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Systematic analysis of spectroscopic characteristics of the lanthanide and actinide ions with the $4f^N$ and $5f^N$ ($N = 1 \dots 14$) electronic configurations in a free state



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ABSTRACT

Systematic consideration of the spectroscopic properties of the di-, tri- and tetravalent lanthanide and actinide ions in a free state is presented. Variations of the Hartree–Fock calculated Slater parameters F^2, F^4, F^6 , spin–orbit interaction constant ζ and averaged values of the $4f, 5f$ electrons' radial coordinate across both series were considered; functional dependencies between the mentioned quantities were obtained. It has been shown that the F^2, F^4, F^6 parameters grow up linearly with the atomic number Z . The spin–orbit interaction constant $\zeta^{1/4}$ is also proportional to Z , and, therefore, to the Slater integrals as well. Moreover, the ratios F^4/F^2 and F^6/F^2 are practically constant for the isovalent ions in the considered series. The energy barycenters of all electronic configurations and the third, fourth and fifth ionization energies were all calculated. The energy barycenter moves up with increasing number of f -electrons until the f -shell becomes half-filled (7 f electrons) and then moves down. The ionization energies increase linearly with atomic number across the considered series. The established relations between F^2, F^4, F^6 and ζ reduce the number of independent parameters in the free ion Hamiltonian and can be further applied to the case of crystal-field fitting calculations as the empirical constraints.

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1. Introduction

There are two particular groups of chemical elements in the periodic table, which share a certain similarity in their properties. These are the so called “lanthanides” and “actinides”, which have the $4f$ and $5f$ unfilled electron shells, respectively. These names are derived from those of the first elements opening the considered groups: lanthanum ($Z = 57$) and actinium ($Z = 89$). Their f -electron shells are gradually built up by adding one additional electron when moving across the considered series until the f shell becomes completed with 14 electrons. It has also to be mentioned that the unfilled $4f$ (lanthanides) and $5f$ (actinides) shells are screened by the completely filled $5s^2 5p^6$ and $6s^2 6p^6$ shells, respectively, which strongly decreases influence of environment of these ions on their inner f shells.

The lanthanide ions – also known as the rare earth ions – are widely used in various optical applications, such as laser materials,

infrared to visible up-conversion materials, phosphors [1–7] and references therein. Recently, the lanthanide ions have increasing utility in biomedical applications [8]. The actinide ions, although resembling lanthanides from the point of view of electronic structure, stand apart due to their radioactivity, which determines their specific areas of application in nuclear energetic and military spheres [9]. For example, the photophysics and photochemistry of actinide ions has been developed to address the safety and security issues arising from nuclear fission [10].

The physical fact behind these applications of lanthanide and actinide ions is that their intraconfigurational f – f transitions manifest themselves as very sharp narrow lines in the experimental absorption/emission spectra due to the screening effect of the completely filled $5s^2 5p^6$ and $6s^2 6p^6$ shells on the inner f orbitals. Thus, the main emphasis in the article is placed on the properties of the f electron configurations f^N , with N varying from 1 to 14.

In Table 1 we give the number of energetic J -manifolds (many of which are degenerated) and the number of states for each considered configuration. Those energetic J -manifolds arise from the Coulomb interaction between the f electrons and the f electron's spin–orbit (SO) coupling interaction (it should be

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Table 1
Electronic configurations and the number of possible states for the f^N configurations.

Electron configuration	Number of states (including possible orientation of spin)	Number of J manifolds (number of energy levels of free ions)
f^1	14	2
f^2	91	13
f^3	364	41
f^4	1001	107
f^5	2002	198
f^6	3003	295
f^7	3432	327
f^8	3003	295
f^9	2002	198
f^{10}	1001	107
f^{11}	364	41
f^{12}	91	13
f^{13}	14	2
f^{14}	1	1

emphasized that the Slater parameters describing the Coulomb interaction in the f^N configurations cannot be determined for $N = 1, 13$ and 14). Almost all those levels are highly degenerated and can be split further by a crystal field, to form rich energy level schemes with numerous sharp absorption/emission lines in a wide spectral region, from infrared to ultraviolet, depending on the ion considered.

The semi-empirical effective Hamiltonian model operating within the f^N electron configurations has been well developed to understand the electronic energy level structures observed in the f – f transition spectra of lanthanide and actinide ions in solids [1,11,12]. In the model, each effective interaction within the f^N configuration can be expressed as the product of the radial (depending on the radial coordinates of f -electrons only) fitting parameter and the angular (depending on the angular coordinates of f -electrons only) operator. The matrix elements of all operators entering the free ion Hamiltonian acting between the basis wave functions $|f^N, \eta SLJM\rangle$ (S, L, J, M stand for the quantum numbers of the spin, orbital momentum, total momentum and its projection, respectively; η denotes all other quantum numbers needed to distinguish between the states with identical S, L, J, M sets) can be derived from the Racah–Wigner algebra. The values of the radial fitting parameters can be obtained by minimizing the root-mean-square (rms) deviation between the theoretical and experimental energy levels. Such a theoretical method has been systematically implemented for successful interpretation of spectra of trivalent lanthanide and actinide ions in LaCl_3 and LaF_3 by Carnall and his coworkers, and the trend of the obtained fitting parameter values across the whole f -element series has been also analyzed and discussed (see the review article of Liu [13] for more details and literature references). After that, that trend has been applied to other spectroscopic studies of trivalent lanthanide ions in solids to reduce the number of the fitting energy parameters [14].

More recently, Duan and Tanner have also demonstrated the similar trend of the energy parameters of trivalent ions in $\text{Cs}_2\text{-NaYCl}_6$ across the whole lanthanide series [15]. It is noticeable that in those above-mentioned publications the main studied objects are the trivalent lanthanide and actinide ions in crystals. However, some other oxidation states of these ions can be encountered. The divalent lanthanide ions (first of all, Eu^{2+}) can be found in some materials and they are of paramount importance for persistent phosphors as we all know. Recently, a comparative study of the spectroscopic properties of four isoelectronic ions with the $4f^2$ configuration ($\text{La}^+, \text{Ce}^{2+}, \text{Pr}^{3+}, \text{Nd}^{4+}$) was also published [16]. Obviously, it is very desirable to further extend the trend study to the cases of other oxidation states of all lanthanide and actinide ions – this is one of the main aims of the present study.

In addition, the SO constant ζ_f is linearly related to the atomic number Z to the fourth power according to the theory of atomic structure and spectra proposed by Cowan [17]. Therefore, the relation between the SO constant ζ_f and the atomic number Z given by the previous works will need a complete re-analysis.

Recently we have considered how the spectroscopic properties of the ions with unfilled 3d [18] and 4d/5d shells [19] vary across the whole groups depending on the atomic number and/or oxidation state. In particular, we have shown that the Racah parameters A, B and C and SO constant ζ_d for those 3d, 4d, and 5d ions are all related to the atomic number Z ; the linear trends obtained by the scheme we developed in our earlier two papers reduce the number of independent parameters needed for a proper description of the free ions spectra.

In the present paper we continue this line of research to explore the main spectroscopic parameters of the 4f and 5f ions, i.e., to perform a thorough analysis of the electrostatic (the so called Slater integrals F^2, F^4, F^6) and SO interaction parameters for all the doubly, triply, and quadruply charged lanthanide and actinide ions in a free state. We also calculate the averaged values of the second, fourth and sixth power of the 4f or 5f electrons radial coordinate ($\langle r^2 \rangle, \langle r^4 \rangle, \langle r^6 \rangle$), since these quantities are necessary to calculate the crystal field parameters. The barycenter energies E_{avg} of all considered f^N electron configurations and first ionization energies E_I were calculated and are reported here. We believe that all data accumulated and discussed in this paper will be useful for an analysis of the 4f and 5f ions spectra in various materials.

