A relativistic crystal field for S-state f electron ions

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Abstract
In order to improve the theoretical reproduction of the splitting of the energy levels for S-state f electron ions, a model in which the relativistic effects are included in an effective way is used. Although the effective operators act within the spin-orbital space, and the radial integrals involve the *large* and *small* components of the relativistic theory, all the required matrix elements are evaluated within the intermediate coupling scheme. The approach is illustrated by the results of numerical calculations performed for the representative ions: Gd^{3+}, Cm^{3+}, and Bk^{4+}. The results of the analysis support the expectation that for such large systems the relativistic effects indeed play an important role. In addition, it is concluded that the fitting procedure applied for the determination of the crystal field parameters has to be performed within the parametrization scheme that includes the relativistic weights for the various parameters.

1. Introduction

Magnetic resonance imaging of biological structure is the alternative technique to light-based microscopy. The efficiency of this technique is not limited by the scattering of light by the layers of cells on the surface, and in addition it does not produce toxic substances as do the methods that use dyes and fluorochromes. This is an especially useful method to monitor cellular Ca^{2+} and its role in the physiology of a cell and internal biochemical processes. Recently, the lanthanide ion Gd^{3+} has been used as a contrast agent. This ion is characterized by the half-filled shell of equivalent 4f electrons, and it belongs to the group of so-called S-state ions (their ground state is $[^8S]_{7/2}$). Gadolinium is a good contrast agent due to its high magnetic moment. To avoid toxicity of the aqua ion, all but one of the coordination sites of Gd^{3+} are bound by a chelate. The remaining side is left for the water molecule that produces the signal in all imaging experiments. The authors of the pioneering research claim that [1] *'the agent can be conveniently micro-injected inside cells at an early developmental stage, and subsequent cell movements and calcium fluctuations during development can be monitored over long periods of time'*.

The properties of $LiGdF_4$:Eu, again due to the special properties of gadolinium ion, have led to a technological revolution of a new generation of highly efficient fluorescent lights.

This new phosphor replaces the conventional materials; it emits twice as many photons than it absorbs. One uv photon from Xe (instead of toxic mercury in standard devices) is absorbed by Gd^{3+} and then in two portions it is transferred to two doping Eu ions that act as luminescence centres [2].

These two examples demonstrate the wide range of applications of the Gd ion in various disciplines, and show the motivation for the theoretical research even if, at the first sight, there is no direct connection between basic research and the practical use of its results. In fact, Gd^{3+} by itself is a very interesting system, similarly as all the other ions that represent the so-called S-state elements, Eu^{2+}, Gd^{3+}, Cm^{3+}, Bk^{4+}. In particular, there is a search for an adequate theoretical model that reproduces the observed splitting of their ground state [3–8].

In 1966 Wybourne [3] performed an extensive analysis of various mechanisms that possibly contribute to the splitting of the ground state of Gd^{3+}. In the class of effective operators that represent the interactions within the $4f^7$ configuration the fourth-order terms, associated with the crystal-field parameter B_0^2 of the following form have been taken into account:

$$\langle ^8S|V_{so}|^6P\rangle\langle ^6P|V_{so}|^6D\rangle\langle ^6D|V_{CF}|^6P\rangle\langle ^6P|V_{so}|^8S\rangle$$

where V_{so} denotes the spin-orbit interaction operator, and V_{CF} represents crystal-field potential. In addition, other fourth-order terms were also discussed, namely

$$\langle ^8S|V_{so}|^6P\rangle\langle ^6P|V_{CF}|^6L\rangle\langle ^6L|V_{CF}|^6P\rangle\langle ^6P|V_{so}|^8S\rangle,$$

where $L = D, G, I$. The list of the perturbing operators considered in [3] was completed by the spin–spin interaction operator, V_{ss}, taken into account through the third-order term of the form

$$\langle ^8S|V_{ss}|^6D\rangle\langle ^6D|V_{CF}|^6P\rangle\langle ^6P|V_{so}|^8S\rangle.$$

