $F^2$ and $F^4$, by 2 to 3%. If the lowering of Slater's integrals is taken as an indication of the degree of covalency, it is clear that the more covalent among the rare-earth compounds are the oxides and the oxysulfides.

In this context, the computation of crystal-field parameters from structural data alone is important because it has been proposed[38] that covalency and overlap give a large contribution to the mechanisms which build up the experimentally observed cfp. Newman[38] has listed 10 such mechanisms. In the present work, we have shown that a point-charge calculation plus the computation of the dipolar contribution gives a passably good representation of the experimental crystal-field parameters. This could mean that the other contributions are less important than was assumed, but clearly our demonstration concerning only two rare-earth compounds is not sufficient to establish the point with certainty.

It is difficult to predict the order of magnitude of quadrupole contributions. Hutchings[1] calculated a large quadrupolar correction in the case of $PrCl_3$ and $PrBr_3$. For the two presently investigated compounds, we can suppose it will not be negligible since the dipolar electric field is as strong as the one due to monopoles. However, accidental cancellations or enhancements frequently occur in lattice sums. For instance, a crude comparison of formulas relevant to $(B_0^2)_{PC}$ and $(B_0^2)_D$ (Appendix C) would lead us to assert that the ratio $(B_0^2)_D/(B_0^2)_{PC}$ behaves like $3M_j \cos\omega / q_j R_j$, with $M_j/q_j \leq 0.1$, $R_j > 2$, and $\cos\omega \leq 1$; that is, we could expect a dipolar correction at least ten times smaller than the point-charge value. Instead, the ratio $(B_0^2)_D/(B_0^2)_{PC}$ is only equal to $\frac{1}{3}$ for $(Nd_2O_3)$ and amounts to 2 for $(Nd_2O_2S)$. That means, to our point of view, one must be careful with this sort of prediction and carry out the complete calculation to clear up the matter.

## ACKNOWLEDGMENT

We would like to thank Professor K. Rajnak for a helpful discussion.

## APPENDIX A: DIPOLAR CONTRIBUTION TO THE CRYSTAL-FIELD PARAMETERS

In Eq. (8), we write

$$\vec{\mathrm{M}}_j \cdot \vec{\nabla} \left( \frac{Y_k^{q*}(\alpha_j, \beta_j)}{R_j^{k+1}} \right) = -\tfrac{1}{2}(M_{jx} + iM_{jy}) \left( \frac{-\partial}{\partial x} + \frac{i\partial}{\partial y} \right) \left( \frac{Y_k^{q*}(\alpha_j, \beta_j)}{R_j^{k+1}} \right) + \tfrac{1}{2}(M_{jx} - iM_{jy}) \left( \frac{\partial}{\partial x} + i\frac{\partial}{\partial y} \right) \left( \frac{Y_k^{q*}(\alpha_j, \beta_j)}{R_j^{k+1}} \right) + M_{jz} \frac{\partial}{\partial z} \left( \frac{Y_k^{q*}(\alpha_j, \beta_j)}{R_j^{k+1}} \right). \tag{A1}$$

Taking into account the following identities between partial derivatives,

$$\frac{\partial}{\partial x} = \sin\alpha\cos\beta\frac{\partial}{\partial R} + \frac{\cos\alpha\cos\beta}{R_j}\frac{\partial}{\partial\alpha} - \frac{\sin\beta}{R_j\sin\alpha}\frac{\partial}{\partial\beta},$$
$$\frac{\partial}{\partial y} = \sin\alpha\sin\beta\frac{\partial}{\partial R} + \frac{\cos\alpha\sin\beta}{R_j}\frac{\partial}{\partial\alpha} + \frac{\cos\beta}{R_j\sin\alpha}\frac{\partial}{\partial\beta}, \tag{A2}$$
$$\frac{\partial}{\partial z} = \cos\alpha\frac{\partial}{\partial R} - \frac{\sin\alpha}{R_j}\frac{\partial}{\partial\alpha}.$$