The structure of the paper is as follows: in Section 2 the Hamiltonian of the free f -ions is described; in Section 3 all relations between the main spectroscopic parameters of free ions and atomic number are derived; Section 4 highlights the behavior of the energy barycenters and ionization energies, and, finally, Section 5 contains the final concluding remarks.

2. Free di-, tri- and tetravalent 4f/5f ions: the structure of the Hamiltonian

The parameterized free-ion Hamiltonian H_{FI} of a f^N ($N = 1 \dots 13$) electron configuration can be written as [1,11,12]:

$$H_{FI}(f^N) = E_{avg} + \sum_{k=2,4,6} F^k \mathbf{f}_k + \zeta_f \sum_{i=1}^N \mathbf{l}_i \cdot \mathbf{s}_i + \alpha \mathbf{L}(\mathbf{L} + \mathbf{1}) + \beta \mathbf{G}(\mathbf{G}_2) + \gamma \mathbf{G}(\mathbf{R}_7) + \sum_{i=2,3,4,6,7,8} T^i \mathbf{t}_i + \sum_{h=0,2,4} M^h \mathbf{m}_h + \sum_{k=2,4,6} P^k \mathbf{p}_k \quad (1)$$

where the italic and bold letters represent the radial fitting parameter and the angular operator, respectively. The first term E_{avg} is the f^N configuration barycenter energy, which does not cause any energy splitting and can be easily determined by shifting the whole energy splitting pattern so that the ground-state energy is zero. The second term is the Coulomb interaction between the f electrons, where F^k ($k = 2, 4$ and 6) are the Slater parameters (for obvious reasons, these parameters can be defined only for the ions having more than one electron or one positively charged hole in the electron configuration). The \mathbf{f}_k values are eventually some numerical constants, which can be calculated for a given electron configuration with N electrons as [20]:

$$\mathbf{f}_k = \frac{1}{2} \sum_{i,j=1}^N \frac{4\pi}{2k+1} \sum_{q=-k}^k Y_{kq}^*(\theta_i, \varphi_i) Y_{kq}(\theta_j, \varphi_j), \quad (2)$$

with Y_{kq} being the spherical functions of the f -electrons' coordinates θ, φ with $i \neq j$ for obvious reasons, since this is a pair Coulomb interaction. The third term stands for the f electron's SO interaction, where ζ_f is the SO coupling constant and $\mathbf{l}_i \cdot \mathbf{s}_i$ is the SO interaction operator with the first and second terms being the operators of the angular and spin momenta of an individual electron with index i .

The second and third terms dominate in the Hamiltonian (1) and to a large extent determine the order and sequence of the energy levels. The next four terms are the two- and three-electron Coulomb correlation contributions from the higher configurations with the same parity. The last two terms represent the magnetically and electrostatically correlated interactions. The last six terms only produce very small corrections to the energy levels determined by the second and third terms.

We restrict our analysis to the second and third terms of the Hamiltonian (1) only due to the consideration of the orders of magnitude of the energy splitting caused by each interaction in the free ion Hamiltonian (1). Besides, the calculations of those correction terms are very complicated and as a rule they are treated as the fitting parameters, which can be determined numerically from the procedure of non-linear fitting of the calculated energy level schemes to the experimental ones.

The studied ions were grouped as the di-, tri- and tetravalent ions, whose atomic numbers and electron configurations are listed in Table 2. As seen from the table, increase of the atomic number by unity with keeping the same electric charge of an ion leads to appearance of one additional f-electron in the unfilled shell. Moreover, to cover as many possible oxidation states as possible and to offer a comparative cross-cutting study of spectroscopic properties of the 4f and 5f ions in several groups, we have considered those di-, tri-, and tetravalent ions collected in Table 2.

It should be pointed out that for some divalent ions, due to a particular order in filling the electron shells, the ground state configuration is not of pure f character, but contains one 5d (Gd²⁺) or 6d electron (Ac²⁺, Th²⁺, Pa²⁺, U²⁺, Np²⁺, Cm²⁺). However, the difference between the ground states of these “mixed f–d” and “pure f” configurations is not large. For example, for Gd²⁺, it is about 2400 cm^{−1} [21]. So, being based on this fact, on one hand, and

for the sake of consistency, on the other hand, we consider only pure f configurations for all ions studied in the present paper.

3. Results of calculations: relations between the main spectroscopic parameters for free di-, tri- and tetravalent 4f/5f ions and atomic number Z

The numerical values of the Slater parameters F^2 , F^4 , F^6 and spin-orbit interaction constant ζ_f were calculated by us using the suite of the Cowan programs [17] with relativistic effects taken into account. It should be noted here that there can exist certain discrepancy between the experimentally deduced parameters of the Hamiltonian (1) as reported in various literature sources; the difference can be about 10–20% [20]. As a rule, the Hartree–Fock calculated Slater parameters (and thus, the Racah parameters as well) are somewhat overestimated with respect to those ones, which may be deduced from the experimental spectra; the overall observation is that $F_{\text{exp}}^k \approx 0.8F_{\text{HF}}^k$, $\zeta_{\text{exp}} \approx 0.9\zeta_{\text{HF}}$ [20]. These scaling coefficients can be introduced, if necessary; they do not question the validity of the obtained results, and we did not use them in our analysis. All parameters calculated in the present work are collected in Table 3.

Figs. 1 and 2 show the variation of the F^2 , F^4 , F^6 parameters against the atomic number Z in the considered groups of ions. As can be easily seen from both figures, all three parameters excellently follow the linear trend of the form $F^k(k = 2, 4, 6) = a_1 + a_2Z$. The values of the a_1 , a_2 coefficients obtained after a linear fit of the calculated data points are all collected in Table 4. It can be noticed that the absolute values of the a_1 , a_2 coefficients all decrease in the “ $F^2 \rightarrow F^4 \rightarrow F^6$ ” and “divalent–trivalent–tetravalent ions” directions for both 4f and 5f groups. The strongest dependence of the Slater parameters on Z in each of the di-, tri- and tetravalent ions’ groups is realized for the F^2 parameter; the weakest – for the F^6 parameter. If the 4f and 5f ions are compared, then the Slater parameters also behave in a similar way: the a_2 coefficient is the greatest for the F^2 parameter, and the difference between the a_2 coefficients for the 4f and 5f ions decreases when moving in the “ $F^2 \rightarrow F^4 \rightarrow F^6$ ” direction.

Moreover, it is possible to reduce further the number of the independent electrostatic parameters by considering the so called hydrogenic ratios F^4/F^2 and F^6/F^2 [22] (assuming that the 4f (or 5f) radial wave function is the hydrogen-like one).

Fig. 3 shows these calculated ratios for all considered series of isovalent ions. The F^4/F^2 and F^6/F^2 ratios are pretty constant across the considered groups, very slightly depending on the atomic number. In Fig. 3 we give the averaged values of those hydrogenic ratios for each group. Thus, for the di-, tri- and tetravalent 4f ions $\langle F^4/F^2 \rangle = 0.622, 0.626, 0.629$; $\langle F^6/F^2 \rangle = 0.446, 0.450, 0.453$, respectively. For the di-, tri- and tetravalent 5f elements, we obtained the following values: $\langle F^4/F^2 \rangle = 0.646, 0.652, 0.656$; $\langle F^6/F^2 \rangle = 0.471, 0.478, 0.482$, correspondingly.