The perturbing influence of the excited configurations has been included via the second-order terms

$$\langle ^8S|V_{CF}|Xx\rangle\langle Xx|V_E|^8S\rangle,$$

where V_E denotes the Coulomb interaction operator, X represents the excited configuration $4f^5 5d^2$, and x stands for its various states. The effects of electrostatic interactions have been taken into account at the third order by the terms that involve the spin-orbit interactions within the $4f^7$ shell, and the inter-shell interactions via the crystal field potential

$$\langle ^8S|V_{so}|^6P\rangle\langle ^6P|V_{CF}|Xx\rangle\langle Xx|V_E|^8S\rangle.$$

The fifth-order terms analysed in [3] represent the configuration interaction modified by the interactions via spin-orbit operator and crystal-field potential, namely

$$\langle ^8S|V_E|Xx_1\rangle\langle Xx_1|V_{so}|Xx_2\rangle\langle Xx_2|V_{CF}|Xx_3\rangle\langle Xx_3|V_{so}|Xx_4\rangle\langle Xx_4|V_E|^8S\rangle.$$

Unfortunately all these non-relativistic corrections did not improve the results of calculations, and they did not reproduce the observed splitting of the ground state of gadolinium ethyl sulphate. The problem was also not solved when the particular relativistic contributions were taken into account. The energy corrections evaluated from the following effective term [9]:

$$B_0^2\langle ^8S|V_{so}|^6P\rangle\langle ^6P|W^{(11)2}|^8S\rangle$$

led to the splitting of the ground terms of opposite sign than observed.

The aim of the present investigation is to verify the importance of the relativistic effects that are taken into account within the approach in which the interactions via the crystal-field potential result in the splitting of the ground state. The relativistic effects are included here in an effective way, and the energy of Kramer's components are evaluated as first-order corrections.

2. Relativistic crystal-field potential

In the non-relativistic approach the energy of crystal-field splitting is evaluated as a matrix of the following operator:

$$V_{\mathrm{CF}} = \sum_{k,q} A_q^k \sum_i r_i^k C_q^{(k)}(\theta_i \phi_i), \tag{1}$$

where A_q^k are the structural parameters. The crystal-field potential defined in equation (1) in terms of unit tensor operators has the form

$$V_{\mathrm{CF}}^{\mathrm{eff}} = \sum_{k,q} A_q^k \sum_i \langle n\ell | r_i^k | n\ell \rangle \langle \ell || C^{(k)} || \ell \rangle u_{i,q}^{(k)}(\ell\ell), \tag{2}$$

where the product $A_q^k \langle n\ell | r_i^k | n\ell \rangle$ is usually denoted by B_q^k, and it defines the so-called crystal-field parameters.

Following the idea of Wybourne from 1965 [9], and applying the method of Sandars and Beck [10] (see also Smentek and Wybourne [11,12]), it is rather straightforward, using standard tensor operator techniques [13], to evaluate the crystal-field splitting within the relativistic model, and at the same time avoid the troublesome calculations of the matrix elements within the j–j coupling scheme. Thus, in the relativistic approach, instead of the effective operator of equation (2), the following operator is taken into consideration:

$$V_{\mathrm{CF}}^R = \sum_{k,q} A_q^k \sum_{\kappa t} b_k(\kappa t) \sum_i w_{i,q}^{(\kappa t)k}(\ell\ell), \tag{3}$$

where $w_{i,q}^{(\kappa t)k}(\ell\ell)$ denotes the unit double tensor operator, and $\sum_i w_{i,q}^{(\kappa t)k}(\ell\ell) = W_q^{(\kappa t)k}$. The coefficient $b_k(\kappa t)$ from equation (3) contains the main information about the transformation from the non-relativistic to the relativistic approach [9], and it has the form

$$b_k(\kappa t) = (-1)^{\kappa+k+t} \sum_{j_\pm, j'_\pm} (-1)^{j'_\pm+1/2}[k]^{-1/2}[\kappa, t]^{1/2}[j_\pm, j'_\pm]$$

$$\times \begin{pmatrix} j'_\pm & k & j_\pm \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \begin{Bmatrix} \ell & \ell & t \\ \frac{1}{2} & \frac{1}{2} & \kappa \\ j'_\pm & j_\pm & k \end{Bmatrix} R_{j_\pm, j'_\pm}^k. \tag{4}$$

The radial integrals contain the *large* and *small* components and are defined as follows:

$$R^k(j_\pm, j'_\pm) = \langle P^{j_\pm} | r^k | P^{j'_\pm} \rangle + \langle Q^{j_\pm} | r^k | Q^{j'_\pm} \rangle, \tag{5}$$

where $j_\pm = \ell \pm \frac{1}{2}$ and $j'_\pm = \ell \pm \frac{1}{2}$.

