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Crystal-Field Shielding Parameters for Nd^{3+} and Np^{4+}†

D. SENGUPTA
Department of Physics, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

AND

J. O. ARTMAN
Departments of Physics and Electrical Engineering, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

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The crystal-field shielding parameters σ_n for $Nd^{3+}(4f^3)$ and $Np^{4+}(5f^3)$ have been computed by the Sternheimer method. For Nd^{3+}, we find $\sigma_2=0.792$, $\sigma_4=0.139$, and $\sigma_6=-0.109$. For Np^{4+}, we find $\sigma_2=0.881$. These shielding parameters, in conjunction with monopole lattice-sum data, are used to compute numbers for comparison with crystal-field splittings determined experimentally from optical data taken on Nd^{3+}- and Np^{4+}-doped $PbMoO_4$. The over-all correlation is poor. Inclusion of dipole lattice-sum contributions does not help. It is concluded that more sophisticated crystal-field analyses are required in doped scheelite systems.

I. INTRODUCTION

IN recent years, there has been increasing interest in crystal-field shielding effects in the rare earths.[1–5] The $4f$ electrons in the rare earths are shielded from external electric fields primarily by the $5s^2p^6$ electronic clouds. The effects are much larger than those found in transition-metal ions, for example, where comparable electronic configurations, of course, are absent. These shielding parameters are used in *ab initio* calculations of crystal-field components—which can be compared with the deductions made primarily from optical and secondarily from microwave spectroscopy. The calculations also yield the quadrupolar Sternheimer antishielding factor γ_∞ and the quadrupolar polarizability α_q. The γ_∞ factor enters in the determination of the nuclear electronic quadrupolar splittings[6–9]; α_q would enter in the determination of higher-order multipole contributions to ionic-type crystal fields.

The first rare-earth shielding calculation was done for $Pr^{3+}(4f^2)$ by Ray[1] using the Das and Bersohn[2] variational method. Sternheimer developed another technique involving solution of the inhomogeneous Schrödinger equation. Using the latter method, shielding calculations were done for Pr^{3+} and $Tm^{3+}(4f^{12})$ by Sternheimer and his co-workers[3,4] and by Ghatikar and others.[5] The results were used in the crystal-field analysis of the optical splittings of the Pr^{3+}-$LaCl_3$ system.[1]

We present in this paper shielding calculations for $Nd^{3+}(4f^3)$ by the Sternheimer method. We include γ_∞ and α_q results. The values are compared with the Pr^{3+} and the Tm^{3+} parameters. We also include a calculation for one of the shielding terms in a $5f$ system analogous to Nd^{3+}:$Np^{4+}(5f^3)$. In view of our recent interest in rare-earth-doped scheelites,[10–12] we discuss briefly the computation of the pertinent lattice sums in such crystals and their correlation (including shielding effects) with the experimentally determined crystal-field splittings.

We are indebted to Dr. J. B. Mann of the Los Alamos Scientific Laboratory for providing us with Nd^{3+} and Np^{4+} Hartree-Fock wave functions. The computations were done on the Univac 1108 of the Carnegie-Mellon University computation center.

II. SHIELDING CORRECTIONS

We treat the crystal-field potential as a perturbation on the free-ion states. The solution of the problem is

TABLE I. Shielding parameter σ_2 for Nd^{3+} (values for Pr^{3+} and Tm^{3+} also listed).

Perturbation	σ_{2-d}	σ_{2-e}	$\sigma_2=\sigma_{2-d}+\sigma_{2-e}$
$5s\to d$	0.430	−0.070	0.360
$5p\to f$	0.515	−0.069	0.446
$5p\to p$	−0.189	+0.036	−0.153
$4s\to d$	0.042	−0.011	0.031
$4p\to f$	0.052	−0.014	0.038
$4d\to s$	0.029	−0.012	0.017
$4d\to g$	0.071	−0.018	0.053
Total	0.950	−0.158	0.792
Pr^{3+}[a]	0.7778	−0.1063	0.672
Tm^{3+}[b]	0.6189	−0.0741	0.545

[a] Data from Tables I and III, Ref. 3 and Tables VII and VIII, Ref. 4.
[b] Data from Tables II and IV, Ref. 3 and Tables VII and IX, Ref. 4.