As far as the SO constant ζ variation is concerned, it is a well-established fact that it grows linearly with the fourth power of the atomic number $\zeta \sim Z^4$. In other words, a plot of $\zeta^{1/4}$ against Z should be a straight line, as confirmed by Fig. 4. The derived linear equations for $\zeta^{1/4}$ (measured then in cm^{−1/4}) are as follows (Z^* denotes an effective nuclear charge):

divalent 4f : $\zeta^{1/4}$

$$= (-6.39991 \pm 0.17977) + (0.19556 \pm 0.00283)Z \\ = 0.19556(Z - 32.73) = 0.19206Z^*$$

trivalent 4f : $\zeta^{1/4}$

$$= (-5.43241 \pm 0.09300) + (0.18275 \pm 0.00144)Z \\ = 0.18275(Z - 29.73) = 0.18275Z^*$$

Table 2

Atomic numbers and electron configurations for the considered di-, tri- and tetravalent 4f and 5f ions. The ground state configurations (if different) are given in the parentheses.

Atomic number Z	Symbol	Divalent	Trivalent	Tetravalent
<i>Electron configuration 4fⁿ</i>				
57	La	4f ¹	–	–
58	Ce	4f ²	4f ¹	–
59	Pr	4f ³	4f ²	4f ¹
60	Nd	4f ⁴	4f ³	4f ²
61	Pm	4f ⁵	4f ⁴	4f ³
62	Sm	4f ⁶	4f ⁵	4f ⁴
63	Eu	4f ⁷	4f ⁶	4f ⁵
64	Gd	4f ⁸ (4f ⁷ 5d)	4f ⁷	4f ⁶
65	Tb	4f ⁹	4f ⁸	4f ⁷
66	Dy	4f ¹⁰	4f ⁹	4f ⁸
67	Ho	4f ¹¹	4f ¹⁰	4f ⁹
68	Er	4f ¹²	4f ¹¹	4f ¹⁰
69	Tm	4f ¹³	4f ¹²	4f ¹¹
70	Yb	4f ¹⁴	4f ¹³	4f ¹²
71	Lu	–	4f ¹⁴	4f ¹³
<i>Electron configuration 5fⁿ</i>				
89	Ac	5f ¹ (6d ¹)	–	–
90	Th	5f ² (6d ²)	5f ¹	–
91	Pa	5f ³ (5f ² 6d)	5f ²	5f ¹
92	U	5f ⁴ (5f ³ 6d)	5f ³	5f ²
93	Np	5f ⁵ (5f ⁴ 6d)	5f ⁴	5f ³
94	Pu	5f ⁶	5f ⁵	5f ⁴
95	Am	5f ⁷	5f ⁶	5f ⁵
96	Cm	5f ⁸ (5f ⁷ 6d)	5f ⁷	5f ⁶
97	Bk	5f ⁹	5f ⁸	5f ⁷
98	Cf	5f ¹⁰	5f ⁹	5f ⁸
99	Es	5f ¹¹	5f ¹⁰	5f ⁹
100	Fm	5f ¹²	5f ¹¹	5f ¹⁰
101	Md	5f ¹³	5f ¹²	5f ¹¹
102	No	5f ¹⁴	5f ¹³	5f ¹²
103	Lr	–	5f ¹⁴	5f ¹³

Table 3
Calculated energy parameters (in cm^{-1}), radial integrals (in \AA^k) and first-ionization energies (in eV) of the f^N configurations for the considered di-, tri- and tetravalent 4f and 5f ions.