It is seen from equation (3) that κ denotes the rank of part of a double tensor operator that acts within the spin space, and therefore $\kappa = 0, 1$. For the case of $\kappa = 0$, $t = k$; for $\kappa = 1$ when the rank of crystal field potential $k = 2$: $t = 1, 3$, for $k = 4$: $t = 3, 5$, and finally, for $k = 6$: $t = 5$. Thus, the energy correction due to the perturbing operator defined in equation (3) is determined by the matrix elements of at most eight effective operators.

In order to simplify the comparison of the results of the present analysis with the values obtained from the non-relativistic approach it is convenient to define the following terms:

$$H_{M_J M_{J'}}^k = \sum_q A_q^k \langle n\ell | r^k | n\ell \rangle \langle \ell || C^{(k)} || \ell \rangle \langle U_q^{(k)} \rangle_{\Psi\Psi'}, \tag{6}$$

where Ψ is an appropriate wavefunction defined within the intermediate coupling scheme, and $\langle U_q^{(k)} \rangle_{\Psi\Psi'}$ denotes a matrix element of the unit tensor operator. In addition, for the purpose of the numerical analysis the product of radial integral and the reduced matrix element in equation (6) is denoted in the discussion by N-RCF since it represents the non-relativistic contribution.

As a counterpart for the $H_{M_J M_{J'}}^k$ terms in equation (6), the following matrix elements of the relativistic approach are taken into account:

$$\mathcal{H}_{M_J M_{J'}}^k = \frac{1}{\sqrt{2}} \sum_q A_q^k b_k(0k) \langle U_q^{(k)} \rangle_{\Psi \Psi'}$$
$$+ \sum_q A_q^k \sum_{\kappa \neq 0} \epsilon(\kappa + t + k) \sum_t b_k(\kappa t) X_q^{(\kappa t)k}(\Psi, \Psi') \langle U_q^{(k)} \rangle_{\Psi \Psi'}. \tag{7}$$

The first part of the expression in equation (7) represents the terms subtracted from equation (3) for $\kappa = 0$, and the factor $1/\sqrt{2}$ originates from the reduction of the double tensor operator $W^{(0k)k}$ to the unit tensor operator $U^{(k)}$. This part of the relativistic contributions to the crystal-field corrections, denoted by RCF in the further discussion, can be compared directly to the non-relativistic terms, N-RCF, from equation (6); indeed, N-RCF and RCF are associated with the same unit tensor operators. It is important to note that the structural parameters A_q^k are common for both terms. Thus, it is possible at this point to extract from the analysis the uncertainty of crystal-field parameters, and also disregard the matrix elements of U operators. This means that the contributions that are evaluated exactly serve as a basis for the conclusions on the relative importance of both types of N-RCF and RCF; this part of the numerical analysis is *ab initio* in nature.

The tensorial structure of equation (3) for $\kappa \neq 0$ is different from the terms previously analysed since it is associated with double tensor operators. In order to simplify the analysis, a new symbol $X_q^{(\kappa t)k}(\Psi, \Psi')$ is introduced in equation (7), and it denotes the following ratio of matrix elements:

$$X_q^{(\kappa t)k}(\Psi, \Psi') = \langle \ell^N [\alpha SL] J M_J | W_q^{(\kappa t)k} | \ell^N [\alpha' S' L'] J' M_{J'} \rangle / \langle \ell^N [\alpha SL] J M_J | U_q^{(k)} | \ell^N$$
$$\times [\alpha' S' L'] J' M_{J'} \rangle. \tag{8}$$

This technical step makes it possible to directly compare the part of the relativistic contribution that originates from the crystal-field interactions within the spin-orbital space, S-OCF, to the values of the non-relativistic, N-RCF, and the other relativistic, RCF, terms.