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conveniently expressed in terms of shielding parameters. Specifically, we set $\sigma_{k,q}$ equal to the shielding parameter corresponding to the crystal-field potential term $A_k{}^q r^k Y_k{}^q$; that is, we replace $A_k{}^q$ by $A_k{}^q(1-\sigma_{k,q})$. It has been shown that $\sigma_{k,q}=\sigma_{k,0}$.[4] Thus, for a given k, it is sufficient to calculate the shielding factor for just the $r^k Y_k{}^0$ term which we will denote simply as σ_k. The contributions to σ_k can be classified in two groups: the direct terms (denoted by σ_{k-d}) and the exchange terms (denoted by σ_{k-e}). The quadrupolar antishielding and polarizability factors (γ_∞ and α_q) follow from a simple extension of the calculations. The details of the theory have been given by Sternheimer[3,4] and will not be repeated here.

The contributions from different excitations to σ_2, σ_4, and σ_6 for Nd^{3+} are listed, respectively, in Tables I–III. The σ_2 compilation includes contributions from the 4s, 4p, and 4d electrons which we find to be small, but not negligible, compared to the 5s and 5p contributions. Radial excitation terms of the form $4p\to p$ and $4d\to d$ are very small and have been neglected. The net σ_2 factor is quite large and positive (0.792), indicating strong shielding. The σ_4 coefficient, as a consequence of the near compensation of the direct and exchange term effects, is small and positive (0.139). The σ_6 value is -0.109 indicating small antishielding. We also have entered the Pr^{3+} and Tm^{3+} tabulations from Sternheimer's papers. The results are quite similar. It is difficult to discern specific trends, particularly since we used Hartree-Fock wave functions while Sternheimer used Hartree functions.

Our Nd^{3+} result for γ_∞ was -65. From examination of Tables I and II of Ref. 3, the equivalent results for Pr^{3+} and Tm^{3+} are -72.6 and -64.5, respectively. Using the more reliable nuclear quadrupole perturbation method, Sternheimer (Table V, Ref. 3) found Pr^{3+} and Tm^{3+} γ_∞ values of -80.9 and -75.3, respectively. (We have not made the Nd^{3+} calculation equivalent to these latter two.) It should be recollected that the γ_∞ calculation is sensitive to the form of the perturbed wave function near the origin; in view of the different type of wave functions used by us and Sternheimer, the most that can be said is that no particular trend seems to exist. Finally, we compute a Nd^{3+} α_q value of 0.9212 $(\text{Å})^5$ as compared to the Pr^{3+} and Tm^{3+} values of 1.731 (Table I, Ref. 3; Table VIII, Ref. 4) and 0.729 (Table II, Ref. 3; Table IX, Ref. 4), respectively.

TABLE II. Shielding parameter σ_4 for Nd^{3+} (values for Pr^{3+} and Tm^{3+} also listed).

Perturbation	σ_{4-d}	σ_{4-e}	$\sigma_4=\sigma_{4-d}+\sigma_{4-e}$
$5s\to g$	0.076	-0.047	0.029
$5p\to h$	0.120	-0.059	0.061
$5p\to f$	0.330	-0.281	0.049
Total	0.526	-0.387	0.139
Pr^{3+} [a]	0.3264	-0.2355	0.091
Tm^{3+} [b]	0.2987	-0.2112	0.088

[a] Data from Table II, Ref. 4.
[b] Data from Table III, Ref. 4.

TABLE III. Shielding parameter σ_6 for Nd^{3+} (values for Pr^{3+} and Tm^{3+} also listed).