Utilizing also the derivative properties of the Legendre functions,[39] it is straightforward to show that

$$\left(-\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\left(\frac{Y_k^{q*}(\alpha_j,\beta_j)}{R_j^{k+1}}\right) = -\left(\frac{(2k+1)}{(2k+3)}(k+q+1)(k+q+2)\right)^{1/2}\frac{Y_{k+1}^{q+1*}(\alpha_j,\beta_j)}{R_j^{k+2}},$$
$$\left(\frac{\partial}{\partial x} + i\frac{\partial}{\partial y}\right)\left(\frac{Y_k^{q*}(\alpha_j,\beta_j)}{R_j^{k+1}}\right) = -\left(\frac{(2k+1)}{(2k+3)}(k-q+1)(k-q+2)\right)^{1/2}\frac{Y_{k+1}^{q-1*}(\alpha_j,\beta_j)}{R_j^{k+2}}, \tag{A3}$$
$$\frac{\partial}{\partial z}\left(\frac{Y_k^{q*}(\alpha_j,\beta_j)}{R_j^{k+1}}\right) = -\left(\frac{(2k+1)}{(2k+3)}(k-q+1)(k+q+1)\right)^{1/2}\frac{Y_{k+1}^{q*}(\alpha_j,\beta_j)}{R_j^{k+2}}.$$

Equations (A1) and (A3) in Eq. (8), give the final expression for the dipolar contribution to the crystal-field parameters

$$(B_q^k)_D = e\langle r^k\rangle\left(\frac{4\pi}{(2k+3)}\right)^{1/2}\sum_j\{-\tfrac{1}{2}(M_{jx}+iM_{jy})[(k+q+1)(k+q+2)]^{1/2}Y_{k+1}^{q+1*}(\alpha_j,\beta_j)$$
$$+\tfrac{1}{2}(M_{jx}-iM_{jy})[(k-q+1)(k-q+2)]^{1/2}Y_{k+1}^{q-1*}(\alpha_j,\beta_j)$$
$$+M_{jz}[(k-q+1)(k+q+1)]^{1/2}Y_{k+1}^{q*}(\alpha_j\beta_j)\}/R_j^{k+2}. \tag{A4}$$

## APPENDIX B

Details on Ewald method may be found elsewhere.[5,6,40] We shall only recall what is necessary for our practical calculations. It is based on the identity

$$\sum_j\frac{1}{|R_j|} = \frac{\pi}{v}\sum_{\vec{g}} e^{i\vec{g}\cdot\vec{R}_{j0}}\frac{e^{-g^2/4G^2}}{g^2/4} + \sum_j\frac{1}{|R_j|}\operatorname{erfc}|GR_j|. \tag{B1}$$

The first right-hand term is a sum over the points of the reciprocal lattice, the second one is over the sites of the direct lattice. $\vec{R}_j$ is a vector joining the origin to a point charge. The first sum concerns the atoms of *one* unit cell ($\vec{R}_{j0}$). It may be the nearest to the origin or any other because of the translational invariance of the lattice. $\vec{g}$ is a vector of the reciprocal lattice, $v$ the volume of the unit cell, and $G$ is an arbitrary constant with dimensions of inverse length, chosen so as to make both series rapidly convergent. The partial derivatives of Eq. (B1) also converge rapidly and it is easy to derive from Eq. (B1) that the $z$ component of the electric field produced at $P$ by point charges $C_{j'}$ located at $P'$ is equal to

$$(E_{Pz})_{PC} = \frac{\pi}{v}\sum_{\vec{g},j_0'} iC_{j'0}eg_z e^{i\vec{g}\cdot\vec{R}j_0'}\frac{e^{-g^2/4G^2}}{g^2/4}$$
$$-\sum_{j'}C_{j'}e\left(\frac{z_{j'}}{R_{j'}^3}\operatorname{erfc}|GR_{j'}| + \frac{2Gz_{j'}}{R_{j'}^2\pi^{1/2}}e^{-(GR_{j'})^2}\right). \tag{B2}$$

