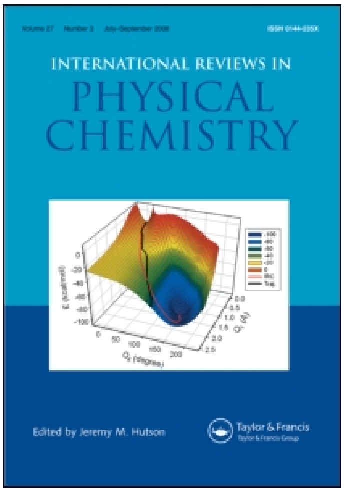

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Regularities in *f*-element properties

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A review of the regularities in various lanthanide and actinide properties considered as functions of atomic number is given. The regularities, which have been called the tetrad or the double–double effect, are due to symmetry of the *f*-shell and can be conveniently depicted with the use of the expression for the ground energy term in the Racah representation. The tetrad effect has its lower and upper boundaries, imposing certain restrictions on the relative changes in the Racah parameters. Since the tetrad effect in stability constants depends on the magnitude of the nephelauxetic effect, the region of the possible relative nephelauxetic changes of Racah parameters is also presented. The regularities serve as a basis for a semiempirical approach for determination of ionic radii, $f^q \to f^{q-1}d$ transition energies, oxidation potentials and other properties of the lanthanides and actinides. In connection with the regularities in $f^q \to f^{q-1}d$ transition energies and oxidation potentials, the relative stabilities of various valence states of the *f*-elements are considered.

1. Introduction

When dealing with various physical and chemical properties of the lanthanides and actinides, one faces the fact that often the properties behave regularly if regarded as functions of the atomic number *z*, or of the number of *f*-electrons *q*. For example the plots of ionization energies, $f^q \to f^{q-1}d$ transitions, and oxidation potentials, which have similar patterns, can be divided into two analogous parts with a minimum at the beginning, a maximum at the end, and some kind of a 'plateau' in the middle (see figure 1). The discontinuity in the middle of the plot is the well known half-filled-shell effect. In the literature such dependence is sometimes called 'irregularities' or 'quasi-irregularities', but we shall rather use the term 'regularity', having in mind the apparent symmetry of the plot.

It was found that beside the half-filled-shell effect, some lanthanide and actinide properties can exhibit also the one-quarter and three-quarters effects (Fidelis and Siekierski 1966, Peppard *et al.* 1969). In their study of the separation factor β for neighbouring Ln^{3+} ions, Fidelis and Siekierski (1966) revealed a regularity which can be depicted as shown in figure 2. Again the plot has a characteristic pattern with a distinct division into two similar parts. Beside the main division, a subdivision exists in each of the two parts, where two maxima and two minima occur. Since the separation factor β is connected with the standard free energy change ΔG^0 of the extraction process: $\Delta(\Delta G^0) = -RT\ln\beta$, where $\Delta(\Delta G^0) \equiv \Delta G^0_{z+1} - \Delta G^0_z$, an investigation of ΔG^0 was undertaken, which had shown that the regularities in the values of β displayed in figure 2 are caused by the regular variation of ΔG^0 with the atomic number *z*. The regular pattern of ΔG^0 is represented for Ln(III) in figure 3. Thus figure 2 reflects the variation of the difference between the adjacent values of ΔG^0 with *z*.

Siekierski (1971) and Siekierski and Fidelis (1972) worked on extensive experimental data to demonstrate that if lanthanide or actinide compounds are considered that have similar crystal structures, then the regularity resembling the one shown in figure 3 is

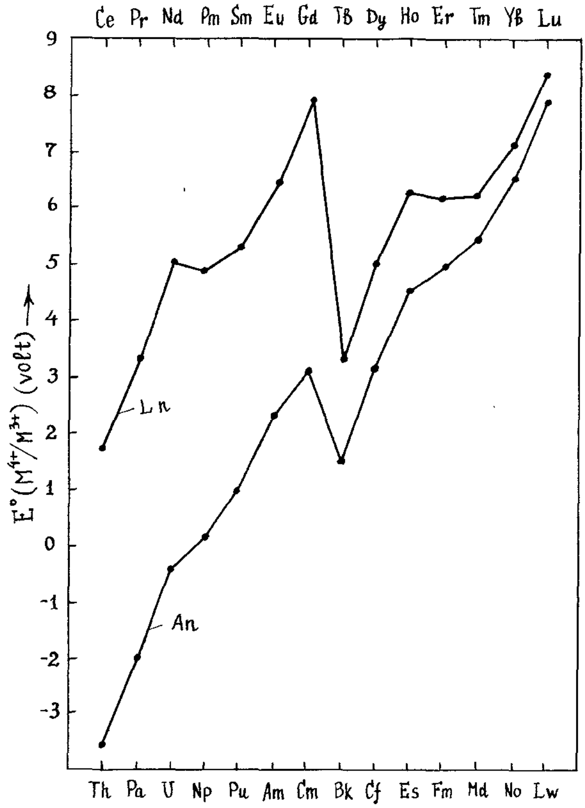

Figure 1. The standard oxidation potentials $E^0(M^{4+}/M^{3+})$ (relative to the normal hydrogen electrode) of the lanthanides and actinides. In the regions Nd–Pm–Sm and Ho–Er–Tm of the lanthanide series, two 'plateaus' occur. The tendency to form 'plateaus' is obvious also for the actinides in the regions U–Np–Pu and Es–Fm–Md.

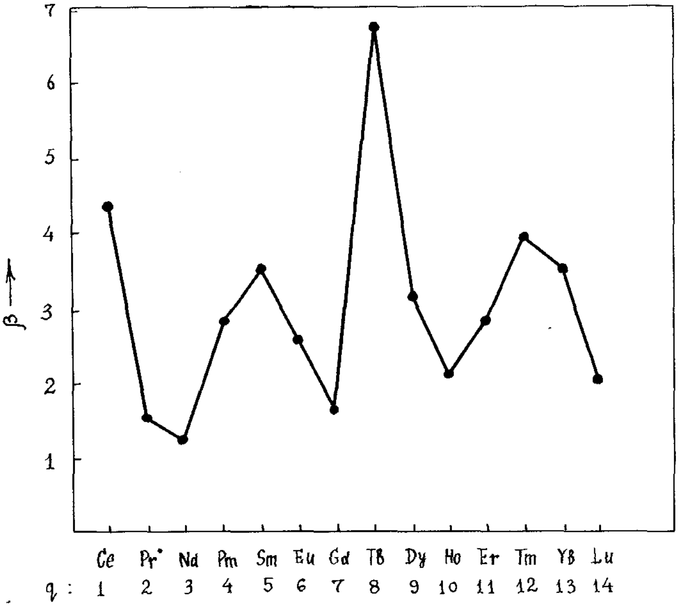

Figure 2. Variation of the separation factor β for neighbouring Ln(III) along the series (extraction with 2-ethylhexylphenyl phosphonic acid).