Perturbation	σ_{6-d}	σ_{6-e}	$\sigma_6=\sigma_{6-d}+\sigma_{6-e}$
$5s\to i$	0.015	-0.025	-0.010
$5p\to h$	0.059	-0.159	-0.100
$5p\to j$	0.028	-0.027	$+0.001$
Total	0.102	-0.211	-0.109
Pr^{3+} [a]	0.0461	-0.0861	-0.040
Tm^{3+} [b]	0.0508	-0.0940	-0.043

[a] Data from Table V, Ref. 4.
[b] Data from Table VI, Ref. 4.

In Table IV, we present a listing of the various contributions to σ_2 for Np^{4+}. The numerical trends are similar to the Nd^{3+} case (Table I); as expected, the net result is larger (0.881).

III. CRYSTAL-FIELD CALCULATIONS

$CaWO_4$ and $PbMoO_4$ are representative of the scheelites. The structure corresponds to the space group $I4_1/a(C_{4h}{}^6)$. The Ca (or Pb) and W (or Mo) positions are fixed in terms of the c and a lattice parameters. The oxygen sites require additional special position parameters (x, y, z) for specification. Rare-earth ions are believed to substitute at Ca^{2+} (or Pb^{2+}) sites. The charge compensation is believed to be nonlocal; the site symmetry remains unaltered as S_4. Each such site has eight nearest-neighbor oxygens which are grouped into two sets of four each—these constitute two distorted interpenetrating tetrahedra. Each oxygen, in turn, is associated with a different tetrahedral WO_4 (or MoO_4) complex. Now it is clear from crystallographic and from general chemical data that significant covalent bonding exists—the existence of tightly bound $(MoO_4)^{2-}$ and $(WO_4)^{2-}$ complexes is common knowledge. Hence, even though the Ca—(or Pb)—O distances are quite large and the $Ca^{2+}(Pb^{2+})$ sites may be considered to be "ionic," a simple crystal-field picture may be inadequate when describing the charge distribution in the crystal.

Unfortunately, a detailed picture of the charge distribution within these hosts is not available presently from x-radiation analysis. To gain some insight into

TABLE IV. Shielding parameter σ_2 for Np^{4+}.

Perturbation	σ_{2-d}	σ_{2-e}	$\sigma_2=\sigma_{2-d}+\sigma_{2-e}$
$6s\to d$	0.365	-0.062	0.303
$6p\to f$	1.048	-0.419	0.629
$6p\to p$	-0.129	$+0.043$	-0.086
$5s\to d$	-0.037	$+0.008$	-0.029
$5p\to f$	0.047	-0.013	0.034
$5d\to s$	-0.030	$+0.005$	-0.025
$5d\to g$	0.074	-0.019	0.055
Total	1.338	-0.457	0.881

TABLE V. Experimental and calculated crystal-field parameters for Nd^{3+}- and Np^{4+}-doped $PbMoO_4$.[a]

	$A_2^0\langle r^2\rangle$	$A_4^0\langle r^4\rangle$	$A_6^0\langle r^6\rangle$	$A_4^4\langle r^4\rangle$	$A_6^4\langle r^6\rangle$	$A_4'^4\langle r^4\rangle$	$A_6'^4\langle r^6\rangle$
Nd^{3+} [b]	331.3	−86.3	−5.3	−808.7	−3367.6	−4.9	−4.5
Nd^{3+} [c]	252.6	−49.4	−0.2	−97.1	−32.5	−151.4	−35.3
Np^{4+} [d]	1290.4	−441.8	−92.3	−2376.7	−3726.2	−754.8	−1186.3
Np^{4+} [c]	226.3						

[a] All tabulations are in units of cm^{-1}.

[b] Experimental results from Ref. 10.

[c] Computed from monopole lattice sums using crystallographic data from J. Leciejewicz, Z. Krist. **121**, 158 (1965); $\langle r^n\rangle$ data from Ref. 16, and shielding data from present paper.