An analogous procedure can be applied to calculate the dipolar field (13). The $z$ component of Eq. (13) is written as

$$(E_{Pz})_D = \sum_{j'u_{j'}} M_{j'u_{j'}}\left(\frac{3z_{j'}u_{j'}}{R_{j'}^5} - \frac{\delta(z_{j'}u_{j'})}{R_{j'}^3}\right)$$
$$u_{j'} = x_{j'}, y_{j'}, z_{j'}. \tag{B3}$$

Since

$$\frac{\partial^2(1/R)}{\partial x\partial y} = \frac{3xy}{R^5} - \frac{\delta(xy)}{R^3}, \tag{B4}$$

the development of Eq. (B3) as a Ewald sum can be deduced from that of $\sum\partial^2(1/R)/\partial x\partial y$ as given in Ref. 40:

$$\sum_j\frac{\partial^2(1/R)}{\partial x\partial y} = \frac{\pi}{v}\sum_{\vec{g}j0} -g_xg_ye^{i\vec{g}\cdot\vec{R}_{j0}}\frac{e^{-g^2/4G^2}}{g^2/4} + \sum_j\left[\frac{2GR_j}{\pi^{1/2}}\frac{e^{-(GR_j)^2}}{R_j^3}\left(\frac{3x_jy_j}{R_j^2} - \delta x_jy_j + 2G^2x_jy_j\right)\right.$$
$$\left. + \frac{\operatorname{erfc}|GR_j|}{R_j^3}\left(\frac{3x_jy_j}{R_j^2} - \delta x_jy_j\right)\right] + \frac{4G^3}{3\pi^{1/2}}\delta(x_jy_j)R_j \to 0. \tag{B5}$$

Equation (B5) in Eq. (B3) yields the final result

$$(E_{Pz})_{\mathrm{D}} = \frac{\pi}{v} \sum_{\vec{g},u,j_0}{}' -g_z g_u M_{j'0,u} e^{i\vec{g}\cdot\vec{R}_{j'0}} \frac{e^{-g^2/4G^2}}{g^2/4} + \sum_{j'u_{j'}} M_{j'u_{j'}} \left[ \frac{2GRj'}{\pi^{1/2}} \frac{e^{-(GR_{j'})^2}}{R^3_{j'}} \left( \frac{3z_{j'}u_{j'}}{R^2_{j'}} - \delta(z_{j'}u_{j'}) + 2G^2 z_{j'}u_{j'} \right) + \frac{\mathrm{erfc}|GR_{j'}|}{R^3_{j'}} \left( \frac{3z_{j'}u_{j'}}{R^2_{j'}} - \delta(z_{j'}u_{j'}) \right) \right] + \frac{4}{3\pi^{1/2}} G^3 M_{j'z_{j'}} ,$$

$$(|\vec{R}_{j'}| = 0) \quad \text{(B6)}$$

with $u = x, y, z$.

The infinite sums (B2) and (B6) do not run over $R$ or $g = 0$. The subtraction of the effect of the dipole at the origin on itself leads to the additional term $4G^2 M_{j'z_{j'}}/3\pi^{1/2}$ in Eq. (B6). There is no constant term in Eq. (B2) because there exists an exact cancellation between

$$\frac{-z_{j'}\mathrm{erfc}|GR_{j'}|}{R^3_{j'}} - \frac{2Gz_{j'}\exp(-G^2R^2_{j'})}{R^2_{j'}\pi^{1/2}}$$

and

$$z_{j'}/R^3_{j'} ,$$

when $R_{j'} \to 0$.

No correction term appears for $g = 0$ in Eqs. (B2) and (B6) since the summation is carried over a neutral centrosymmetrical lattice.