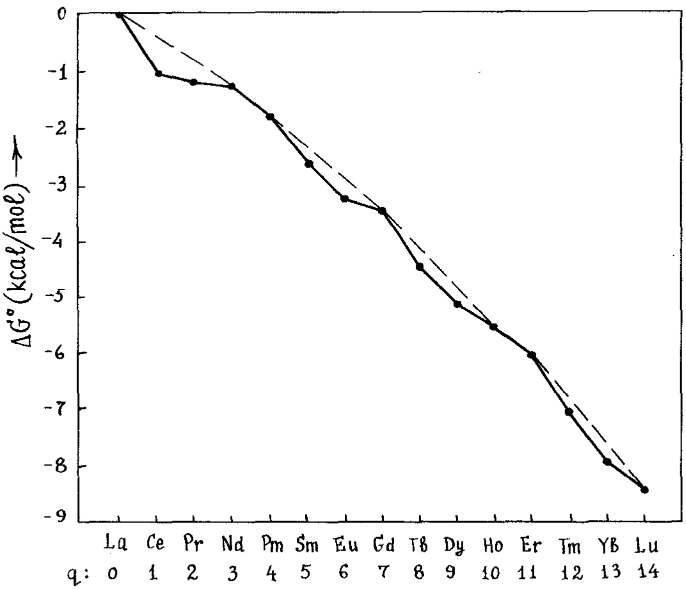

Figure 3. Variation of the respective standard free energy ΔG^0 of extraction for Ln(III) along the series (extraction with 2-ethylhexylphenyl phosphonic acid). The values of ΔG^0 are relative to ΔG^0 of La(III). The dashed lines facilitate distinguishing the regularity in ΔG^0.

also displayed by the lanthanide and actinide unit cell volumes, lattice constants and ionic radii. It should be stressed that the division of the plot of the lattice constant '*C*' versus *z* of the lanthanide sesquioxides into two similar parts by the break at gadolinium was discovered as far back as 1939 (Bommer 1939). The gadolinium discontinuity exists as well in the values of the ionic radii of Ln^{3+} given by Templeton and Dauben (1954). The studies of Siekierski (1971) and Siekierski and Fidelis (1972) revealed that, besides the singularity in the middle of the plot, a minute effect of departure from smooth convexity exists in both parts of the plots, which is usually obscured by experimental errors or by the non-existence of the same stable crystal structure for all members of the series.

The regularity similar to that shown in figure 3 was found also by Peppart *et al.* (1969, 1970) for the logarithm of the distribution ratio. It was shown that the corresponding plot for the trivalent lanthanides can be divided into four analogous parts. Each of the parts consists of four points and represents a 'tetrad'. Similar behaviour holds for the actinides in those regions of the series where the same stable valence form exists. Peppard *et al.* (1969) called this kind of a dependence 'the tetrad effect' and gave the following definition (Peppard *et al.* 1970):

> In systems involving all 15 lanthanides(III) the points on a plot of the logarithm of a suitable numerical measure of a given property of these elements versus *z* may be grouped through the use of four smooth curves without inflections into four tetrads with the gadolinium point being common to the second and third tetrads and the extended smooth curves intersecting additionally in the 60–61 and 67–68 regions.

The plots of the logarithm of the distribution ratio versus *z* for the trivalent lanthanides and actinides are shown in figure 4. Comparing the plots in figures 3 and 4, one can see that the tetrad effect for the logarithm of the distribution ratio may be represented by

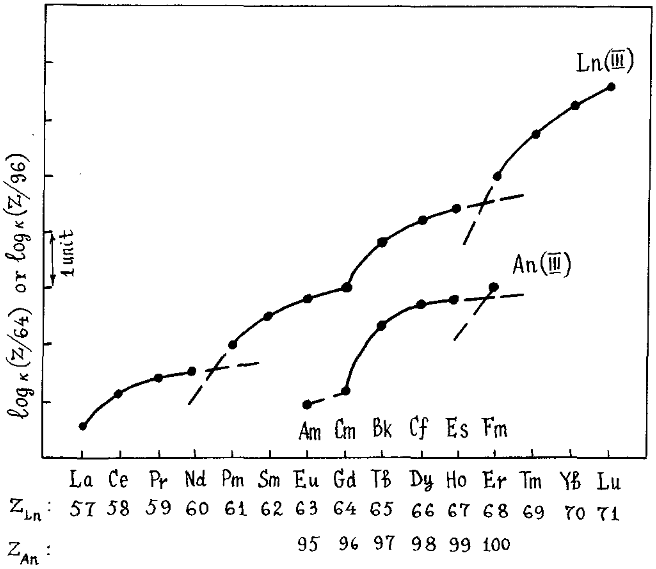

Figure 4. Variation along the series of the values of the logarithm of the distribution ratio κ for Ln(III) and An(III). The values of κ are counted from the value of the logarithm of the distribution ratio for the middle member of the corresponding series (extraction with 2-ethylhexyl phosphoric acid).

the 'turned-over' plot of ΔG^0. It is easy to understand, since the logarithm of the distribution ratio is proportional to $-\Delta G^0$. Along with the term 'the tetrad effect', the term 'the double–double effect' proposed by Fidelis and Siekierski (1971) is also used. We want to stress that actually two main types of regularities exist: the one depicted in figures 3 and 4, and the one demonstrated in figure 2. Though closely connected, they look totally different and should have different designations. To distinguish between the two types of regularities, we shall use the term 'the tetrad effect' for the regularity shown in figures 3 and 4, and the term 'the double–double effect effect' for the regularity shown in figure 2, where no tetrads can be allocated. The plots in figure 1 can be said to have degenerate double–double character, since the intermediate maxima and minima in both halves of the plots are changed by two plateaus.

Spitsyn *et al.* (1983 a) demonstrated that the 'graphic' definition of the tetrad effect given by Peppard *et al.* (1970) can be reformulated in terms of a system of inequalities. The tetrad effect for property A is equivalent to the system

$$\left.\begin{array}{lll} 2A_q-A_{q-1}-A_{q+1}<0\ (>0) & (i<q<i+3; i=0,4,7,11) \\ -2A_q+A_{q-1}+A_{q+1}<0\ (>0) & (i<q<i+3;\ i=2,9) \\ -2A_q+A_{q-1}+A_{q+1}<0\ (>0) & (q=7) \end{array}\right\} \qquad (1)$$

which also can be written in a more compact form

$$\Delta A_q-\Delta A_{q+1}\left\{\begin{array}{ll} <0\ (>0) & (i<q<i+3;\ i=0,4,7,11) \\ >0\ (<0) & (i<q<i+3;\ i=2,9) \\ >0\ (<0) & (q=7) \end{array}\right. \qquad (2)$$

where $\Delta A_q = A_q - A_{q-1}$. The subscript i marks the first point of each of the four tetrads, and q indicates two of their intermediate points. The first inequality expresses the fact that the intermediate points of all of the four tetrads simultaneously are below (or above) the line segments which connect the limiting points of the tetrads and provides a condition that the points of each tetrad lie on a 'curve without inflections'. The second inequality guarantees that inverse tetrads exist between the first and second, and the third and fourth tetrads (see figure 3), which is equivalent to 'intersecting of the extended smooth curves in the 60–61 and 67–68 regions'. The third inequality describes the break in the middle of the plot at $q=7$. The change of sign shown in parentheses in (1) and (2) leads to the inverse tetrad effect, as in figure 4. System (2) is equivalent to system (1) and clearly indicates that if property A satisfies the definition of the tetrad effect, then ΔA must exhibit the double–double effect (cf. figure 2).