Ion	La ²⁺	Ce ²⁺	Pr ²⁺	Nd ²⁺	Pm ²⁺	Sm ²⁺	Eu ²⁺	Gd ²⁺	Tb ²⁺	Dy ²⁺	Ho ²⁺	Er ²⁺	Tm ²⁺	Yb ²⁺	
4f ^N	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
E_{avg}	940	10,238	25,915	39,478	50,221	67,310	94,022	72,092	59,295	51,817	38,122	18,200	3726	0	
F^2	–	80,374	85,636	90,328	94,615	98,622	102,408	106,014	109,486	112,834	116,084	119,256	122,343	125,372	
F^4	–	49,798	53,142	56,116	58,825	61,352	63,734	65,999	68,176	70,271	72,303	74,283	76,208	78,095	
F^6	–	35,647	38,065	40,212	42,167	43,989	45,705	47,335	48,901	50,408	51,867	53,290	54,672	56,026	
ζ_f	470	580	698	825	960	1106	1264	1433	1615	1810	2019	2244	2484	2740	
r^2	0.5704	0.5041	0.4469	0.4038	0.3699	0.3419	0.3184	0.2984	0.2809	0.2653	0.2516	0.2393	0.2282	0.2181	
r^4	0.8618	0.6821	0.5366	0.4398	0.3711	0.3193	0.2792	0.2473	0.2212	0.1997	0.1815	0.1661	0.1529	0.1415	
r^6	2.6921	1.9440	1.3713	1.0301	0.8085	0.6548	0.5433	0.4598	0.3953	0.3445	0.3037	0.2703	0.2431	0.2200	
E_i	19.558	20.468	21.733	22.794	23.694	24.473	25.148	25.731	26.241	26.678	27.055	27.380	27.646	27.869	
4f ^N	La ³⁺	Ce ³⁺	Pr ³⁺	Nd ³⁺	Pm ³⁺	Sm ³⁺	Eu ³⁺	Gd ³⁺	Tb ³⁺	Dy ³⁺	Ho ³⁺	Er ³⁺	Tm ³⁺	Yb ³⁺	Lu ³⁺
E_{avg}	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
F^2	–	1378	12,709	30,985	46,244	58,030	76,814	105,850	80,893	66,373	57,825	42,459	20,393	4359	0
F^4	–	–	96,681	100,645	104,389	107,971	111,416	114,742	117,981	121,132	124,214	127,240	130,201	133,119	135,996
F^6	–	–	60,533	63,030	65,383	67,630	69,786	71,865	73,886	75,850	77,768	79,650	81,489	83,300	85,085
ζ_f	–	689	808	937	1075	1225	1387	1561	1749	1950	2165	2396	2643	2906	3187
r^2	–	0.3724	0.3472	0.3215	0.2999	0.2812	0.2648	0.2504	0.2374	0.2258	0.2153	0.2057	0.1969	0.1888	0.1814
r^4	–	0.3156	0.2785	0.2409	0.2113	0.1874	0.1678	0.1514	0.1375	0.1256	0.1154	0.1064	0.0986	0.0916	0.0855
r^6	–	0.5070	0.4300	0.3505	0.2918	0.2473	0.2123	0.1846	0.1620	0.1435	0.1281	0.1151	0.1042	0.0948	0.0866
E_i	–	38.510	39.164	40.423	41.534	42.530	43.421	44.219	44.941	45.584	46.163	46.685	47.140	47.548	47.910
4f ^N	Ac ⁴⁺	Pr ⁴⁺	Nd ⁴⁺	Pm ⁴⁺	Sm ⁴⁺	Eu ⁴⁺	Gd ⁴⁺	Tb ⁴⁺	Dy ⁴⁺	Ho ⁴⁺	Er ⁴⁺	Tm ⁴⁺	Yb ⁴⁺	Lu ⁴⁺	
E_{avg}	0	1	2	3	4	5	6	7	8	9	10	11	12	13	
F^2	–	1826	14,864	35,383	52,216	65,021	85,385	116,427	88,967	73,029	63,578	46,661	22,591	5048	
F^4	–	–	109,481	112,901	116,217	119,442	122,583	125,662	128,677	131,639	134,560	137,430	140,266	143,071	
F^6	–	–	69,009	71,147	73,217	75,226	77,180	79,093	80,965	82,801	84,611	86,387	88,142	89,875	
ζ_f	–	–	49,736	51,271	52,757	54,198	55,599	56,970	58,311	59,626	60,921	62,192	63,447	64,687	
r^2	–	913	1047	1190	1345	1512	1692	1885	2093	2315	2553	2806	3077	3365	
r^4	–	0.2876	0.2726	0.2568	0.2427	0.2301	0.2188	0.2085	0.1992	0.1906	0.1827	0.1754	0.1686	0.1623	
r^6	–	0.1746	0.1590	0.1424	0.1284	0.1165	0.1063	0.0974	0.0897	0.0829	0.0769	0.0715	0.0668	0.0625	
E_i	–	0.1916	0.1697	0.1456	0.1262	0.1105	0.0975	0.0867	0.0776	0.0699	0.0632	0.0575	0.0525	0.0481	
5f ^N	Ac ²⁺	Th ²⁺	Pa ²⁺	U ²⁺	Np ²⁺	Pu ²⁺	Am ²⁺	Cm ²⁺	Bk ²⁺	Cf ²⁺	Es ²⁺	Fm ²⁺	Md ²⁺	No ²⁺	
E_{avg}	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
F^2	–	1636	9354	21,752	32,802	42,253	56,642	71,912	59,772	53,162	48,586	37,347	20,725	7056	0
F^4	–	–	53,181	58,224	62,604	66,534	70,161	73,533	76,733	79,767	82,689	85,493	88,219	90,855	93,433
F^6	–	–	33,835	37,220	40,164	42,805	45,240	47,503	49,648	51,679	53,633	55,505	57,324	59,080	60,796
ζ_f	–	24,509	27,025	29,217	31,184	32,998	34,685	36,283	37,796	39,251	40,646	41,999	43,306	44,583	
r^2	818	1087	1356	1631	1914	2209	2516	2838	3175	3530	3906	4290	4704	5133	
r^4	1.4234	1.1504	0.9669	0.8404	0.7466	0.6732	0.6138	0.5645	0.5228	0.4870	0.4559	0.4284	0.4041	0.3822	
r^6	4.5026	2.9579	2.0678	1.5511	1.2170	0.9849	0.8171	0.6893	0.5906	0.5119	0.4484	0.3960	0.3526	0.3157	
E_i	26.2187	14.3456	8.4146	5.4809	3.8230	2.7931	2.1168	1.6469	1.3118	1.0628	0.8753	0.7299	0.6162	0.5248	
5f ^N	Ac ³⁺	Th ³⁺	Pa ³⁺	U ³⁺	Np ³⁺	Pu ³⁺	Am ³⁺	Cm ³⁺	Bk ³⁺	Cf ³⁺	Es ³⁺	Fm ³⁺	Md ³⁺	No ³⁺	Li ³⁺
E_{avg}	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14
F^2	–	2658	12,459	27,098	39,501	49,930	65,955	81,142	67,488	60,002	54,583	41,763	23,338	8117	0
F^4	–	–	65,387	69,091	72,526	75,769	78,840	81,792	84,622	87,370	90,028	92,626	95,153	97,635	100,058
F^6	–	–	42,303	44,790	47,094	49,268	51,324	53,298	55,187	57,021	58,792	60,521	62,200	63,848	65,456
ζ_f	–	–	30,883	32,737	34,455	36,076	37,607	39,078	40,486	41,851	43,169	44,456	45,705	46,931	48,126
r^2	–	1329	1588	1860	2143	2440	2751	3078	3420	3780	4162	4553	4975	5411	5868
r^4	–	0.8614	0.7690	0.6903	0.6275	0.5755	0.5321	0.4945	0.4623	0.4338	0.4088	0.3862	0.3660	0.3478	0.3310
r^6	–	1.4303	1.1496	0.9261	0.7657	0.6447	0.5515	0.4773	0.4176	0.3684	0.3276	0.2930	0.2638	0.2386	0.2169
E_i	–	4.0689	2.9820	2.1695	1.6401	1.2745	1.0141	0.8210	0.6759	0.5630	0.4748	0.4040	0.3472	0.3004	0.2618
5f ^N	Th ⁴⁺	Pa ⁴⁺	U ⁴⁺	Np ⁴⁺	Pu ⁴⁺	Am ⁴⁺	Cm ⁴⁺	Bk ⁴⁺	Cf ⁴⁺	Es ⁴⁺	Fm ⁴⁺	Md ⁴⁺	No ⁴⁺	Li ⁴⁺	
E_{avg}	0	1	2	3	4	5	6	7	8	9	10	11	12	13	
F^2	–	–	3624	15,230	31,862	45,583	57,071	74,847	89,448	74,777	66,664	60,424	46,190	25,980	9237
F^4	–	–	–	74,359	77,494	80,497	83,371	86,158	88,849	91,478	94,033	96,541	98,990	101,402	103,764
F^6	–	–	–	48,597	50,695	52,702	54,621	56,480	58,272	60,022	61,720	63,386	65,010	66,609	68,173
ζ_f	–	–	–	35,658	37,222	38,718	40,148	41,533	42,867	44,170	45,433	46,672	47,879	49,068	50,229
r^2	–	–	1812	2083	2369	2669	2985	3317	3665	4031	4421	4819	5249	5693	6158
r^4	–	–	0.6514	0.5995	0.5519	0.5116	0.4769	0.4464	0.4198	0.3960	0.3747	0.3554	0.3380	0.3220	0.3075
r^6	–	–	0.7625	0.6508	0.5532	0.4764	0.4150	0.3647	0.3232	0.2883	0.2589	0.2335	0.2117	0.1928	0.1763
E_i	–	–	1.4563	1.1640	0.9183	0.7385	0.6041	0.5007	0.4203	0.3562	0.3048	0.2626	0.2282	0.1994	0.1754
	–	–	44.371	45.817	47.775	49.639	51.402	53.101	54.719	56.286	57.786	59.244	60.642	62.004	63.313