## APPENDIX C: POINT-CHARGE CONTRIBUTION TO THE CRYSTAL-FIELD PARAMETERS

$$(B^2_0)_{\mathrm{PC}} = -e\frac{\langle r^2\rangle}{2} \sum_j C_j(3\cos^2\alpha_j - 1)/R^3_j ,$$

$$(B^4_0)_{\mathrm{PC}} = -e\frac{\langle r^4\rangle}{8} \sum_j C_j(35\cos^4\alpha_j - 30\cos^2\alpha_j + 3)/R^5_j ,$$

$$(B^4_3)_{\mathrm{PC}} = e\frac{\langle r^4\rangle(35)^{1/2}}{4} \times \sum_j C_j\cos\alpha_j \sin^3\alpha_j (\cos3\beta_j - i\sin3\beta_j/R^5_j ,$$

$$(B^6_0)_{\mathrm{PC}} = -e\frac{\langle r^6\rangle}{16} \sum_j C_j(231\cos^6\alpha_j - 315\cos^4\alpha_j + 105\cos^2\alpha_j - 5)/R^7_j ,$$

$$(B^6_3)_{\mathrm{PC}} = e\frac{\langle r^6\rangle(105)^{1/2}}{16} \times \sum_j C_j\cos\alpha_j\sin^3\alpha_j(11\cos^2\alpha_j - 3) \times (\cos3\beta_j - i\sin3\beta_j)/R^7_j ,$$

$$(B^6_6)_{\mathrm{PC}} = -e\frac{\langle r^6\rangle(231)^{1/2}}{32} \times \sum_j C_j\sin^6\alpha_j(\cos6\beta_j - i\sin6\beta_j)/R^7_j .$$

Dipolar contribution to the crystal field parameters:

$$(B^2_0)_{\mathrm{D}} = \tfrac{3}{2}e\langle r^2\rangle \sum_j M_{jz}\cos\alpha_j(5\cos^2\alpha_j - 3)/R^4_j ,$$

$$(B^4_0)_{\mathrm{D}} = \frac{5}{8}e\langle r^4\rangle \sum_j M_{jz}\cos\alpha_j \times (63\cos^4\alpha_j - 70\cos^2\alpha_j + 15)/R^6_j ,$$

$$(B^4_3)_{\mathrm{D}} = -\frac{(35)^{1/2}}{4}e\langle r^4\rangle \times \sum_j M_{jz}\sin^3\alpha_j(9\cos^2\alpha_j - 1) \times (\cos3\beta_j - i\sin3\beta_j)/R^6_j ,$$

$$(B^6_0)_{\mathrm{D}} = \frac{7}{16}e\langle r^6\rangle \times \sum_j M_{jz}\cos\alpha_j(429\cos^6\alpha_j - 693\cos^4\alpha_j + 315\cos^2\alpha_j - 35)/R^8_j$$

$$(B^6_3)_{\mathrm{D}} = -\frac{(105)^{1/2}}{16}e\langle r^6\rangle \times \sum_j M_{jz}\sin^3\alpha_j(143\cos^4\alpha_j - 66\cos^2\alpha_j + 3) \times (\cos3\beta_j - i\sin3\beta_j)/R^8_j$$

$$(B^6_6)_{\mathrm{D}} = \frac{(39039)^{1/2}}{32}e\langle r^6\rangle \times \sum_j M_{jz}\sin^6\alpha_j\cos\alpha_j(\cos6\beta_j - i\sin6\beta_j)/R^8_j .$$

The spherical harmonics necessary for the derivation of these expressions can be found in Refs. 9, 41, and 42.

---

[1] M. T. Hutchings and D. K. Ray, Proc. Phys. Soc. London 81, 663 (1963).

[2] C. A. Morrison, Solid State Commun. 18, 153 (1976).

[3] P. Caro, J. Derouet, L. Beaury, and E. Soulié, J. Chem. Phys. 70, 2542 (1979).

[4] J. C. Souillat, J. Rossat-Mignod, and C. Linares, Phys. Status Solidi B 52, 601 (1972).

