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Role of the electrostatic model in calculating rare-earth crystal-field parameters

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Abstract

The Sternheimer method is used to derive shielding parameters and antishielding factors for the whole series of rare earths using relativistic wavefunctions. It is found that the shielding parameter σ_2 of the 4f electronic shell is decreased compared to earlier calculations. The σ_4 and σ_6 parameters are calculated for the first time for all rare-earth ions. In all cases, they are found to be small. The influence of the various calculated parameters on the crystal-field parameters for the cases Nd:LiYF$_4$ and Pr:LiYF$_4$ is studied. Present corrections result in ab initio crystal-field parameters that are in excellent agreement with experimentally fitted phenomenological parameters. The nuclear antishielding factors γ_∞ are found to essentially agree with earlier findings. These are also found to agree with some early experiments. The various wavefunctions used are derived from a relativistic Desclaux code. These are more external compared to standard Hartree–Fock wavefunctions. © 1998 Elsevier Science S.A.

Keywords: Crystal-field parameters; Electrostatic model; Rare earths; Sternheimer method

1. Introduction

For many years, it has been known that the use of the popular electrostatic model to calculate crystal-field parameters (CFP) gives poor agreement with the experimentally fitted phenomenological B_{tp}'s. A great number of different models for fitting or calculating CFP have been developed since the 1960s. An almost complete review may be found in Ref. [1]. The present work will return to the electrostatic model for primarily host materials where covalency effects are unimportant. The traditional relation to the direct lattice sums (A_{tp}) is $B_{tp} = A_{tp}\langle r^t \rangle_{4f}$. Particularly, the simple point-charge (PC) model in its original form has often been unsuccessful. The usual observations as noted by Morrison (pp. 485–486 in Ref. [2]) are: the calculated PC B_{2p}'s are by far too large, the PC B_{4p}'s are too small and the PC B_{6p}'s are even smaller. Shortly after the advent of the electrostatic model, it was realized by Judd [3], Satton [4] and particularly by Sternheimer [5] that the crystal field experienced by a 4f electron is shielded by the polarized adjacent filled electronic shells. The effect of shielding results in the modified expression $B_{tp} = (1 - \sigma_t)A_{tp}\langle r^t \rangle_{4f}$. Taking shielding into account largely rectifies the discrepancy seen in the B_{2p} parameters, although they now become a bit small. The deviations observed in B_{4p} and particularly in the B_{6p} parameters remained, however. This led many authors to the conclusion that the electrostatic model is inappropriate for these parameters. One should note, however, that early CFP calculations were often based on simple point charges, and also that account was taken only of nearest neighbours. To remedy the situation, some authors extended the simple point charge model by including the interactions from the whole crystal by direct summation far out into the lattice or by Ewald summation techniques [6]; and also by including higher moments considering the contributions from consistently induced dipoles and quadrupoles [7,8]. Unfortunately, these generalizations usually only helped a little. As pointed out by Morrison [2] and others, it is a well-known fact that the Slater integrals F^k based on Hartree–Fock radial wavefunctions are too large when compared with F^k fitted to experiment (*nephelauxetic effect*). It was, however, shown by Rajnak and Wybourne that the inclusion of the configuration interaction (CI) will reduce the electron–electron interactions resulting in an effective shielding of the Slater integrals [9,10]. Unfortunately, this theoretical formulation contains several numerically difficult parameters (excited states) making it difficult to compute accurate results. On the other hand, in the experimental fitting process of F^k, CI become to a large extent included