tetravalent 4f : $\zeta^{1/4}$

$$= (-4.86638 \pm 0.05956) + (0.17606 \pm 0.00009)Z$$

$$= 0.17606(Z - 27.64) = 0.17606Z^*$$

divalent 5f : $\zeta^{1/4}$

$$= (-14.97853 \pm 0.69153) + (0.23113 \pm 0.00723)Z$$

$$= 0.23113(Z - 64.81) = 0.23113Z^*$$

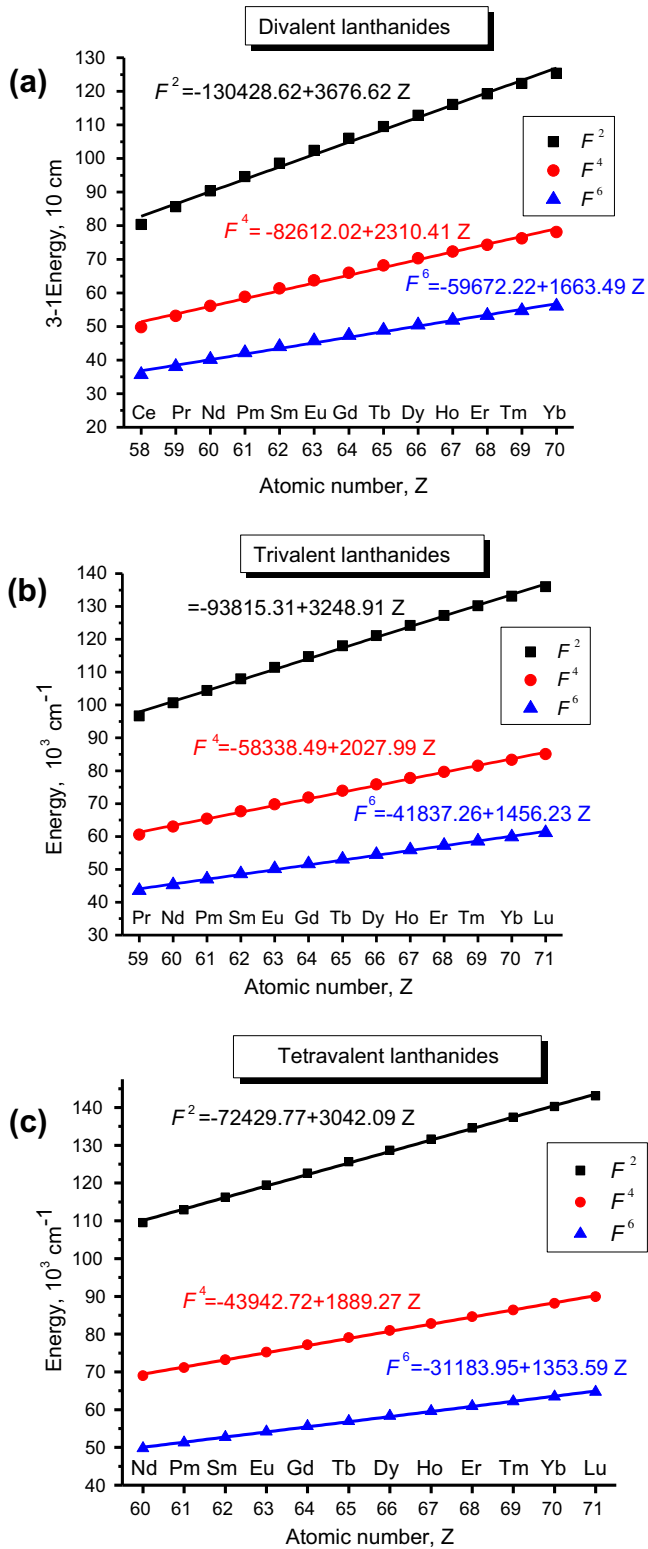


Fig. 1. Dependence of the F^2 , F^4 , F^6 parameters on the atomic number for the divalent (a), trivalent (b) and tetravalent (c) 4f ions.

trivalent 5f : $\zeta^{1/4}$

$$= (-12.35019 \pm 0.36986) + (0.20563 \pm 0.00383)Z$$

$$= 0.20563(Z - 60.06) = 0.20563Z^*$$

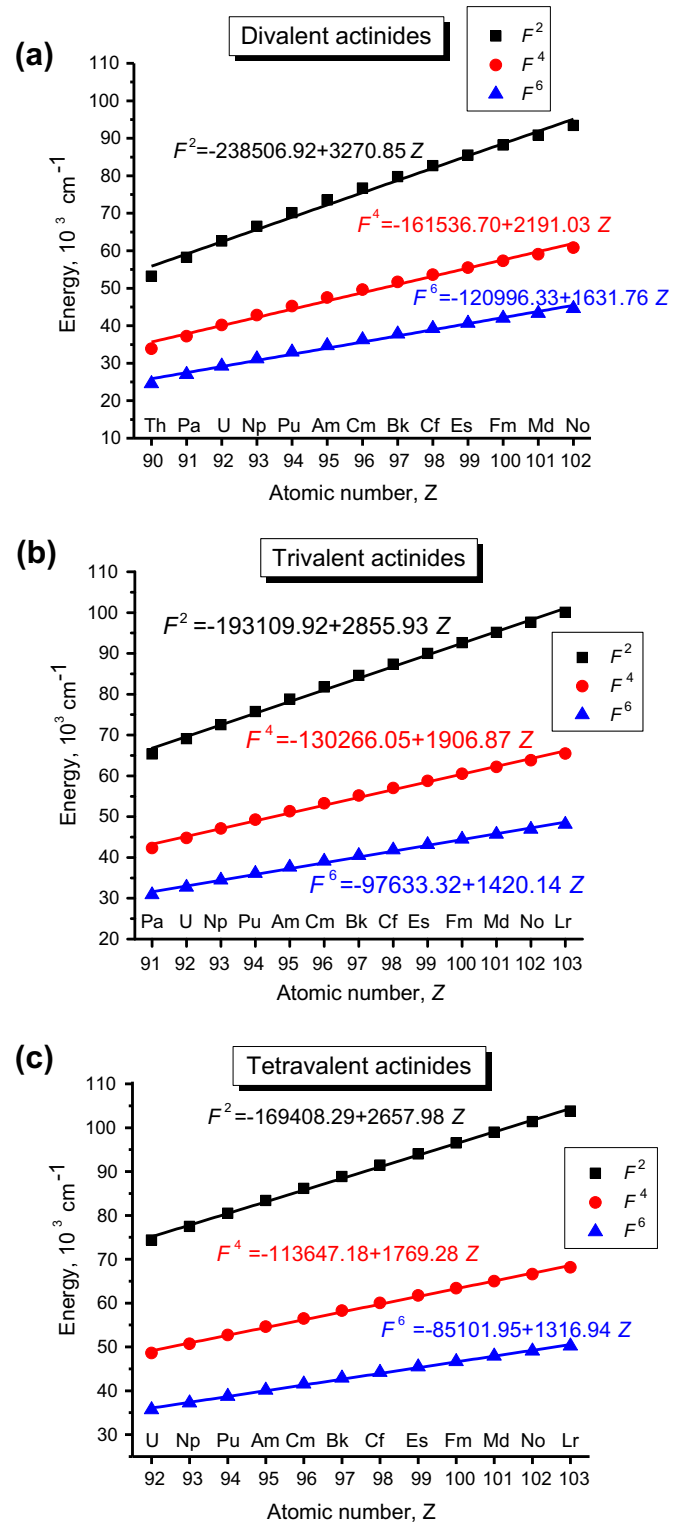


Fig. 2. Dependence of the F^2 , F^4 , F^6 parameters on the atomic number for the divalent (a), trivalent (b) and tetravalent (c) 5f ions.