[5] P. P. Ewald, Ann. Phys. (Leipzig) 64, 253 (1921).

[6] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, New York, 1965), p. 40.

[7] B. G. Wybourne, *Spectroscopic Properties of Rare Earths* (Wiley, New York, 1965), p. 164.

[8] J. B. Gruber, W. F. Krupke, and J. M. Poindexter, J. Chem. Phys. 41, 3363 (1964).

[9] N. Karayanis, C. A. Morrison, *Rare Earth Ion-Host Lattice Interactions 1. Point Charge Lattice Sums in Scheelites,* (HDL-TR-1648, Washington, D. C. 20438, 1973).

[10] C. A. Morrison and R. P. Leavitt, J. Chem. Phys. 71, 2366 (1979).

[11] E. F. Bertaut, J. Phys. (Paris) 39, 1331 (1978).

[12] F. W. de Wette and G. E. Schacher, Phys. Rev. 137, A78 (1965).

[13] O. J. Sovers and T. Yoshioka, J. Chem. Phys. 51, 12 (1969).

[14] W. H. Zachariasen, Z. Phys. Chem. (Leipzig) 123, 134 (1926).

[15] W. H. Zachariasen, Z. Krystallogr. 70, 187 (1929).

[16] L. Pauling, Z. Kristallogr. A 69, 415 (1928).

[17] W. C. Koehler and E. O. Wollan, Acta Crystallogr. 6, 741 (1953).

[18] H. Muller-Buschbaum and H. G. Schnering, Z. Anorg. Allg. Chem. 340, 232 (1965).

[19] J. X. Boucherle and J. Schweizer, Acta Crystallogr. Sec. B 31, 2745 (1975).

[20] R. S. Roth and J. Schneider, J. Res. Nat. Bur. Stand. Sec. A 64, 309 (1960).

[21] H. A. Eick, J. Am. Chem. Soc. 80, 43 (1958).

[22] W. H. Zachariasen, Acta Crystallogr. 2, 60 (1949).

[23] B. Morosin and D. J. Newman, Acta Crystallogr. Sec. B 29, 2647 (1973).

[24] A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[25] J. R. Tessman and A. H. Kahn, W. Shockley, Phys. Rev. 92, 890 (1953).

[26] G. Burns, Phys. Rev. 128, 2121 (1962).

[27] M. Faucher and P. Caro, J. Chem. Phys. 63, 446 (1975).

[28] P. Porcher and P. Caro, J. Chem. Phys. 65, 89 (1976).

[29] C. E. Schäffer and C. K. Jorgensen, Mol. Phys. 9, 401 (1965).

[30] M. R. Kibler, Int. J. Quantum. Chem. 9, 403 (1975).

[31] C. Linares and A. Louat, J. Phys. (Paris) 36, 717 (1975).

[32] G. Grenet, M. Kibler, C. Linares, A. Louat, and F. Gaume, Chem. Phys. Lett. 51, 160 (1977).

[33] J. C. Gacon, G. Grenet, J. C. Souillat, and M. Kibler, J. Chem. Phys. 69, 868 (1978).

[34] P. Caro and J. Derouet, Bull. Soc. Chim. 46 (1972).

[35] J. R. Henderson, M. Muramoto, and J. B. Gruber, J. Chem. Phys. 46, 2515 (1967).

[36] D. Sengupta and J. O. Artmann, Phys. Rev. B 1, 2986 (1970).

[37] G. Burns, J. Chem. Phys. 42, 377 (1965).

[38] D. J. Newman, Adv. Phys. 20, 197 (1971).

[39] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University, Press, Princeton, N. J., 1960), p. 24.

[40] M. Faucher and P. Caro, J. Chem. Phys. 66, 1273 (1977).

[41] J. L. Prather, Natl. Bur. Stand. (U.S.), Monogr. 19, 4 (1961).

[42] J. A. Detrio, J. Chem. Phys. 57, 5012 (1972).