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automatically. One simplified way to decrease the ab initio F^k to the experimental values was to introduce a scaling parameter $1/\tau$ that expands the 4f wavefunction [2,11]. The new radial integrals are then given by $\tau^{-t}\langle r^t\rangle_{4f}$. Although the model has met some success in the case of PC-CFP for a few host crystals [8,12,13], we feel that this approach is unsatisfactory. In the first place, CI does not cause the radial 4f wavefunction to expand so much. Rather it comes in as angular corrections in the calculation of the electrostatic energy for the interacting 4f electrons; and the use of the suggested scaling $1/\tau \sim 1.3$ for the radial wavefunction causes the higher order ($t=4,6$) $\tau^{-t}\langle r^t\rangle_{4f}$ to "explode" so that the PC $B_{tp} = A_{tp}\tau^{-t}\langle r^t\rangle_{4f}(1-\sigma_t)$ become almost an order of magnitude too large (e.g., $LiYF_4$). Neither is it consistent to expand the 4f radial wavefunction and at the same time keep the original shielding parameters σ_t. We see that an artificial scaling to this extent must be dismissed. In an attempt to revive the electrostatic model, we note that many authors still use rather contracted Hartree–Fock wavefunctions (e.g., those of Freeman and Watson [14]). Instead, we will use a modified Desclaux code [15] with relativistic effects included, resulting in considerably more expanded wavefunctions. Of course to be consistent, the shielding parameters σ_t must be recalculated for the same wavefunctions. The shielding parameters have been calculated partially in a number of earlier papers; see, for example, Refs. [5,11,16–19]. The influence on the CFP ($B_{tp} = A_{tp}\langle r^t\rangle_{4f}(1-\sigma_t)$) is twofold since current work alters both $\langle r^t\rangle_{4f}$ and σ_t. It will be shown below that B_{2p} increases (as it should), because $\langle r^2\rangle_{4f}$ increases and σ_2 decreases compared to previous calculations. B_{4p} also increases and B_{6p} even more (again as it should), mainly due to the moderate increase of $\langle r^4\rangle_{4f}$ and $\langle r^6\rangle_{4f}$. The A_{tp} parameters will be derived from Ref. [7] which used the best ab initio polarizabilities available [20,21] for the host material studied here.

2. Theory and computation

The full details of the theory have been given previously by Sternheimer [16]. We will just summarize the expressions (in a.u.) needed to calculate the shielding parameters. The shielding parameters σ_t ($t=2$, 4, 6) for the 4f shell can be calculated according to

$$\sigma_t = \sum_{nl\to l'} \sigma_t(nl\to l') = \sum_{nl\to l'} [\sigma_{t,\mathrm{D}}(nl\to l') + \sigma_{t,\mathrm{E}}(nl\to l')]$$

The sum is performed over the various perturbations $nl\to l'$ considered; the direct (D) and exchange (E) terms are given by

$$\sigma_{t,\mathrm{D}}(nl\to l') = (C_\mathrm{D}/\langle r^t\rangle_{4f})\int_0^\infty P_{4f}^2 f_t(r)\mathrm{d}r$$

$$\sigma_{t,\mathrm{E}}(nl\to l') = -\sum_{L=|l'-3|}^{l'+3} (C_\mathrm{E}/\langle r^t\rangle_{4f})\int_0^\infty u_0 P_{4f} g_L(r)\mathrm{d}r$$

The angular parameters are

$$C_\mathrm{D} = \frac{8(2l+1)(2l'+1)}{2t+1}\begin{pmatrix} l' & t & l \\ 0 & 0 & 0\end{pmatrix}^2$$

$$C_\mathrm{E} = 4(-1)^L(2l+1)(2l'+1) \times \begin{pmatrix} l & t & l' \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l & L & 3 \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} l' & L & 3 \\ 0 & 0 & 0\end{pmatrix} \times \begin{Bmatrix} t & 3 & 3 \\ L & l & l'\end{Bmatrix} \Big/ \begin{pmatrix} 3 & t & 3 \\ 0 & 0 & 0\end{pmatrix}$$