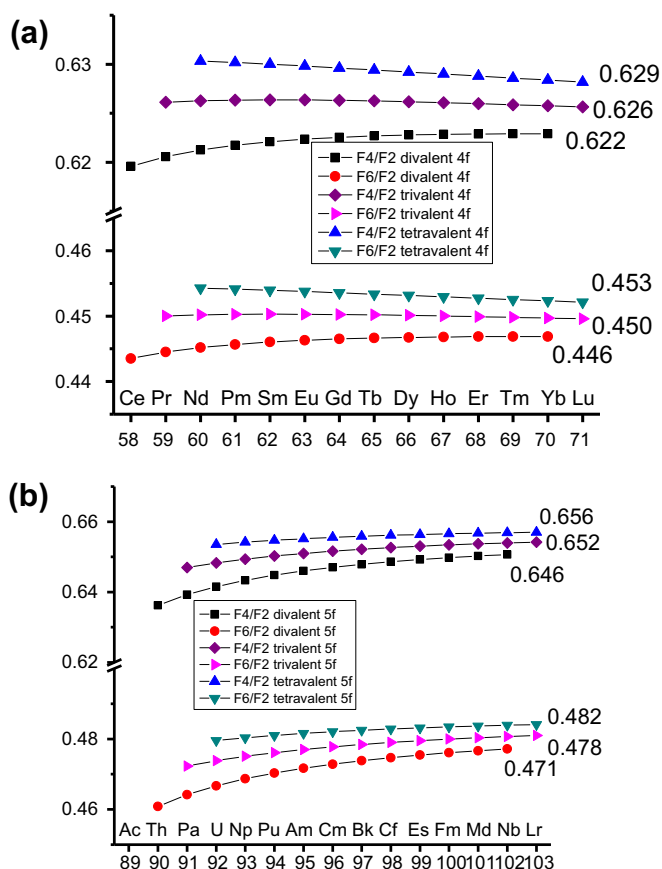
tetravalent 5f : $\zeta^{1/4}$

$$= (-10.97840 \pm 0.24443) + 0.19305 \pm 0.00252 Z$$

$$= 0.19305(Z - 56.87) = 0.19305Z^*$$

Table 4Linear approximations $a_1 + a_2Z$ of the Slater parameters F^2 , F^4 and F^6 as functions of the atomic number Z .

		4f ions		5f ions	
		a_1, cm^{-1}	$a_2, \text{cm}^{-1}/\text{at.number}$	a_1, cm^{-1}	$a_2, \text{cm}^{-1}/\text{at.number}$
Divalent ions	F^2	$-130,428.62 \pm 3676.62$	3676.62 ± 89.23	$-238,506.92 \pm 9350.29$	3270.85 ± 97.32
	F^4	$-82,612.02 \pm 3737.27$	2310.41 ± 58.30	$-161,536.70 \pm 6360.04$	2191.03 ± 66.20
	F^6	$-59,672.22 \pm 2728.48$	1663.49 ± 42.56	$-120,996.33 \pm 4734.37$	1631.76 ± 49.28
Trivalent ions	F^2	$-93,815.31 \pm 3248.91$	3248.91 ± 46.12	$-193,109.92 \pm 5193.31$	2855.93 ± 53.50
	F^4	$-58,338.49 \pm 1969.81$	2027.99 ± 30.25	$-130,266.05 \pm 3575.50$	1906.87 ± 36.83
	F^6	$-41,837.26 \pm 1440.70$	1456.23 ± 22.13	$-97,633.32 \pm 2681.56$	1420.14 ± 27.62
Tetravalent ions	F^2	$-72,429.77 \pm 1900.76$	3042.09 ± 28.98	$-169,408.29 \pm 3488.87$	2667.98 ± 35.76
	F^4	$-43,942.72 \pm 1248.61$	1889.27 ± 19.04	$-113,647.18 \pm 2412.12$	1769.28 ± 24.72
	F^6	$-31,183.951 \pm 912.90$	1353.59 ± 13.92	$-85,101.95 \pm 1819.53$	1316.94 ± 18.65

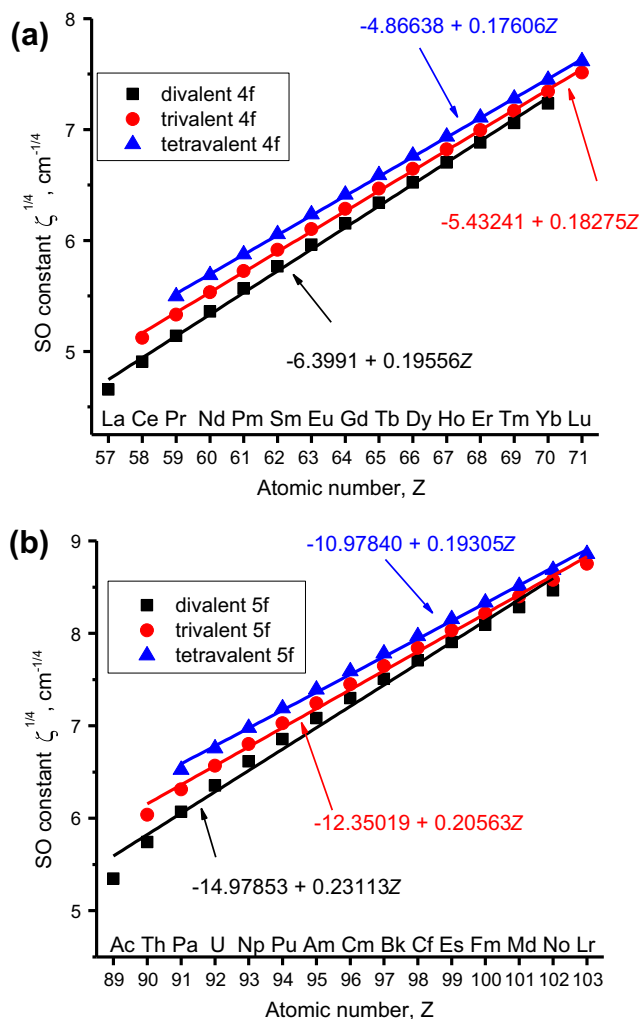
**Fig. 3.** Dependence of the F^4/F^2 and F^6/F^2 ratios on the atomic number for the divalent, trivalent and tetravalent 4f (a) and 5f (b) ions. The lines are the guides to the eye only. The averaged values of the ratios are given in the figure.

Again, the slopes of these linear dependences all decrease when increasing the ions' oxidation state. It can be observed that the $\zeta^{1/4}$ dependence for the 5f ions is steeper than for the 4f ones.

Since the F^2 , F^4 and F^6 parameters and the SO constant $\zeta^{1/4}$ are proportional to the atomic number Z , they should be also proportional to each other, as is evidenced by Fig. 5. The linear relations between them are given below. All calculated results are expressed in cm^{-1} ; the coefficient before $\zeta^{1/4}$ is measured in $\text{cm}^{-3/4}$.

Divalent 4f ions:

$$\begin{aligned} F^2 &= (-12522.97 \pm 1443.08) + (19173.54 \pm 234.08)\zeta^{1/4} \\ F^4 &= (-8528.79 \pm 978.11) + (12050.29 \pm 158.66)\zeta^{1/4} \\ F^6 &= (-6334.88 \pm 723.06) + (8676.59 \pm 117.28)\zeta^{1/4} \end{aligned} \quad (3)$$

**Fig. 4.** Linear dependencies of the $\zeta^{1/4}$ value on the atomic number for the di-, tri- and tetravalent 4f (a) and 5f (b) ions.