The cause of the tetrad or double–double effect remained unidentified for some time. Fidelis (1970) pointed out the correlation of the effect with the ground term quantum number of the total orbital angular momentum L of the lanthanide and actinide ions in a fixed oxidation state (see figure 5). The quantum number L, along with the quantum number S of the total spin, defines the energy terms, which, in the Russell–Saunders approximation, characterizes the states of free atoms and ions. For the ground term of an ion with a pure f^q-configuration, L and S can be expressed through the number of f-electrons q as follows:

$$\left.\begin{aligned} L&=\frac{q(7-q)}{2} \\ S&=\frac{q}{2} \end{aligned}\right\}(q\leqslant 7) \qquad \left.\begin{aligned} L&=\frac{(14-q)(q-7)}{2} \\ S&=\frac{14-q}{2} \end{aligned}\right\}(q>7) \tag{3}$$

It is seen from (3) that for ions with a pure f^q-configuration both L and S have the same values for q and $14-q$ electrons in the f-shell ($q\leqslant 7$). This reflects the well-known

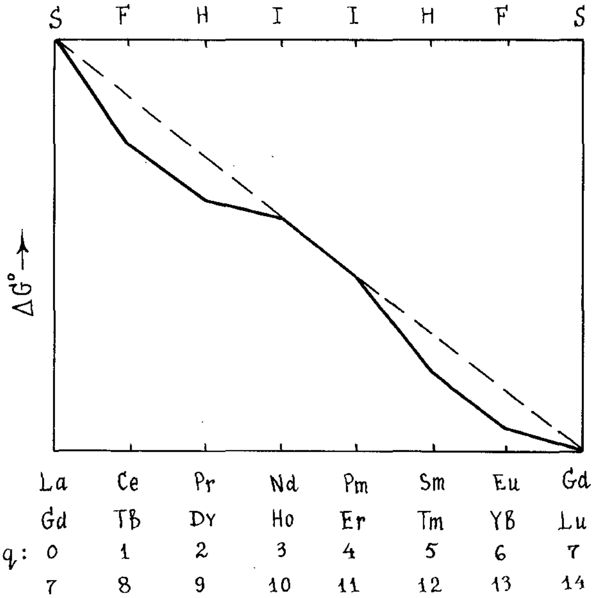

Figure 5. The idealized plot of the standard free energy ΔG^0 of complex formation, indicating a correlation of ΔG^0 with the quantum number of the total orbital angular momentum L.

principle of electron–hole symmetry of atomic shells. Beside electron–hole symmetry, there is additional symmetry for L, which has the same values for ions with q and $7-q(q \leqslant 7)$, and, consequently, with $14-q$ and $q+7(q \leqslant 7)$ f-electrons. Thus one can see that the tetrad effect displays the symmetry which the f-shell has in the Russell–Saunders approximation. The possibility of such a unique display of free-ion shell symmetry in properties of f-ions in compounds is due to the lanthanide and actinide contraction. The contraction involves localization of $4f$- and $5f$-electrons (the localization, though, is much less for $5f$- than for $4f$-electrons in the first half of the actinide series) and, thereby, the screening of these electrons by outer closed shells. This prevents $4f$- and $5f$-shells from being much perturbed by ligands and leaves L and S relatively good quantum numbers. Since energy terms, characterized by L and S, result from interelectronic repulsion of f-electrons, this interaction of f-electrons is responsible for generation of the tetrad effect in various characteristics of the lanthanides and actinides and their compounds. The conclusion about the source of the tetrad (or double–double) effect can also be drawn from the similarity of the double–double plot shown in figure 2 with the plot shown in figure 1, for interelectronic repulsion of f-electrons is known to be the cause of the regular pattern of the latter plot (see, for example, Jørgensen 1962 a, Johnson 1969). These qualitative arguments lead up to the theory of the tetrad effect in the properties characterizing extraction processes which was presented independently by Jørgensen (1970) and Nugent (1970).

2. The theory of the tetrad effect

Let us consider the explanation of the tetrad effect given by Jørgensen (1970) and Nugent (1970) in more detail. The energy of a term resulting from interelectronic repulsion of f-electrons can be written either in Slater–Condon representation or in Racah representation, but for our purpose it is convenient to use the latter. Then the energy of a term is written as

$$\varepsilon = \sum_{n=0}^{3} e_n E^n \tag{4}$$

Here E^n are Racah parameters and e_n depends on quantum numbers. The immediate advantage of Racah representation is that $e_2 = 0$ for the values of S given by (3) (see, for example, Judd 1963). Another advantage is that the dependence of the ground energy term on L and S is separated in different coefficients e_n. The coefficients e_n for the ground energy term have the form (Judd 1963)

$$e_0 = \frac{q(q-1)}{2}; \quad e_1 = \begin{cases} 0 & (q \leqslant 7) \\ 9(q-7)(q>7) \end{cases}; \quad e_3 = 3\left[U - \frac{L(L+1)}{2}\right] \tag{5}$$

where L is defined by (3). U in (5) denotes a combination of some quantum numbers which has the same symmetry as L (see (3)). So it is sufficient to give the values of $U(q)$ only for $q = 0, 1, 2, 3$. From Judd (1963) we have

$$U(0)=0; \quad U(1)=6; \quad U(2)=12; \quad U(3)=14 \tag{6}$$

Thus with L defined by (3), $e_3(q)$ assumes the values: $e_3(0)=0$; $e_3(1)=0$; $e_3(2)=-9$; $e_3(3)=-21$. It is easy to verify by direct calculation that the expression for e_1 in (5) can be rewritten in the following way:

$$e_1 = \frac{18}{13} S\left(\frac{1}{2} - S\right) + \frac{9}{13}\frac{q(q-1)}{2}$$

where S is defined by (3). The second term in the right-hand side of the latter expression for e_1, being multiplied by E^1, can be combined in (4) with e_0E^0 to form a baricentre or a centre of gravity of the f^q-configuration (see Jørgensen 1962 b), with the baricentre parameter $E^B = E^0 + 9/13E^1$. The baricentre is used as a standard reference point for all energy terms of a configuration. The energy of the ground term counted from the baricentre is

$$E_{st} = k_1(S)E^1 + k_3(L)E^3 \tag{7}$$

where $k_1(S) = 18/13S(1/2 - S)$; $k_3 \equiv e_3$. The first term in (7) is what Jørgensen (1962 b) called "the spin-pairing energy". Since $k_1 \leqslant 0$, $k_3 \leqslant 0$, $E^1 > 0$, $E^3 > 0$, the ground term energy is non-posititive, indicating that the ground term is stabilized (hence st in E_{st}) relative to the baricentre when k_1 and k_3 (or one of them) are not zero. So the first term in (7) presents the effect which coupling of spins of f-electrons into the total spin S has on the stabilization. Analogously the second term in (7) expresses the effect of coupling of the orbital angular momenta of f-electrons into the total orbital angular momentum L. It is well known that for the lanthanides and actinides the influence of L and S coupling into the total angular momentum J, i.e. spin–orbit interaction, becomes increasingly important. We can take it into account approximately by adding the spin–orbit correction term in (4). Later it will be shown that the term does not contribute to the tetrad regularity, defined by (1).