For the perturbations studied in the current work the multipolarity L is limited to $0\le L\le 6$. $u_0(nl)$ is the unperturbed radial wavefunction times r for a particular electronic shell nl (effective). The somewhat intricate functions $f_t(r)$ and $g_L(r)$ are defined by

$$f_t(r) = (1/r^{t+1})\int_0^r u_0(nl)u_1(nl\to l')r'^t\,\mathrm{d}r' + r^t\int_r^\infty u_0(nl)u_1(nl\to l')r'^{-t-1}\,\mathrm{d}r'$$

$$g_L(r) = (1/r^{L+1})\int_0^r u_1(nl\to l')P_{4f}r'^L\,\mathrm{d}r' + r^L\int_r^\infty u_1(nl\to l')P_{4f}r'^{-L-1}\,\mathrm{d}r'$$

The perturbed radial wavefunction $u_1(nl\to l')$ is obtained by solving the inhomogeneous Schrödinger equation numerically:

$$\left[\frac{-\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l'(l'+1)}{r^2} + 2(V_0(nl) - E_0(nl))\right]u_1(nl\to l') = u_0(nl)[r^t - \langle r^t\rangle_{nl}\delta_{ll'}]$$

In the case $l=l'$ the orthogonality condition must be satisfied, i.e. $\langle u_0|u_1\rangle = 0$. Since the solutions u_1 behave as $r^{l'+1}$ near the origin [16], the appropriate boundary condition is $u_1 = 0$ close to the origin. Far from the origin (here: $r=10$ a.u.) it is easily realised that the tail of u_1 behaves as $e^{-\sqrt{\varepsilon_0}r}$, $\varepsilon_0 = |E_0(nl)|$. The proper outer boundary condition is therefore $u_1 = 0$, $\mathrm{d}u_1/\mathrm{d}r = 0$. The consistency of the results was checked by trying different steplengths h. Complete convergence was achieved using $h = 10^{-4}$ a.u.

3. Results

In Table 1 we summarize the resulting shielding parameters, radial integrals and antishielding factors for the

Table 1
The resulting shielding parameters, radial integrals (a.u.) and antishielding factors from the present work. For each relevant column, the first value is the standard result, and the second theoretical value also has the contribution from the 4f perturbations included

	σ_2		σ_4		σ_6		$\langle r^2\rangle$	$\langle r^4\rangle$	$\langle r^6\rangle$	γ_∞	
Ce^{3+}	0.510		0.0132		−0.0294		1.456	5.437	42.26	−65.5,	−66.0
Pr^{3+}	0.514,	0.515	0.0150,	0.0138	−0.0302,	−0.0301	1.327	4.537	32.65	−64.2,	−65.0
Nd^{3+}	0.515,	0.518	0.0164,	0.0130	−0.0307,	−0.0310	1.222	3.875	26.12	−62.8,	−64.0
Pm^{3+}	0.512,	0.519	0.0175,	0.0109	−0.0309,	−0.0314	1.135	3.366	21.46	−61.8,	−63.3
Sm^{3+}	0.507,	0.519	0.0184,	0.0077	−0.0309,	−0.0317	1.061	2.964	17.99	−60.8,	−62.6
Eu^{3+}	0.502,	0.520	0.0190,	0.0033	−0.0308,	−0.0319	0.997	2.638	15.34	−59.8,	−61.9
Gd^{3+}	0.494,	0.521	0.0192,	−0.0031	−0.0304,	−0.0318	0.942	2.381	13.36	−58.8,	−61.3
Tb^{3+}	0.486,	0.523	0.0193,	−0.0107	−0.0300,	−0.0318	0.893	2.163	11.75	−58.1,	−60.8
Dy^{3+}	0.477,	0.527	0.0193,	−0.0199	−0.0295,	−0.0316	0.849	1.977	10.44	−57.2,	−60.3
Ho^{3+}	0.469,	0.534	0.0192,	−0.0306	−0.0289,	−0.0313	0.810	1.816	9.345	−56.4,	−59.9
Er^{3+}	0.460,	0.544	0.0190,	−0.0427	−0.0283,	−0.0310	0.773	1.677	8.431	−55.6,	−59.4
Tm^{3+}	0.450,	0.554	0.0188,	−0.0567	−0.0277,	−0.0306	0.740	1.555	7.659	−54.9,	−59.0
Yb^{3+}	0.441,	0.571	0.0185,	−0.0725	−0.0270,	−0.0300	0.710	1.448	7.003	−54.2,	−58.7
Lu^{3+}	0.431,	0.588	0.0182,	−0.0902	−0.0263,	−0.0294	0.682	1.353	6.441	−53.6,	−58.4