[d] Experimental results from Ref. 12.

this problem by comparatively simple techniques, we investigated the monopolar and dipolar contributions to a lattice-sum crystal-field calculation. We chose the geometrical crystal parameters from recent neutron diffraction analyses. The summations were performed by a version of the chargeless cluster method.[13,14] Since the scheelite unit cell is tetragonal (caa), the cluster contributions were taken within successively larger ellipsoids of revolution—the semi-major and -minor axes being proportional to c and a. Only the oxygens occupy sites of nonzero electric field in scheelites. The oxygen dipole vector p follows from solution of the matrix equation $\mathbf{p}=(1-\boldsymbol{\alpha}\mathbf{K})^{-1}\boldsymbol{\alpha}\mathbf{E}$, where $\boldsymbol{\alpha}$ represents the polarizability tensor, $\mathbf{K}$ is the dipole reaction matrix, and $\mathbf{E}$ is the monopolar electric field. For these scheelite geometries, K was sufficiently large that p was *independent* of α for representative α values.

The crystal-field potential energy appropriate for an f electron at a site of S_4 symmetry has the form[12]

$$V=B_0^2C_0^2+B_0^4C_0^4+B_0^6C_0^6+B_4^4(C_4^4+C_{-4}^4)$$
$$+iB_4'^4(C_4^4-C_{-4}^4)+B_4^6(C_4^6+C_{-4}^6)+iB_4'^6(C_4^6-C_{-4}^6)\,.$$

The B_m^n are related to the Elliot-Stevens A_n^m parameters as follows[15]:

$$B_0^2=2A_2^0\langle r^2\rangle\,,\quad B_0^4=8A_4^0\langle r^4\rangle\,,\quad B_0^6=16A_6^0\langle r^6\rangle\,,$$
$$B_4^4=[8(70)^{1/2}/55]A_4^4\langle r^4\rangle\,,\quad B_4^6=[(14)^{1/2}/21]A_6^4\langle r^6\rangle\,,$$

where $\langle r^n\rangle\equiv\langle r^n\rangle_{4f}$. The extensions to primed parameters and to $5f$ systems are obvious. The $\langle r^n\rangle$ values[16] of interest here in units of $(\text{Å})^n$ are

$$Nd^{3+}{:}\langle r^2\rangle=0.281\,,\quad \langle r^4\rangle=0.180\,,\quad \langle r^6\rangle=0.223;$$
$$Np^{4+}{:}\langle r^2\rangle=0.440\,,\quad \langle r^4\rangle=0.342\,,\quad \langle r^6\rangle=0.439\,.$$

In Table V, we compare the experimental crystal-field parameters for Nd^{3+}- and Np^{4+}-doped $PbMoO_4$ with some simple monopolar lattice calculations which include the shielding parameters. The point-charge model value for $A_2^0\langle r^2\rangle$ for Nd^{+3} is 1214.5 cm^{-1} which, upon multiplication by $1-\sigma_2$, yields 252.6 cm^{-1}, in good agreement with the experimental data. However, for $n=4$, 6 the agreement is not very good. For example, the computed $A_6^4\langle r^6\rangle$ term (including shielding) is too small by over two orders of magnitude. In the case of Np^{4+}, for which we have computed only σ_2, the final computed $A_2^0\langle r^2\rangle$ term is one-sixth of the experimental value. Inclusion of the dipolar lattice-sum contribution is not too helpful. For A_2^0 and A_4^0, the dipolar contribution was about ten times the monopolar contribution. This would destroy the "agreement" in the Nd^{3+} case and yield a crude agreement in the Np^{4+} case.

Operationally, these large dipolar contributions cast doubt upon the validity of the convergence of a multipolar lattice-sum analysis. Inclusion of a quadrupolar oxygen polarizability would provide at least one additional parameter at our disposal, however, we do not find speculations in this direction attractive. Of further interest are the crystal-field "exclusion-model" calculations discussed in a series of papers[17–20] by Ellis, Newman, and others. For the $Pr^{3+}{:}LaCl_3$ system they found a major contribution to the crystal field from overlap and exchange interaction between the metal-ion and the nearest-neighbor ligand wave functions. This exclusion model can provide substantial contributions to the higher-order crystal-field components and may be able to reduce the discrepancies. Finally, since we are considering a substituent, there may be changes in the local environment that would affect all these calculations. Further crystal-field analysis beyond the scope of the present paper is indicated.

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