Using the values of the Racah parameters E^1 and E^3 for the trivalent lanthanide and actinide aqua ions compiled in table 1 (parentheses indicate linear extrapolated values), and calculating the energy of the ground term E_{st} by equation (7), we can see that E_{st} satisfies the definition of the tetrad effect (1). The regularity in E_{st} values is generated by regular variation of k_1 and k_3, which in its turn is caused by repetitions of S, L and U values, defined by (3) and (6). For Racah parameters the approximate ratio $E^3/E^1 \approx 0{\cdot}1$ is valid. So the question arises: will an expression of the type (7) satisfy the tetrad effect inequalities (1) when the ratio E^3/E^1 is far from 0·1? This is considered later.

In figure 6 the plot of E_{st} versus q for Ln^{3+} is shown. The dashed lines have been added to help to distinguish the tetrads. It is seen that Nd^{3+} and Pm^{3+}, Ho^{3+} and Er^{3+}, and Gd^{3+} are stabilized relative to the interpolated values which would lie on the imaginary line segments connecting the points of Pr^{3+} and Sm^{3+}, Dy^{3+} and Tm^{3+}, and Eu^{3+} and Tb^{3+} respectively. The stabilization of Nd^{3+}, Pm^{3+}, Ho^{3+} and Er^{3+} is

Table 1. The values of Racah parameters E^1 and E^3 for Ln^{3+} and An^{3+} aqua ions.

Ln^{3+}	E^1(eV)	E^3(eV)	An^{3+}	E^1(eV)	E^3(eV)
Pr^{3+}	0·5639	0·0579	Pa^{3+}	(0·320)	(0·032)
Nd^{3+}	0·5876	0·0602	U^{3+}	0·3859	0·0355
Pm^{3+}	0·6102	0·0652	Np^{3+}	0·4208	0·0394
Sm^{3+}	0·6815	0·0689	Pu^{3+}	0·4621	0·0434
Eu^{3+}	0·6910	0·0691	Am^{3+}	0·517	(0·047)
Gd^{3+}	0·7142	0·0722	Cm^{3+}	0·5730	0·0495
Tb^{3+}	0·7466	0·0755	Bk^{3+}	(0·616)	(0·540)
Dy^{3+}	0·7587	0·0756	Cf^{3+}	(0·667)	(0·0577)
Ho^{3+}	0·7985	0·0774	Es^{3+}	(0·716)	(0·0614)
Er^{3+}	0·8393	0·0802	Fm^{3+}	(0·765)	(0·0650)
Tm^{3+}	0·8855	0·0836	Md^{3+}	(0·815)	(0·0687)

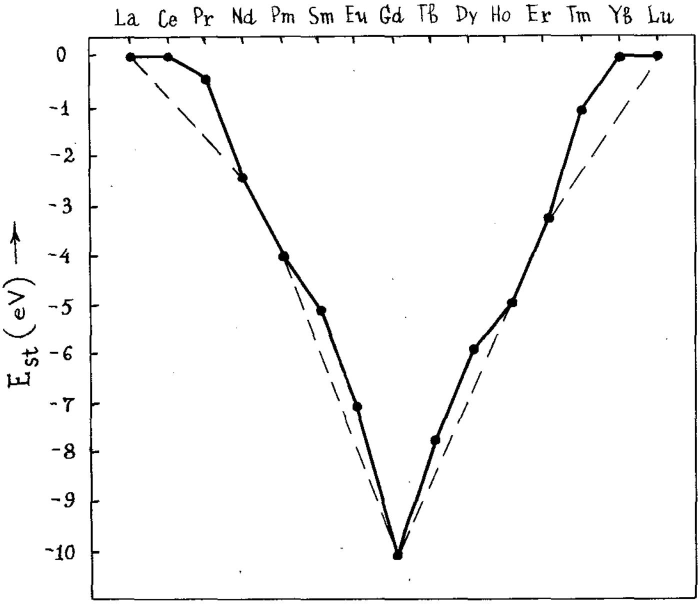

Figure 6. The stabilizing contribution E_{st} of interelectronic repulsion of *f*-electrons for Ln^{3+} aqua ions.

caused by the term in k_3 in (7), which has minimum values at $q = 3, 4, 10, 11$. At the same time the stabilization of Gd^{3+} is due to the term in k_1, which has its minimum at $q = 7$.

Now we can consider, following Jørgensen (1970) and Nugent (1970), how interelectronic repulsion of *f*-electrons generates the tetrad effect in the standard free energy changes which characterize the extraction process. When an aqua ion attaches ligands in an extraction process, *f*-electrons spread slightly into the region of the ligands, which leads to a decrease of the *f*-electron interelectronic repulsion. This is called the nephelauxetic effect (see, for example, Jørgensen 1971). So the contribution from the E_{st} change in the extraction process is

$$\delta E_{st} = k_1 \delta E^1 + k_3 \delta E^3 \tag{8}$$

where δE^1 and δE^3 are nephelauxetic changes of the corresponding Racah parameters in (7). Since the parameters decrease in the extraction process, i.e. δE^1 and δE^3 are negative, δE_{st} is positive (or equal to zero when both k_1 and k_3 are equal to zero). Thus δE_{st} presents a destabilizing contribution. Usually the decrease of the parameters E^1 and E^3 in the extraction process is about 1–2% (Nugent 1970). For an ion doped in a crystal the decrease is 3–5% (Wensky and Moulton 1970). If $\delta E^3/\delta E^1$ is not very far from the value 0·1, then δE_{st} can be depicted by a plot as in figure 6 but which is turned over the horizontal axis. A tetrad plot similar to that shown in figure 3 can be obtained by adding the tetrad contribution (8) to a suitable curve approximating the smooth part of ΔG^0 (for a crude approximation a straight line may be used).

Among Ln^{3+}, the maximum values of the relative destabilization (8) are found for Nd^{3+}, Pm^{3+}, Gd^{3+}, Ho^{3+} and Er^{3+}, i.e. the ions which have had, until the extraction process, maximum values of the relative stabilization. This can explain the existence of three crystallochemical instability regions where transitions between various crystal structures with unchanged stoichiometry (or vice versa) are most often observed, and which were revealed by Bandurkin (1964) in the lanthanide series.

3. The boundaries of the tetrad effect

It was shown previously that when the ratio of the parameters in (8) is approximately 0·1, then the contribution δE_{st} may induce the tetrad effect in ΔG^0. It is of interest to find the range of the ratio $R = \delta E^3/\delta E^1$ for which the tetrad effect in ΔG^0 is possible. For this we have to solve the system of inequalities (1) for R in

$$\delta E_{st}(q) = [k_1(q) + k_3(q)R]\delta E^1 \tag{9}$$

(see Spitsyn *et al.* 1983 a). Placing (9), where R and δE^1 are assumed to be constant, in (1), one finds that each of the inequalities will be satisfied, no matter what the value of δE^1 is, if