whole series of rare-earth ions. In the case of Lu^{3+} the 4f shell is complete and should therefore be included. We have excluded the self-interaction contributions according to Ref. [22] (p. 551). This can be treated by first calculating the $\sigma_t(4f \rightarrow l')$ as usual (complete shell) and then simply multiply by 13/14. In present work, it was realized that an approximate way to include the 4f contributions for the other ions is to first consider the 4f shell complete, and then multiply $\sigma_t(4f \rightarrow l')$ by a self-interaction factor given by $k(k-1)/n^2$, where k is the number of electrons and n is the total number of electrons for the filled shell (i.e. 14). As expected, in the case of one electron ($k=1$) the contribution is seen to be zero. The antishielding factors $\gamma_\infty(4f \rightarrow l')$ were derived approximately by multiplying these by the fraction of the shell which is filled (k/n). Both cases (4f included and excluded) are tabulated to make it possible to compare with earlier results in the literature. The resulting shielding parameters σ_2 in Table 1 compared to earlier calculations [16,18,19], show that all our σ_2 are smaller. This result is due to the fact that the present wavefunctions are more external. Comparing the individual perturbations between Ref. [19] and the present work, it was found that the 5p→f and 5s→d perturbations are mainly responsible for the differences.

The various antishielding factors are also tabulated in Table 1. The measurable quantity in a Mössbauer experiment is $Q(1-\gamma_\infty)/[(1-\sigma_2)\langle r^2\rangle_{4f}]$, where Q is the nuclear quadrupole moment. This quantity is given by 1.011×10^{-5} a.u. in the case of Tm_2O_3 [23]. The same paper lists a theoretical nuclear quadrupole moment given by $Q\approx 5.4\times 10^{-8}$ a.u. for the 8.4 keV state. By dividing the above expression by Q, the experimental value 187 is obtained. We obtain $(1-\gamma_\infty)/[(1-\sigma_2)\langle r^2\rangle_{4f}]=137$ or 182 if the 4f contribution is included. Another experiment [24] combined nuclear alignment and optical measurements for Lu^{3+} to obtain the ratio $(1-\gamma_\infty)/(1-\sigma_2)=155$ based on the value $Q=13\times 10^{-8}$ a.u. From Table 1, we obtain 96 or 144 if the 4f contribution is included. We should finally note that in the current work we have not included the 3p→p, 2p→p, etc. perturbations in the calculation of γ_∞. It can be seen from Ref. [19] that such an inclusion would alter all the present results for γ_∞ by about −2, e.g. −1.763 for Pr^{3+} (−62.227→−63.99 in Table 2 of Ref. [19]). Consistency effects (i.e., the inclusion of electron–electron interactions) would also reduce the present results for γ_∞ somewhat. A reduction of about −0.9 was calculated in the case of Fe^{3+} [25]. The reduction is expected to be slightly higher for rare-earth ions. If these (rather small) effects had been included, the agreement would have improved further.