It is seen from equation (7), followed by a definition in equation (8), that the contributions S-OCF are state dependent through X, and they have to be evaluated for every energy level separately. It should be mentioned at the same time that this part of the numerical analysis has lost the features of *ab initio* calculations. Actually, the matrix elements involve the wavefunctions defined within the intermediate coupling scheme, and the coefficients of the linear combinations are determined through the semi-empirical procedure. However, it is still possible to continue the crystal-structure independent analysis leaving aside the crystal-field parameters, and comparing terms for the same value of k.

3. Numerical results

In order to verify the importance of relativistic contributions to the crystal-field energy splitting, the radial one electron basis sets have been generated separately for the non-relativistic and relativistic models. The free ion, non-relativistic calculations were performed for the average energy of the configuration at the level of the Hartree–Fock method using Froese Fischer's MCHF program [14]. The relativistic radial integrals were evaluated within the Dirac–Hartree–Fock method using the GRASP^2 package [15]. The orbitals were generated from the average-energy formalism with all the relativistic configuration state functions arising from the f^7 open-shell configurations included in the optimization procedure. There were 42 and 50 configuration state functions involved for the states with $J = 5/2$ and $7/2$.

Table 1. Radial integrals from non-relativistic and relativistic free ion calculations for Gd^{3+} ($4f^7$) and Bk^{4+} ($5f^7$).

	Gd^{3+} ($4f^7$)					Bk^{4+} ($5f^7$)				
k	$\langle 4f|r^k|4f\rangle$	(++)	(+−)	(−−)	η (%)[a]	$\langle 5f|r^k|5f\rangle$	(++)	(+−)	(−−)	η (%)[a]
2	0.7921	0.8722	0.8659	0.8546	8	1.2363	1.4718	1.4366	1.4043	14
4	1.4647	1.8734	1.8164	1.7626	19	2.7065	4.0017	3.8037	3.6217	30
6	5.4459	8.2046	7.8112	7.4426	30	9.8579	18.6240	17.2133	15.9399	43

[a] $\eta = [\langle \frac{7}{2}|r^k|\frac{7}{2}\rangle_{Av} - \langle nf|r^k|nf\rangle]/\langle \frac{7}{2}|r^k|\frac{7}{2}\rangle_{Av} \times 100\%$, where $\langle \frac{7}{2}|r^k|\frac{7}{2}\rangle_{Av} = \frac{1}{3}(R_{++} + R_{+-} + R_{--})$.

Table 2. Results of non-relativistic and relativistic free ion calculations for Gd^{3+} and Bk^{4+} ($E_{HF}^{Av} = -10\,818.8469$, $E_{HF}^{Av} = -29\,096.6479$, $E_{DHF}^{Av}(\frac{7}{2}) = -13\,309.521$, $E_{DHF}^{Av}(\frac{7}{2}) = -37\,833.4864$).

	Gd^{3+} ($4f^7$)					Bk^{4+} ($5f^7$)			
nl	$-\varepsilon_{HF}$	$-\varepsilon_{DHF}$	$\langle r\rangle_{nl}^{HF}$	$\langle r\rangle_{nl}^{DHF}$	nl	$-\varepsilon_{HF}$	$-\varepsilon_{DHF}$	$\langle r\rangle_{nl}^{HF}$	$\langle r\rangle_{nl}^{DHF}$
5s	2.90	3.15	1.4274	1.3456	6s	3.24	4.00	1.5257	1.3150
5p−	2.09	2.26	1.5790	1.4857	6p−	2.47	3.02	1.6703	1.4323
5p+	2.09	2.08	1.5790	1.5665	6p+	2.47	2.47	1.6703	1.6374
4f−	1.82	1.65	0.7943	0.8211	5f−	2.40	2.06	1.0260	1.0889
4f+	1.82	1.61	0.7943	0.8317	5f+	2.40	1.98	1.0260	1.1155

The quality of the numerical calculations performed at this initial step is illustrated in tables 1 and 2 where certain radial integrals along with the values of energies for Gd^{3+} and Bk^{4+} are collected. The Hartree–Fock radial functions have been applied to evaluate the radial integrals of N-RCF defined in equation (6), while the Dirac–Hartree–Fock *small* and *large* components have been used for evaluation of the radial integrals of relativistic contributions represented by $b_k(\kappa t)$ in equation (3) (and defined by equation (4)); all these radial integrals are presented in table 1.