$$R > 0{\cdot}058 \tag{10}$$

The upper boundary of the tetrad effect can be obtained when the feature common to all the tetrad plots of $\Delta G^0(q)$ known from experiment is considered. Namely, the difference $\Delta G^0(q) - \Delta G^0(q-1)$ has minimum at $q=1$ for the first half of the f-shell, and/or at $q=8$ for the second half of the f-shell. This corresponds to a maximum appearing on the plot of $\beta(q)$ at $q=1$ and/or at $q=8$ (see figure 2). It was shown (Spitsyn *et al.* 1982) that the necessary condition for this is conservation of the sign of the difference $\delta E_{st}(q) - \delta E_{st}(q-1)$ for $0 < q \leqslant 7$ and for $7 < q \leqslant 14$. The condition is easy to derive when the smooth part $\overline{\Delta G}^0(q)$ of the standard free energy variation $\Delta G^0(q)$ is approximated by a straight line, so that $\overline{\Delta G}^0(q) - \overline{\Delta G}^0(q-1)$ is constant. Taking into account the conservation of the sign of the difference between the adjacent values of $\delta E_{st}(q)$ within each half of the f-shell, and using (9), one finds the upper boundary of the tetrad effect (Spitsyn *et al.* 1982)

$$R < 0{\cdot}231$$

So with the lower boundary defined by (10) the range of R values corresponding to the tetrad effect is

$$0{\cdot}058 < R < 0{\cdot}231 \tag{11}$$

The parameter δE^1 in (9) plays the role of a scaling factor defining the magnitude of the tetrad contribution to $\Delta G^0(q)$. Thus there may be no appreciable tetrad effect in $\Delta G^0(q)$ when δE^1 is relatively small, despite R being within the boundaries of the tetrad effect.

4. The influence of the spin–orbit correction

Now we can consider if the first-order spin–orbit correction resulting from the spin–orbit interaction (s–o correction) takes part in generating the tetrad regularity. The stabilization given by the s–o correction to the ground J level may be written as

$$E_{so} = k_{so}(L, S, J)\zeta_{nf} \tag{12}$$

where ζ_{nf} is the s–o interaction parameter, and the subscript n is 4 for the lanthanides and 5 for the actinides. The values of k_{so} are defined by

$$k_{so} = \pm\frac{1}{4S}[J(J+1) - L(L+1) - S(S+1)] \tag{13}$$

Here for $q \leqslant 7$ the total angular momentum J is equal to $|L-S|$ and the upper sign is taken, and for $q > 7$ J is equal to $L+S$ and the lower sign is taken. It can be deduced from (13) that k_{so} has symmetry which is partly similar to that of k_3

$$k_{so}(q)=k_{so}(7-q),\quad k_{so}(q+7)=k_{so}(14-q),\quad (q\leqslant 7)$$

though the electron–hole symmetry $q\leftrightarrow 14-q$ is not valid. Because of the considerable value of ζ_{nf}, the s–o term (12) for the lanthanides is comparable with the term k_3E^3 in (7), and for the actinides even exceeds it. Since $k_3\delta E^3$ in (8) is responsible for the appearance of the tetrads, we shall investigate in an analogous manner the term $k_{so}\delta\zeta_{nf}$, placing it into (8) instead of $k_3\delta E^3$

$$\delta E'_{st}=(k_1+k_{so}R')\delta E^1 \tag{14}$$

where $R'=\delta\zeta_{nf}/\delta E^1$. Trying to solve (1) for R' in (14), we find that no single value of R' exists which would satisfy simultaneously all the inequalities in (1) (Spitsyn *et al.* 1983 a). For instance when the sign >0 is used, the first inequality in (1) for $q=2, 5$ has the solutions $R'<18/13$, whereas from the second inequality for $q=3, 4$ it follows that $R'>18/13$. The result is independent of $\delta\zeta_{nf}$ and does not change when the increase of $\delta\zeta_{nf}$ with the atomic number is taken into account. So the conclusion is reached that the s–o stabilization affects the values of ΔG^0 numerically, but does not contribute to the tetrad regularity. In general the s–o interaction does not cause sharp deviations in the variation of ΔG^0 along the lanthanide and actinide series, since the changes in k_{so} values are small. For instance when moving from Pr^{3+} to Nd^{3+}, k_{so} changes by 0·5, whereas the corresponding change in k_3 is 12. Beside this, the nephelauxetic change in ζ_{nf} must be much less than those of E^1 and E^3. It is due to the fact that the main contribution to ζ_{nf} comes from the region of the wavefunction which is closer to the core of an ion and which is therefore less perturbed by outer influences (Wong and Richman 1962). That the change of ζ_{nf} is small can be seen also from the spectral data presented by Dieke (1968). The data show that s–o splitting of the ground energy terms of the lanthanide ions is approximately the same for aqua ions and for the ions doped in crystals. Analysis of the nephelauxetic effect made by Jørgensen (1971) confirms the invariance of ζ_{nf} in chemical compounds. These arguments prove that despite the considerable contribution of the s–o interaction to the energetics of the lanthanides and actinides, the main source of regularities in their properties is interelectronic repulsion of *f*-electrons.

5. The range of possible values of $\delta E^3/\delta E^1$

As discussed previously, the standard free energy change of extraction can exhibit the tetrad regularity if the value of the parameter $R=\delta E^3/\delta E^1$ belongs to region (11). On the other hand, conditions exist (Spitsyn *et al.* 1982) which put certain limits on R by the very nature of this parameter. Indeed, the Racah parameters E^1 and E^3 may be expressed in terms of the Slater–Condon parameters F^2, F^4 and F^6. For convenience, the parameters F_2, F_4 and F_6, proportional to F^2, F^4 and F^6 respectively, are more often used. The parameters E^1 and E^3, expressed through F_2, F_4 and F_6, have the form

$$\left.\begin{aligned} E^1&=(70F_2+231F_4+2002F_6)/9\\ E^3&=(5F_2+6F_4-91F_6)/3 \end{aligned}\right\} \tag{15}$$

Wensky and Moulton (1970) have noted that for the correct description of the compression of free-ion energy levels which takes place when a free ion is doped into a crystal, it is necessary that, in going from the free ion to a crystal, the changes in F_2, F_4

and F_6 are negative. Assuming that this is also true for extraction, and considering both directions of the process, we suppose that δF_2, δF_4 and δF_6 have the same sign. Then expressions (15) show that this will impose certain restrictions on the relative changes of the parameters E^1 and E^3. With the use of (15) the expression for R can be found

$$R=\frac{15+18g_1-273g_2}{70+231g_1+2002g_2} \tag{16}$$

where $g_1=\delta F_4/\delta F_2$, $g_2=\delta F_6/\delta F_2$. Since δF_i $(i=2,4,6)$ have the same sign, it follows that $g_1 \geqslant 0$, $g_2 \geqslant 0$. Using (16) we have, for g_1,

$$g_1=\frac{15-273g_2-(70+2002g_2)R}{231R-18} \geqslant 0 \tag{17}$$

where the value $R=18/231$ must be excluded. Assuming $g_2 \to 0$ $(\delta F_2 \neq 0,\ \delta F_6 \to 0)$ and $R>18/231$, we find the upper limit for R

$$R \leqslant \frac{15}{70}$$

Analogously when $g_2 \to \infty (\delta F_2 \to 0,\ \delta F_6 \neq 0)$ and $R<18/231$ the lower limit is derived

$$R \geqslant -\frac{273}{2002}$$

Including the value $R=18/231$, we obtain the region of the possible values of R

$$-\frac{273}{2002} \leqslant R \leqslant \frac{15}{70} \tag{18}$$

or approximately

$$-0{\cdot}136<R<0{\cdot}214 \tag{19}$$

So the relative changes g_1 and g_2 of the parameters F_2, F_4 and F_6 may have arbitrary values from 0 to ∞, but the values of the relative change R of the parameters E^1 and E^3 are restricted to the region (19). It is seen from (19) and (11) that the minimal value of R is less than the lower boundary of the tetrad effect and has a negative sign, indicating that the parameters E^1 and E^3 may change in opposite directions. On the other hand, the maximum possible value of R does not exceed the upper boundary of the tetrad effect, though this value is rather close to it.