We will now derive crystal-field parameters for a few test hosts ($Nd{:}LiYF_4$ and $Pr{:}LiYF_4$) since a considerable number of measurements and calculations exist in the literature. Serious lattice sum calculations were made for several crystals by Faucher and Garcia [7]. Their calculations involved contributions from point charges, consistent dipoles and quadrupoles. Convergence was achieved using Ewald summation techniques. They used accurate dipole polarizabilities from Refs. [20,21]. One exception was the chosen value for Nd^{3+} which was set arbitrarily equal to Ba^{2+} given by 2.24 $Å^3$. This has also been calculated here; it should instead be $\alpha_D\sim 1.297$ $Å^3$. Also, their quadrupole polarizability is too high. In their mathematical formulation, they had to divide the standard α_Q by 6. They used the value 0.372 $Å^5$ (also for Ba^{2+}) while our theoretical result is $\alpha_Q/6\sim 0.163$ $Å^5$. However, these deviations will presumably not have too large an influence on the CFP calculations of Ref. [7]. The A_{tp} parameters were derived by dividing the B_{tp} parameters in Table 10 of Ref. [7] by their choice of $\langle r^t\rangle_{4f}$. These A_{tp} parameters can be used for Nd^{3+} and adjacent RE ions (e.g., Pr^{3+}) since the polarizabilities are quite close. The new B_{tp} were then transformed according to $A_{tp}\langle r^t\rangle_{4f}(1-\sigma_t)$ using our Table 1. The result of this is tabulated and compared with experiment in Table 2. Surprisingly good agreement

Table 2
Comparison between experimentally fitted and theoretical crystal field parameters (in cm^{-1}). The theoretical lattice sums A_{tp} with consistent dipoles and quadrupoles included are derived from Ref. [7]; the B_{tp} parameters are then calculated using σ_t and $\langle r^t \rangle_{4f}$ from our Table 1 (4f perturbations included). The first theoretical value is the dipole result, the second is the result if the quadrupole contribution is also included (see Ref. [7]). The experimental values are taken from Ref. [2]. R and I represent the real and the imaginary part, respectively

CFP	Nd^{3+}:LiYF_4	Pr^{3+}:LiYF_4
B_{20} (theory)	461, 441	504, 482
B_{20} (exp.)	441, 401, 480, 502	489, 485
B_{40} (theory)	−755, −1070	−883, −1251
B_{40} (exp.)	−906, −973, −964, −1008	−1043, −1061
B_{44} (theory)	1144, 1417	1338, 1658
B_{44} (exp.)	1115, 1119, 1105, 1230	1242, 1296
B_{60} (theory)	32, −46	40, −57
B_{60} (exp.)	−26, −60, −27, 30	−42, −57
RB_{64} (theory)	516, 632	645, 790
RB_{64} (exp.)	1073, 1051, 1019, 1074	1213, 1186
IB_{64} (theory)	166, 7	207, 9
IB_{64} (exp.)	21, 49, 35, 0	23, 0

between theory and experiment is observed considering that the highest deviation is only about 30%. Deviations of this order are indeed expected. The standard phenomenological parameters derived from various fitting programs cannot be compared with calculated CFP directly because of many reasons (even if the ab initio CFP were exact!). A few frequent experimental limitations are: (a) CI is not fully taken into account in the fitting to the energy levels (see p. 279 of Ref. [1]); (b) possible neglect of J–J mixing; (c) simplified point symmetry assumed; (d) the use of non-orthogonal operators in the model Hamiltonian; (e) the event of several sets of different parameters giving equally good fit to the energy levels; (f) a general problem is the possible local structure distortion when a RE ion is introduced as a dopant in the host material; (g) incorrect labeling of energy levels; (h) the parameters are not varied simultaneously, etc.

We would like to emphasize that the standard model used to fit the CFP experimentally does not result in the same CFP compared with a more sophisticated model (including more CI effects); see p. 279 of Ref. [1]. Using these two models to fit CFP to experiment results in differences of up to 30%. Since none of our results when compared to experimental CFP (standard model) deviate by more than about 30%, the electrostatic model alone cannot be ruled out for the host material studied here. In the case of a more covalent host material, it is most probably necessary to include the covalent contributions as well, e.g. see Ref. [26]. Bearing all the above difficulties in mind, instead of comparing ab initio and experimental CFP, it seems more appropriate to calculate the energy levels and intensities directly, and then compare with experiment. This has been done by us recently for the same hosts considered here [27], or in the case of Nd^{3+}:YAG [28], and indeed the results are found to be in good agreement with the experimental findings.

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