In addition to the values of radial integrals the deviation of non-relativistic values in relation to the average of the relativistic ones is also presented in terms of η. It is seen from the table that in all cases the relativistic values are greater by a non-negligible amount; this conclusion is important for further analysis since the radial integrals are the messengers of the individual properties of each ion. The remaining parts of the energy corrections that are defined within both approaches, as angular factors, are common for all systems of equivalent electrons (see equation (4) for example). It is also interesting to compare the values of energies and the expectation values of r in various one electron states; these are presented in table 2. In the case of the lanthanide ion illustrated in the first part of the table, Gd^{3+}, so-called *spatial shrinkage* of the 4f function is observed, and this property is demonstrated by the non-relativistic values of the average of r. The lanthanide contraction results from a particular structure of effective potential for 4f electrons [15–17] that is characterized by two rival potential wells. It is interesting to mention that the 4f and 5f orbitals for Xe are almost identical to the hydrogenic functions. At the same time, for La, for example, the 4f orbital exhibits the collapse, while 5f still has the hydrogenic features that show the domination of the well of Coulombic nature [15]. For increasing atomic numbers the situation is changed, and at the beginning of the actinide series the spatial shrinkage of 5f is again observed; this property is well illustrated in table 2 for the Bk^{4+} ion. At the same time it should be noted that 5s and 5p in the case of the lanthanide trivalent ion, and 6s and 6p of the four-valent actinide ion are closed shells, and they actually screen the optically active electrons of the f shell from the direct influence of the environment.

It is known from the literature [15–17] that the relativistic effects cause the radial

Table 3. Non-relativistic crystal-field contributions and their relativistic counterparts (b_k for $\kappa = 0$) for $Gd^{3+}(4f^7)$ and $Bk^{4+}(5f^7)$ ions.

Ion	k	N-REL	RCF[a]	η[b]
Gd^{3+}	2	−1.0822	−0.5303	2.0
	4	1.6525	0.6864	2.4
	6	−6.9528	−2.7869	2.5
Bk^{4+}	2	−1.6892	−0.8815	1.9
	4	3.0535	1.4423	2.1
	6	−12.5856	−6.1685	2.0

[a] $RCF = (1/\sqrt{2})b_k(0k)$.
[b] $\eta = (N - REL)/(RCF)$.

Table 4. Relativistic contributions for $\kappa = 0$, RCF, and the values of the terms originating from the crystal field within the spin-orbital space, S-OCF, for the Bk^{4+} ion.

k	RCF[a]	t	$b_k(1t)$	$X^{(1t)k}$	S-OCF[b]	η (%)[c]
2	−0.8815	1	−0.0180	28.2599	−0.5087	
		3	0.0201	0.4074	0.0082	
Σ_t					−0.5005	57
4	1.4423	3	0.0570	22.0242	1.2554	
		5	−0.0515	0.0427	−0.0022	
Σ_t					1.2532	87
6	−6.1695	5	−0.2473	22.7213	−5.6190	91

[a] $RCF = (1/\sqrt{2})b_k(0k)$.
[b] $S\text{-}OCF = \sum_t b_k(1t)X^{(1t)k}$.
[c] $\eta = (S\text{-}OCF)/(RCF) \times 100\%$.

contraction and stabilization of the energies of the inner orbitals of s and p symmetry. This means that the screening of the nucleus is stronger in the relativistic description, and as a consequence, the orbitals of the outer electrons are more expanded. These general trends are indeed reflected by the values presented in table 2.

In table 3 the values of the non-relativistic contributions to the energy splitting N-REL defined by equation (6) are compared to the relativistic counterparts RCF associated with $b_k(0k)$ (equation (7)). These results are obtained from *ab initio* calculations, and therefore they are free of any uncertainties. It is seen from this table that the signs of the appropriate contributions are preserved, while their magnitude (the absolute values), for both ions analysed, is reduced by approximately a factor of 2 when the relativistic effects are taken into account (see the values of η).