6. The regularities in ionic radii

Let us consider how *f*-electron interelectronic repulsion affects lanthanide and actinide ionic radii. Ionic radii of the lanthanides and actinides are often compared with the radii of maximum electron density of their outer closed shells, i.e. the 5*s*, 5*p* for the lanthanides, and the 6*s*, 6*p* for the actinides. Variation of the calculated radii of the outer shells of Ln along the series (see Pitzer 1979) closely follows that of the radii given by Templeton and Dauben (1954). Qualitatively it can be explained as follows. The stabilization part of the interelectronic repulsion of *f*-electrons (7) induces a certain compression of the *f*-shell. The compression entails a decrease in the effective nuclear charge that outer closed shells feel. This leads to a relative increase in the radii of these shells. Since the stabilization part (7) varies by the tetrad law, it generates a tetrad variation in the relative increase of the outer shell radii, displayed on the background of their monotonic compression along the series.

A semiempirical expression characterizing the variation of the lanthanide ionic radii along the series was derived by Spitsyn *et al.* (1983 a). As a starting point, the crystal-field model and weak-field approximation were used. The total energy of the ground state can approximately be written as

$$E = E_0 + \frac{q(q-1)}{2} E^{\mathrm{B}} + E_{\mathrm{st}} + E_{\mathrm{so}} + \Delta_{\mathrm{cf}} \tag{20}$$

The terms E_{st} and E_{so} are defined by (7) and (12). The first term in (20) includes the core energy of the lanthanide ion, the energy of one-electron interactions of the *f*-electrons and the energy due to the spherically symmetric part of the interaction of the *f*-electrons with the crystal field. The second part of the energy of the interaction of the *f*-electrons with the crystal field—the crystal-field stabilization—is given by the last term in (20). The second term in (20) is the energy of the baricentre (see § 2). The last two terms in (20), corresponding to the s–o and crystal-field stabilizations, can be omitted for convenience without influencing the final result. The effects of these terms on ionic radii will be estimated later. Expression (20) does not include effects of energy-levels mixing by the crystal field, which is small for the lower levels of the lanthanides. Also, following Jørgensen (1970) and Nugent (1970), we did not take into account mixing of the energy terms with different L and S due to the interconfiguration and s–o interaction, despite the fact that the influence of these interactions in the lanthanides and actinides is increasingly large. Though this crude approximation is totally unjustified when excited energy levels of the lanthanides and actinides are considered, it allows us, nevertheless, to depict successfully the variation along the series of spectroscopic and thermodynamic properties, such as the lowest $4f^q \rightarrow 4f^{q-1}5d$ transitions (Jørgensen 1962 a), third ionization energies of the lanthanides (Johnson 1969), and the standard oxidation potentials of the lanthanides and actinides (Nugent *et al.* 1971, 1973, Nugent 1975). We also neglect the mixing of the energy terms in treating the lanthanide and actinide ionic radii and assume that the ground energy is represented sufficiently well by (20).

Combining the first two terms in (20) into one denoted by $\bar{E}$, we have for the ground state,

$$E = \bar{E} + E_{\mathrm{st}} \tag{21}$$

where the energy is represented by smoothly varying part $\bar{E}$ and the tetrad part E_{st}. In the adiabatic approximation, E depends on the distances between the central ion and neighbouring nuclei. It can be assumed for simplicity that only one parameter is sufficient. Let us denote the equilibrium value of this parameter, or the equilibrium distance, by r_0. If the term E_{st} in (21) were equal to zero, then the equilibrium distance would have some other value $\bar{r}$, differing from r_0 by δr

$$r_0 = \bar{r} + \delta r$$

Since the value of E_{st} is small compared with $\bar{E}$, the difference $\delta r = r_0 - \bar{r}$ is also small. Taking the derivative of E with respect to r at the equilibrium point r_0 and expanding the derivative in the power series in δr where only the first two members are considered, we find

$$\delta r = -\left(\frac{\partial E_{\mathrm{st}}}{\partial r}\right)_{\bar{r}} \Big/ \left(\frac{\partial^2 \bar{E}}{\partial r^2}\right)_{\bar{r}} = -\left[k_1\left(\frac{\partial E^1}{\partial r}\right)_{\bar{r}} + k_3\left(\frac{\partial E^3}{\partial r}\right)_{\bar{r}}\right] \Big/ \left(\frac{\partial^2 \bar{E}}{\partial r^2}\right)_{\bar{r}} \tag{22}$$

The denominator in (22) is positive, since $\bar{E}$ has a minimum at $r = \bar{r}$. The derivatives in the numerator are also positive, because a decrease of r is followed by a nephelauxetic decrease in the parameters E^1 and E^3. Since $k_1 \leqslant 0$, $k_3 \leqslant 0$, the equilibrium distance change δr, due to E_{st}, is positive. Thus, as expected previously in the qualitative analysis, the stabilization part of the *f*-electron interelectronic repulsion energy has the effect of increasing the ionic radii. The expression (22) shows that for a constant $(\partial^2 \bar{E}/\partial r^2)_{\bar{r}}$, the magnitude of the increase depends on the values of the derivatives $(\partial E^1/\partial r)_{\bar{r}}$ and $(\partial E^3/\partial r)_{\bar{r}}$. Analogously to the term 'nephelauxetic effect', which might be called the *integral* nephelauxetic effect, the concept of the *differential* nephelauxetic effect could be introduced, which characterizes the rate of variation of the interelectronic repulsion parameters, i.e. the derivatives of the parameters with respect to r. It is seen from (22) that δr has the same form as E_{st} in (7) (with the opposite sign) and hence must vary with the tetrad regularity if the value of the ratio $(\partial E^3/\partial r)_{\bar{r}}/(\partial E^1/\partial r)_{\bar{r}}$ belongs to the region (11).

The contribution from s–o stabilization to the ionic radius may be considered by inclusion of the term $k_{so}(\partial \zeta_{nf}/\partial r)_{\bar{r}}$ into the numerator of (22). As discussed previously, the parameter ζ_{nf} is substantially less sensitive to outer influences than the Racah parameters, so the value of the derivative must be much less than the values of $(\partial E^1/\partial r)_{\bar{r}}$ and $(\partial E^3/\partial r)_{\bar{r}}$. This justifies neglect of the s–o contribution to δr. Since variation of k_{so} along the series is smooth, but at the same time partly resembles the behaviour of k_3 (see § 4), the small s–o contribution to the ionic radius may be taken into account by small changes in the parameters in $\bar{r}$ and δr.