Trivalent 4f ions:

$$\begin{aligned} F^2 &= (1563.49 \pm 858.78) + (17953.47 \pm 132.41)\zeta^{1/4} \\ F^4 &= (1193.84 \pm 588.48) + (11207.31 \pm 90.74)\zeta^{1/4} \\ F^6 &= (909.56 \pm 437.00) + (8047.71 \pm 67.38)\zeta^{1/4} \end{aligned} \quad (4)$$

Tetravalent 4f ions:

$$\begin{aligned} F^2 &= (10878.51 \pm 586.41) + (17390.82 \pm 87.60)\zeta^{1/4} \\ F^4 &= (7793.47 \pm 403.93) + (10800.70 \pm 60.34)\zeta^{1/4} \\ F^6 &= (5882.61 \pm 300.08) + (7738.37 \pm 44.82)\zeta^{1/4} \end{aligned} \quad (5)$$

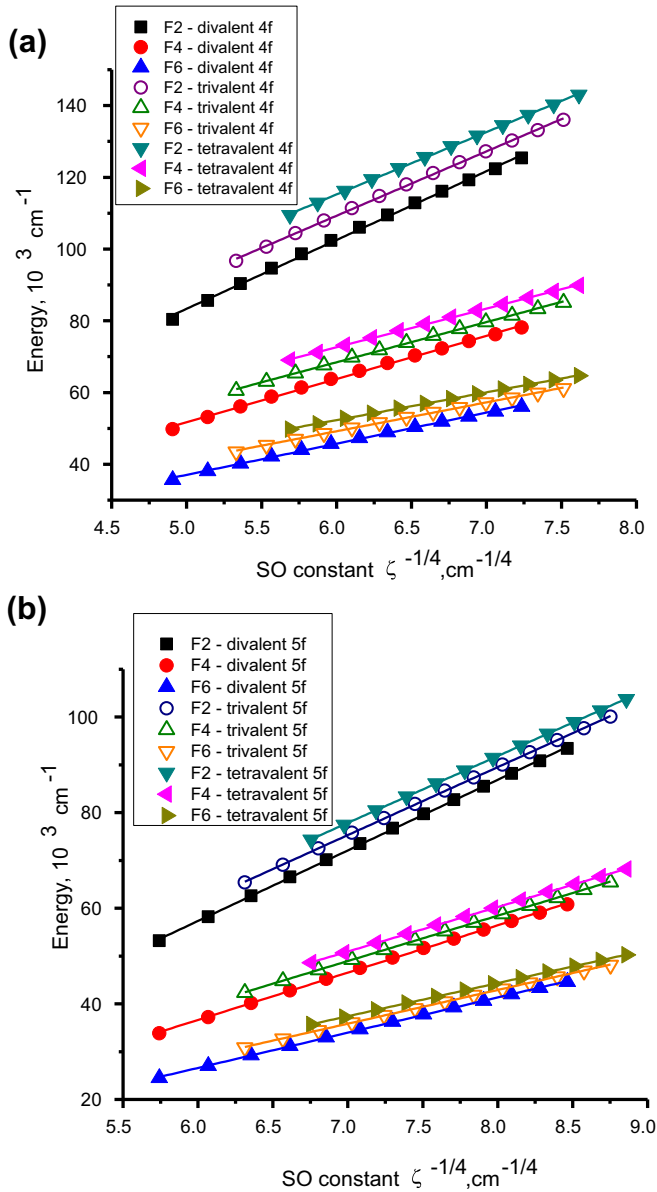


Fig. 5. Dependence of the calculated F^2 , F^4 and F^6 parameters on the $\zeta^{1/4}$ value for the di-, tri- and tetravalent 4f (a) and 5f (b) ions. The straight lines are the linear fits, whose equations can be found in the text.

Divalent 5f ions:

$$\begin{aligned} F^2 &= (-31271.26 \pm 487.73) + (14769.30 \pm 367.03)\zeta^{1/4} \\ F^4 &= (-22725.27 \pm 360.42) + (9894.71 \pm 49.53)\zeta^{1/4} \\ F^6 &= (-17617.14 \pm 36.85) + (7368.99 \pm 36.85)\zeta^{1/4} \end{aligned} \quad (6)$$

Trivalent 5f ions:

$$\begin{aligned} F^2 &= (-24154.33 \pm 284.80) + (14210.35 \pm 37.27)\zeta^{1/4} \\ F^4 &= (-17463.93 \pm 232.40) + (9489.05 \pm 30.41)\zeta^{1/4} \\ F^6 &= (-13625.38 \pm 180.48) + (7067.13 \pm 23.62)\zeta^{1/4} \end{aligned} \quad (7)$$

Tetravalent 5f ions:

$$\begin{aligned} F^2 &= (-20023.65 \pm 213.43) + (13984.44 \pm 27.10)\zeta^{1/4} \\ F^4 &= (-14214.10 \pm 179.65) + (9309.26 \pm 22.81)\zeta^{1/4} \\ F^6 &= (-11091.25 \pm 143.93) + (6929.39 \pm 18.27)\zeta^{1/4} \end{aligned} \quad (8)$$

Therefore, if one out of four parameters (F^2 , F^4 , F^6 , or ζ) is known for any of the di-, tri- or tetravalent 4f (5f) ions, the remaining

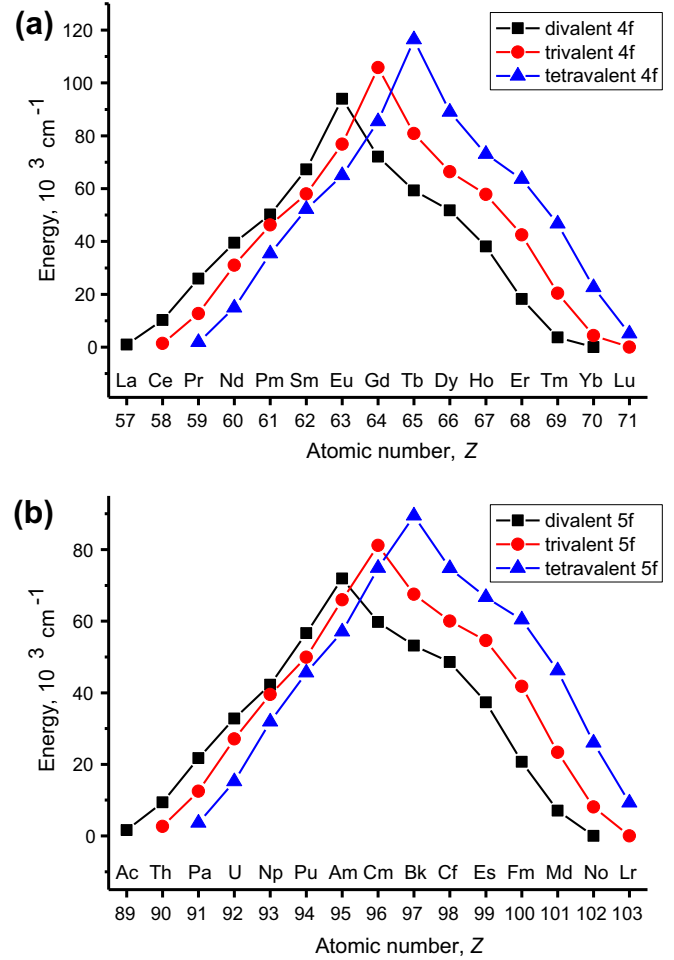


Fig. 6. Calculated barycenter energies E_{avg} of the $4f^n$ (a) and $5f^n$ (b) electron configurations.

three parameters for that ion can all be reliably estimated using the above given linear equations and hydrogenic ratios.

The non-energetical quantities calculated in the present work are the moments of the electron density of the f-electrons for all considered ions, they were found in a standard and a straightforward way by a numerical integration of the following expression:

$$\langle r^k \rangle = \int_0^\infty r^{k+2} |R_{nf}(r)|^2 dr, \quad (9)$$

where $k = 2, 4, 6$; $R_{nf}(r)$ is the corresponding radial wave function with n being a principal quantum number (4 or 5), and f corresponds to the orbital quantum number $l = 3$ for f-electrons. The data given in Table 3 show that the $\langle r^k \rangle$ values systematically decrease with increase of atomic number and oxidation state; the obtained results can be used for calculations of the parameters of crystal field acting upon the 4f and 5f ions in crystals. Considering the decreasing dependence of $\langle r^k \rangle$ related to crystal-field parameters, one can easily conclude that the crystal-field effects on the f electrons should exhibit a decreasing trend across the considered nf series (provided the interatomic distances are kept constant and only the central f ion is changed).