The second part of relativistic contributions in equation (7), S-OCF, originates from the interactions within the spin-orbital space. In table 4 their values for the Bk^{4+} ion are presented together with the former RCF terms. In the fourth and fifth columns the values of the contributing factors $b_k(1t)$ and $X^{(1t)k}$ (see equation (7)) are displayed for certain t; η represents the relative importance of both relativistic contributions. The values presented in table 4 contain the semi-empirical admixture via the coefficients of the intermediate coupling scheme of wavefunctions used for evaluation of the matrix elements in $X^{(1t)k}$ [18].

It is seen from table 4 that both relativistic contributions to the energy, RCF and S-OCF, have the same signs and comparable magnitude; this means that they both have to be included in any calculation. Inspection of table 4 at the same time shows that not all partial contributions to S-OCF are of the same importance. The most dominant terms are for $t = 1$, and this

Table 5. Values of coefficients $b_k(\kappa t)$ of double tensor operators (equation (3)).

k	κ	t	Gd^{3+}	Bk^{4+}
2	1	1	−0.0063	−0.0180
	1	3	0.0070	0.0201
	0	2	−0.7501	−1.2467
4	1	3	0.0165	0.0570
	1	5	−0.0151	−0.0515
	0	4	0.9707	2.0398
6	1	5	−0.0690	−0.2473
	0	6	−3.9413	−8.7254

disproportion is not accidental but rather symptomatic as observed among other terms and for both ions, Gd^{3+} and Bk^{4+}. Indeed, in table 5 the values of the coefficients b_k are presented for various ranks of double tensor operators; among terms for $\kappa = 1$ (these are the ones involved into S-OCF) there is no differentiation between the magnitude of contributions for various t. The values of terms for $\kappa = 0$ which are much larger (contributions to RCF) are collected in this table only for the completeness of analysis. Thus, it is seen that the values of b_k are not the source of various magnitudes of contributions that is noticed in table 4.

In table 6 the reduced matrix elements of unit tensor operators $U^{(k)}$ and double tensor operators $W^{(1t)k}$, together with their ratio $X^{(1t)k}$, evaluated for the ground state $[^8S]_{7/2}$ of Gd^{3+}, Cm^{3+} and Bk^{4+}, are collected [19]. It is apparent that the largest values of the matrix elements of double tensor operators are for the smallest value of rank t, for given k and $\kappa = 1$ (this is the first value of t allowed by the triangular condition). In the case of the Gd^{3+} ion the ratio between the terms for $t = k - 1$ and k exceeds the factor of 10, while for Cm^{3+} and Bk^{4+} this ratio is around 4. Note, that the second largest values of W, for $t = k$, do not contribute to the terms that determine the energy splitting, since for k even and $\kappa = 1$, t must be odd to preserve the Hermiticity of the effective operator (see the second part of equation (7)).

In summary, the disproportion between various contributions to S-OCF in table 4 is explained by the magnitude of values of various matrix elements of unit tensor operators. The general conclusion derived from this part of numerical analysis states that both types of relativistic contributions, RCF and S-OCF, have to be included in the numerical calculations. However, as demonstrated above, it is justified to simplify the expression for the relativistic contributions to the more practical form (instead of equation (7))

$$\mathcal{H}^k_{M_J M_{J'}} = \sum_q A^k_q \left\{ \frac{1}{\sqrt{2}} b_k(0k) + b_k(1k-1) X^{(1k-1)k}_q ([^8S]_{7/2}) \right\} \langle U^{(k)}_q \rangle_{M_J M'_J}, \tag{9}$$

where only the most dominant terms of S-OCF, those for $t = k-1$, are included. It is interesting to mention that this simplification is correct only in the case of the energy correction for the ground state $[^8S]_{7/2}$. Indeed, inspection of table 7 shows that, for example, in the case of $[^6P]_{5/2}$ the values of ratio $X^{(1t)k}$ for $t =$ odd are comparable (except for one element for Gd^{+3}, with $k = 4$ and $t = 3$). A similar situation is observed in the case of state $[^6D]_{7/2}$ for which the values of reduced matrix elements of U for all ranks are comparable with the values of matrix elements of W, and therefore their mutual ratio is small.