The case with the crystal-field contribution is somewhat different. Despite the small value of Δ_{cf}, the derivative $(\partial \Delta_{cf}/\partial r)_{\bar{r}}$ may be comparable with $k_1(\partial E^1/\partial r)_{\bar{r}}$ and $k_3(\partial E^3/\partial r)_{\bar{r}}$. Indeed the potential due to the crystal field is represented by a sum of terms proportional to inverse powers of r (see Judd 1963), and the derivatives of Δ_{cf} with respect to r is of the same order of magnitude as Δ_{cf}, which, for the lanthanides, is $\sim 100\,\mathrm{cm}^{-1}$. Let us assume it to be the absolute value of $(\partial \Delta_{cf}/\partial r)_{\bar{r}}$ and compare the value with the absolute values of $k_1(\partial E^1/\partial r)_{\bar{r}}$ and $k_3(\partial E^3/\partial r)_{\bar{r}}$. Though the derivatives $(\partial E^1/\partial r)_{\bar{r}}$ and $(\partial E^3/\partial r)_{\bar{r}}$ are unknown, rough estimations of their values can be made. As mentioned above, in going from a free lanthanide ion to a crystal, the parameters E^1 and E^3 decrease by 3–4%. Since $E^1 \approx 6000\,\mathrm{cm}^{-1}$, $E^3 \approx 600\,\mathrm{cm}^{-1}$, when the distance between a lanthanide ion and its neighbours in the crystal decreases by ~ 1 Å, the parameters E^1 and E^3 decrease by $\sim 200\,\mathrm{cm}^{-1}$ and $\sim 20\,\mathrm{cm}^{-1}$ respectively. These values can be adopted as the approximate values of $(\partial E^1/\partial r)_{\bar{r}}$ and $(\partial E^3/\partial r)_{\bar{r}}$. Calculating k_1 and k_3 by the formulas of § 2, we can see that the absolute magnitudes of $(\partial \Delta_{cf}/\partial r)_{\bar{r}}$ and $k_3(\partial E^3/\partial r)_{\bar{r}}$ are of the same order. It was shown that the derivatives of the Racah parameters are positive. Then $k_3(\partial E^3/\partial r)_{\bar{r}}$ is negative (or equal to zero) since $k_3 \leqslant 0$. At the same time, the sign of $(\partial \Delta_{cf}/\partial r)_{\bar{r}}$ must be positive, because in going from a free ion to a crystal (r decreases), the crystal-field stabilization, which has a negative sign, increases in absolute value. Hence the terms $(\partial \Delta_{cf}/\partial r)_{\bar{r}}$ and $k_3(\partial E^3/\partial r)_{\bar{r}}$ must partially cancel, and in the numerator of expression (22) only the term $k_1(\partial E^1/\partial r)_{\bar{r}}$ can be left

$$\delta r = -k_1\left(\frac{\partial E^1}{\partial r}\right)_{\bar{r}} \Bigg/ \left(\frac{\partial^2 \bar{E}}{\partial r^2}\right)_{\bar{r}} \tag{23}$$

With the use of (23) and the empirical values of crystal radii of Ln^{3+} obtained by Templeton and Dauben (1954), cited in table 2, the value of $(\partial E^1/\partial r)_{\bar{r}}/(\partial^2 \bar{E}/\partial r_2)_{\bar{r}}$ can be determined in a 'geometric' way (Spitsyn *et al.* 1983 a)

$$\left(\frac{\partial E^1}{\partial r}\right)_{\bar{r}} \Bigg/ \left(\frac{\partial^2 \bar{E}}{\partial r^2}\right)_{\bar{r}} = 5{\cdot}6 \times 10^{-4}\,\text{Å} \tag{24}$$

Table 2. Experimental and calculated ionic radii of Ln^{3+} and Ln^{4+} ions. (Coordination number 6.)

Ln^{3+}	r(Å) exp.	r(Å) calc.	Ln^{4+}	r(Å) exp.	r(Å) calc.
La^{3+}	1·061	1·061	—	—	—
Ce^{3+}	1·034	1·034	Ce^{4+}	0·92	0·92
Pr^{3+}	1·013	1·012	Pr^{4+}	0·90	0·90
Nd^{3+}	0·995	0·992	Nd^{4+}	—	0·89
Pm^{3+}	0·979	0·977	Pm^{4+}	—	0·88
Sm^{3+}	0·964	0·962	Sm^{4+}	—	0·87
Eu^{3+}	0·950	0·950	Eu^{4+}	—	0·86
Gd^{3+}	0·938	0·938	Gd^{4+}	—	0·85
Tb^{3+}	0·923	0·922	Tb^{4+}	0·84	0·84
Dy^{3+}	0·908	0·907	Dy^{4+}	—	0·83
Ho^{3+}	0·894	0·895	Ho^{4+}	—	0·83
Er^{3+}	0·881	0·881	Er^{4+}	—	0·82
Tm^{3+}	0·869	0·869	Tm^{4+}	—	0·82
Yb^{3+}	0·858	0·858	Yb^{4+}	—	0·81
Lu^{3+}	0·848	0·848	Lu^{4+}	—	0·80

Determination of this parameter allows us actually to split the values of crystal radii into the smooth component $\bar{r}$ and δr, which is shown in figure 7. The maximum deviation from the smooth component, caused by the stabilization part of the interelectronic repulsion of *f*-electrons, is approximately 0·008 Å. It is seen from figure 7 that the tetrad effect in r has in fact a degenerate character, which can be explained by partial cancellation of the term in k_3 in the expression for δr by the crystal-field influence. The tendency toward the tetrad regularity is more apparent in the corrected radii and in unit cell volumes obtained by Siekierski (1971) and Siekierski and Fidelis (1972) by a refined approach.

Assuming that for $\bar{E}$ Born's approximation is valid, we can obtain more precise estimates for the magnitude of the differential nephelauxetic effect in the Racah parameters. If the empirical Madelung constant $A = 10$ and Born's exponent $m = 9$, which were applied for $LnCl_3$ (Ladd and Lee 1961), are chosen and the interionic distance is ~ 3 Å, then $(\partial^2 \bar{E}/\partial r^2)_{\bar{r}} = 3 \times 10^5\,\mathrm{cm}^{-1}\,\text{Å}^{-2}$. So it follows from (24) that $(\partial E^1/\partial r)_{\bar{r}} = 168\,\mathrm{cm}^{-1}\,\text{Å}^{-1}$. As mentioned above, $E^3/E^1 \approx 0{\cdot}1$. Supposing that the same value holds for the ratio of the corresponding derivatives, we have $(\partial E^3/\partial r)_{\bar{r}} \approx 17\,\mathrm{cm}^{-1}\,\text{Å}^{-1}$. Thus one can see that the previous rough estimation of the differential nephelauxetic effect in the parameters E^1 and E^3 is in good agreement with the latter more precise values.

Let us now compare the variation of the lanthanide ionic radii with the variation of the ionic radii of *d*-elements. The plots of the ionic radii of *d*-elements are, in general, presented by twin-shouldered curves with a break in the middle. It is somewhat reminiscent of the behaviour of the lanthanide ionic radii, but with the deviation from a smooth variation being much greater. The pattern of the plots is due to the crystal-field influence, which in the case of *d*-elements considerably exceeds the influence of the s–o interaction and the interelectronic repulsion of *d*-electrons. At the points where the number of *d*-electrons is equal to 0, 5 and 10 the electron configuration has spherical symmetry, and the crystal-field splitting is absent. Through these points a curve may be drawn where the values of the ionic radii would lie if the crystal field were equal to zero.