4. Results of calculations: barycenters of the $4f^n$ and $5f^n$ electron configurations

The barycenter energies E_{avg} of all considered f^n electron configurations were calculated by employing the f-shell programs of Reid with the obtained Slater and SO parameter values. The obtained

results are listed in Table 3 and plotted in Fig. 6. There is a characteristic “A-shape”, which is preserved for all considered electron configurations, with the maximal energy E_{avg} achieved for the ions in the middle of the considered series.

For the ions in the first half of the lanthanide and actinide series (before Gd and Cm) the barycenters of the divalent electronic configurations are higher than those of the tri- and tetravalent ones. For the ions following Gd and Cm, the order of the energies is changed and becomes (in the decreasing order): tetravalent–trivalent–divalent. A special case of the Gd and Cm ions is that the order of the barycenters is different from the described above: trivalent (the highest)–tetravalent (medium)–divalent (the lowest). It is also worthwhile noting that inside each group (di-, tri-, and tetravalent ions) the barycenter energy has a maximum value for the half-filled configurations, having 7 f-electrons.

A particular feature of the more-than-half filled electron shells with N electrons is that they can be treated as the “filled” shells with $14-N$ positive holes. As such, the number of states for the f^N and f^{14-N} configurations is equal and is decreasing when moving to the left and to the right from $N = 7$. This decrease of number of states would compress the overall splitting of the f states after going over half-filled electron configurations with $N = 7$. At the same time, it can be noted that the Coulomb interaction parameters and SO constant increase with increasing atomic number. Then, due to increased Hamiltonian parameters, the barycenters of the more-than-half filled configurations are higher than those ones of the conjugate less-than-half filled configurations, thus producing an asymmetric A-shape, as shown in Fig. 6.

An additional energetic characteristic of the considered electronic configurations is the first ionization energy, which is equal

to the energy needed to remove one f electron to convert, for example, a divalent ion into a trivalent one, a trivalent ion into a tetravalent one and so on. This energy has been also calculated (Table 3); it is plotted in Fig. 7 against the atomic number Z . As seen from Fig. 7, for both lanthanide and actinide ions this ionization energy E_i is a practically perfect linear function of the atomic number; the equations of the linear fits are all given in the graph.

The slope of these linear fits of the ionization energies increase with oxidation state (with moving to the ionization energies of higher order), and when moving from the 4f to the 5f ions. We could find the corresponding experimental energies for some ions from the considered group; these data were taken from the well-known web-site <http://www.webelements.com> and are shown in Fig. 7 by the open symbols. As can be seen from that figure, only for the lanthanides there is a complete set of the experimental data on the third and fourth ionization energies. No experimental data are available on the fifth ionization energy, except for Pr. Finally, the experimental ionization energies of the actinides were practically not found at all, except for the third and fourth ionization energies of Th. Overall agreement between the calculated and experimental ionization energies for lanthanides is good (Fig. 7), especially for the first half of the lanthanide series; it can be noticed that for the second half of this group there exists a small systematic overestimation of the calculated energy by about 4–5 eV, which may be related to the well-known overestimation of the Hartree–Fock calculated energies.

5. Conclusions

In the present paper we have given a systematic overview of the spectroscopic parameters of the di-, tri- and tetravalent lanthanide and actinide ions in a free state. We have calculated the Slater parameters F^2 , F^4 and F^6 for all ions in the considered series; these parameters were shown to increase linearly with the atomic number Z . The value of $\zeta^{1/4}$ (where ζ is the SO constant) grows linearly with Z . It has been also demonstrated that the hydrogenic ratios F^4/F^2 and F^6/F^2 remain practically constant within each group of the considered ions.

We also found a linear relation between the F^2 , F^4 and F^6 parameters and $\zeta^{1/4}$. As a main outcome of all these calculations, it turns out to be possible to evaluate all considered parameters using the linear expressions derived in the present paper, which significantly reduces the number of the independent parameters in the free ion Hamiltonian. In other words, knowledge of the atomic number Z and oxidation state of a particular ion from the considered groups is sufficient to restore all four parameters F^2 , F^4 , F^6 and ζ . We also mention that the reported here values of all calculated parameters can be used for crystal field analysis of energy levels of the considered 4f and 5f ions in crystals and/or glasses.

Important energetic characteristics of the considered electron configurations – energy barycenters and third, fourth, and fifth ionization energies – have been all calculated for the considered electronic configurations. The graphs of these quantities against the atomic number revealed that the first one has a clearly-pronounced “A-shape”, reaching its maximum for the configurations with 7 f-electrons (half-filled f-shell), whereas the second one increases monotonically and linearly across the considered series. Comparison of the calculated and experimental (if available) ionization energies yielded good agreement.

As a future prospect and development of the presented in this paper results, we mention that they can be readily applied to the crystal field calculations of energy level splittings of the f^N configurations, because the relations between the Coulomb interaction parameters, SO constants and atomic numbers remain valid for various crystals, as was shown for 4f ions in elpasolites [15] and

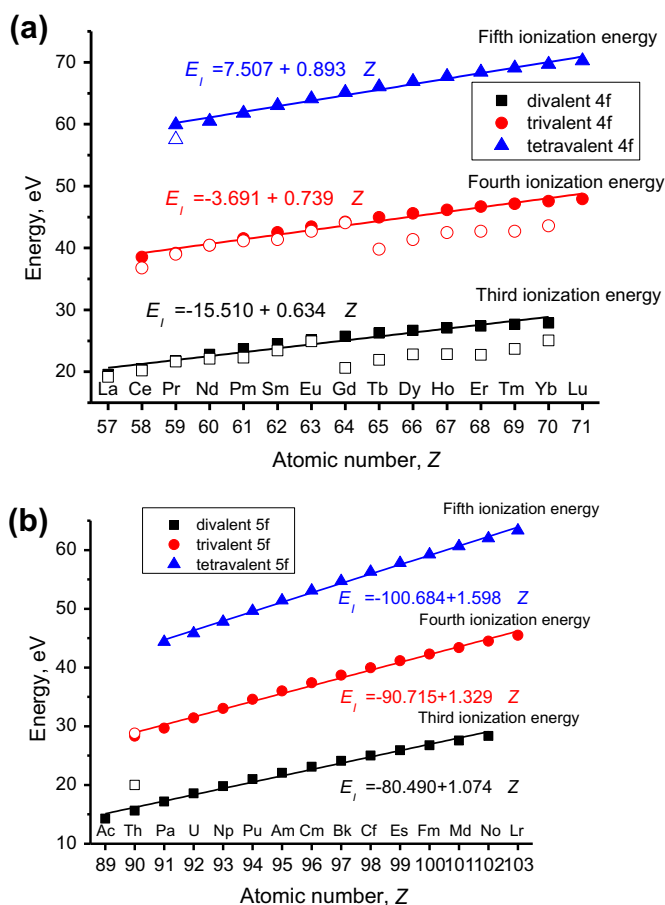


Fig. 7. Calculated first ionization energies E_i for the $4f^N$ (a) and $5f^N$ (b) electron configurations. Experimental data (if available) are shown by empty symbols.

3d ions in garnets [18]. More application-related results based on the developed approach are going to be reported soon by us.

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