In table 5 the values of factors b_k are collected; it is seen from this table that for almost all cases of various ranks, the values for $\kappa = 0$ are two orders of magnitude larger than the remaining ones (for $\kappa = 1$), and there is no dominant contribution among S-OCF to be compared to RCF. Thus, in the light of table 7, the second part of equation (9) for energy states

Table 6. Reduced matrix elements of unit tensor operators U and double tensor operators W (with $\kappa = 1$) for the ground states $[^8S]_{7/2}$ of Gd^{3+}, Cm^{3+} and Bk^{4+} ions (multiplied by 10^2).

Ion	k	$U^{(k)}$	t	$W^{(1t)k}$	$X^{(1t)k} = \dfrac{W}{U}$
Gd^{3+}	2	0.2230	1	58.9091	264.1664
			2	6.0281	27.0318
			3	0.1006	0.4511
	4	0.0074	3	1.4893	201.2568
			4	0.1339	18.0946
			5	0.0014	0.1899
	6	0.0004	5	0.0644	161.0000
			6	0.0061	15.2500
Cm^{3+}	2	4.7438	1	150.6054	31.7478
			2	41.8315	8.8181
			3	1.8265	0.3218
	4	1.1291	3	28.9054	25.6004
			4	6.8174	6.0379
			5	0.0779	0.0689
	6	0.3439	5	8.8378	25.6988
			6	2.0869	6.0683
Bk^{4+}	2	5.6695	1	160.2195	28.2599
			2	45.5919	8.0416
			3	2.3099	0.4074
	4	0.0074	3	34.4043	22.0242
			4	8.6774	5.5550
			5	0.0667	0.0427
	6	0.0004	5	11.9446	22.7213
			6	2.9559	5.6228

Table 7. Values of $X^{(1t)k}$ evaluated for $[^6P]_{5/2}$ of Gd^{3+}, Cm^{3+} and Bk^{4+}.

k	t	$X^{(1t)k}$:Gd^{3+}	$X^{(1t)k}$:Cm^{3+}	$X^{(1t)k}$:Bk^{4+}
2	1	0.73	1.37	1.69
	2	0.28	0.52	0.61
	3	0.30	1.43	1.24
4	3	-11.92[a]	-0.46[a]	-0.28[a]
	4	-2.20[a]	-1.08[a]	-1.09[a]
	5	0.58	0.49	0.52

[a] The value of $W^{(1t)k}$ is negative.

other than $[^8S]_{7/2}$ is negligible in relation to the first term. Consequently, the expression for the energy correction in such cases is further simplified to the term-independent part

$$\mathcal{H}^k_{M_J M_{J'}} = \frac{1}{\sqrt{2}} \sum_q A^k_q b_k(0k) \langle U^{(k)}_q \rangle_{M_J M'_J}.$$

Summarizing, the number of effective operators that determine crystal-field splitting within the relativistic approach is reduced from 8 for the general case (see discussion below equation (5)) to 6 in the case of the ground state $[^8S]_{7/2}$. The ranks of operators in equation (9) are: for $\kappa = 0$ (first part of equation (9)), $k = t = 2, 4, 6$; for $\kappa = 1$ (the second part of equation (9)), the equality $t = k - 1$ must be satisfied, and therefore there are three pairs of permissible values of k and t, namely $(2, 1)$, $(4, 3)$ and $(6, 5)$. At the same time for the other

energy states, for example for $[^6\text{P}]_{5/2}$, the number of operators is reduced to 3 since only the terms for $\kappa = 0$ contribute effectively to the energy.

4. Relativistic parametrization scheme

It is seen from equation (9) that in order to evaluate the energy splitting in addition to the values of various relativistic contributions, also the values of the structural parameters A_q^k for certain system have to be known. As a reliable source of this information the results of the fitting procedure performed for the Bk^{4+} ion presented in [8] have been chosen. The crystal-field parameters reported there divided by the values of non-relativistic radial integrals give the required structural parameters. Unfortunately these crystal field factors applied to equation (7) (rather than to (9) in order not to introduce additional errors at this point of analysis) led to a result at the limit of nonsense. While the order of sublevels of $[^8\text{S}]_{7/2}$ were predicted properly, the crystal-field splitting reached $2500\,\text{cm}^{-1}$ in comparison to $58\,\text{cm}^{-1}$ from experiment. In fact this poor result demonstrates that the crystal-field parameters obtained from the non-relativistic procedure presented in [8] are not appropriate to be used in the present relativistic analysis. In order to verify this conclusion the expression for the crystal-field energy corrections used in [8] has been reconstructed with the relativistic effects taken into consideration. Thus, the following linear combination of the crystal-field parameters and appropriate factors should be used for the fitting procedure if the relativistic effects are taken into account:

$$
\begin{aligned}
\mathcal{H}_{M_J M_{J'}}(\text{Bk}^{4+}\text{:}[^8\text{S}]_{7/2}) = {}& 1.0\{A(4M_J^2 - 21)A_0^2 + B(S_{M_J M_{J'}})A_2^2\} \\
& + 2.4\{C(t_{M_J M_{J'}})A_0^4 + D(u_{M_J M_{J'}})A_2^4 + E(v_{M_J M_{J'}})A_4^4\} \\
& + 9.2\{F(w_{M_J M_{J'}})A_0^6 + G(x_{M_J M_{J'}})A_2^6 + H(y_{M_J M_{J'}})A_4^6 + I(z_{M_J M_{J'}})A_6^6\},
\end{aligned}
\tag{10}
$$

where the factors of crystal-field parameters A_q^k contain the matrix elements of unit tensor operators between the wavefunction of the ground state of Bk^{4+}: $[^8\text{S}]_{7/2}$, and the angular terms originating from, for example Wigner–Eckart theorem; the values of these factors are presented in table 2 of [8]. The most important part of this expression, the numerical factors 1.0, 2.4 and 9.2 represents the relativistic effects. These numbers demonstrate to what extent the non-relativistic relation between various crystal-field parameters that contribute to the energy splitting is changed when the relativistic effects are taken into account. A similar result is obtained for the other S-state ion analysed here, namely

$$
\begin{aligned}
\mathcal{H}_{M_J M_{J'}}(\text{Gd}^{3+}\text{:}[^8\text{S}]_{7/2}) = {}& 1.6\{A'(4M_J^2 - 21)A_0^2 + B'(S_{M_J M_{J'}})A_2^2\} \\
& + 3.5\{C'(t_{M_J M_{J'}})A_0^4 + D'(u_{M_J M_{J'}})A_2^4 + E'(v_{M_J M_{J'}})A_4^4\} \\
& + 10.9\{F'(w_{M_J M_{J'}})A_0^6 + G'(x_{M_J M_{J'}})A_2^6 + H'(y_{M_J M_{J'}})A_4^6 + I'(z_{M_J M_{J'}})A_6^6\}
\end{aligned}
\tag{11}
$$

with the same interpretation of all coefficients of crystal field parameters as before but evaluated for the Gd^{3+} ion.

These two modified expressions for the crystal-field splittings of the ground states of Gd^{3+} and Bk^{4+} demonstrate the strength and importance of relativistic effects. The numerical factors presented in both equations play the role of the weights with which each crystal-field parameter enters the expression for the energy. These factors are large enough to expect a new set of adjusted crystal-field parameters that are different from those obtained from the non-relativistic scheme.

5. Conclusions

Is the recommendation from the literature [20–22] that relativistic effects are important for such large systems as f^N ions fact or fiction? In particular, there is the question whether crystal-field energy splitting requires a relativistic model for better theoretical reproduction. The results of numerical calculations performed for two representative S-state ions, Gd^{3+} and Bk^{4+}, demonstrate clearly that the electronic structure of these systems has to be described in the language of the relativistic approach. This conclusion is very well illustrated by the final results of the calculations with the inclusion of RCF and S-OCF; the relativistic effects are large enough to change the weights of crystal-field parameters that are determined in a standard non-relativistic way.

At the same time it should be pointed out that in the present approach relativistic effects are included, and matrix elements are evaluated within the intermediate coupling scheme (instead of $j-j$ coupling for which the number of required matrix elements would explode); the only price one has to pay for the inclusion of relativity is the inconvenience that part of its contribution depends on the particular electronic state. At the same time, however, this dependence on a particular state might be treated as an additional possibility for including particular features of a distinct state that in turn gives better adjustment of the parameters.

Acknowledgments

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