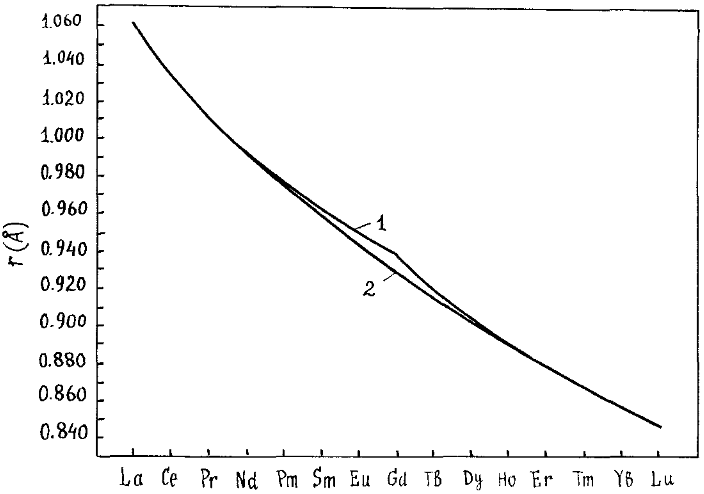

Figure 7. Ionic radii of Ln^{3+} ions (curve 1) and the part of the ionic radii which has smooth variation (curve 2). The break in the middle of the series is due to the 'tetrad' part δr.

Actually the crystal-field stabilization leads to a decrease in the ionic radii in the regions $0<q<5$ and $5<q<10$. The decrease follows from formula (23) where $k_1(\partial E^1/\partial r)_{\bar{r}} \leqslant 0$ is changed by the derivative $(\partial \Delta_{cf}/\partial r)_{\bar{r}} \geqslant 0$, giving a negative δr. Thus for d-elements, the regularity of the ionic radii is due to a relative decrease in their values caused by the crystal-field stabilization, whereas in the case of the lanthanides the regularity is induced by a relative increase of the ionic radii generated by interelectronic repulsion of f-electrons.

A more elaborate approach in treating the ionic radii r of the lanthanides and actinides involves decomposition of r into three parts (Spitsyn *et al.* 1983 b)

$$r = r_l - \left[k_B \left(\frac{\partial E^B}{\partial r} \right)_{\bar{r}} + k_1 \left(\frac{\partial E^1}{\partial r} \right)_{\bar{r}} \right] \Bigg/ \left(\frac{\partial^2 E_0}{\partial r^2} \right)_{\bar{r}} \tag{25}$$

Here r_l represents the purely ionic part of the radius, i.e. the value the radius would have if interelectronic repulsion of the f-electrons were zero, and $k_B = [q(q-1)]/2$. With the use of Born's formula, the expression for r_{li} corresponding to the ith member of the series can be obtained

$$r_{li} = \left(\frac{Q_0}{Q_i} \right)^{1/(m-1)} r_{l0} \tag{26}$$

where m is Born's exponent, $Q_{0(i)}$ is the effective nuclear charge, and r_{l0} is the radius of the initial member of the series for which $q=0$. Formula (26) is similar to Pauling's well known formula which relates the univalent and the crystal radii and is normally applied to the ions having the electron configurations of the atoms of the inert gases (see Pauling 1960). The difference is that (26) links the radii of the ions with incompleted shells and in the same valence state. The effective nuclear charge Q_i of the ith member of the series is expressed through the empirical screening constant σ and the number of f-electrons, q_i, the ith member of the series has

$$Q_i = Q_0 + q_i(1-\sigma) \tag{27}$$

Table 3. Experimental and calculated ionic radii (in Å) of An^{4+}, An^{5+} and An^{6+} ions. (Coordination number 6.)

An	4+ exp.	4+ calc.	5+ exp.	5+ calc.	6+ exp.	6+ calc.
Th	0·99	0·99	—	—	—	—
Pa	0·96	0·96	0·90	0·90	—	—
U	0·93	0·94	0·89	0·89	0·83	0·83
Np	0·92	0·92	0·88	0·88	0·82	0·82
Pu	0·90	0·90	0·87	0·87	0·81	0·81
Am	0·89	0·89	0·86	0·86	0·80	0·80
Cm	0·88	0·88	—	0·85	—	0·79
Bk	0·87	0·87	—	0·84	—	0·78
Cf	—	0·86	—	0·84	—	0·78
Es	—	0·85	—	0·83	—	0·77
Fm	—	0·84	—	0·83	—	0·77
Md	—	0·83	—	0·82	—	0·76
No	—	0·82	—	0·82	—	0·76
Lw	—	0·81	—	0·81	—	0·75

The parameters σ, $(\partial E^{B}/\partial r)_{\bar{r}}/(\partial^{2}E_{0}/\partial r^{2})$ and $(\partial E^{1}/\partial r)_{\bar{r}}/(\partial^{2}E_{0}/\partial r^{2})_{\bar{r}}$ can be found with the use of the empirical values of the ionic radii of any three members of the series other than the initial member. Once the parameters are obtained, one can calculate the ionic radii for the rest of the series by formula (25). Assuming $m=9$ and using the empirical values of the radii of Ce^{3+}, Gd^{3+} and Lu^{3+}, we find for Ln^{3+}: $\sigma=0{\cdot}313$, $(\partial E^{B}/\partial r)_{\bar{r}}/(\partial^{2}E_{0}/\partial r^{2})_{\bar{r}}=5{\cdot}8\times10^{-4}$ Å and $(\partial E^{1}/\partial r)_{\bar{r}}/(\partial^{2}E_{0}/\partial r^{2})_{\bar{r}}=5{\cdot}3\times10^{-4}$ Å. (The value of the parameter $(\partial E^{1}/\partial r)_{\bar{r}}/(\partial^{2}E_{0}/\partial r^{2})_{\bar{r}}$ is close to the previously found 'geometric' value $5{\cdot}6\times10^{-4}$ Å.) The values of the ionic radii of the trivalent lanthanides calculated by formula (25) closely reproduce the corresponding empirical values (see table 2).

In the case of the actinides, absence of the same stable valence form and crystal structure which would exist for all members of the series obscures the tetrad effect in radial characteristics. The same problem also arises for Ln^{4+}. As pointed previously, the use of extensive experimental data allows one to reveal the tetrad regularity in the actinide unit cell volumes and lattice constants (Siekierski 1971, Siekierski and Fidelis 1972). Nevertheless, the actinide ionic radii encountered in the literature do not exhibit the tetrad regularity. We can use the values of the ionic radii of Ln^{4+}, and of An^{4+}, An^{5+} and An^{6+}, which are known for the lighter actinides (Keller 1971), and calculate the hypothetical values of the radii for the rest of both series. Since there is no apparent influence of the interelectronic repulsion of *f*-electrons on the empiric values of the radii, we neglect the last two terms in (25), so that formula (26) can actually be used in calculations. The results for Ln^{4+}, and for An^{4+}, An^{5+} and An^{6+}, are shown in tables 2 and 3 respectively. All the calculated values, with one exception, coincide with the corresponding empirical values. The exception is U^{4+}, where 0·94 Å was obtained instead of 0·93 Å.

7. Regularities in spectroscopic and thermodynamic characteristics and relative stabilities of various valence forms of the lanthanides and actinides

Relative stabilities of various valence forms of the lanthanides and actinides are closely connected with regularities in spectroscopic and thermodynamic characteristics. So knowledge about the dependence of these characteristics on the number of electrons in the f-shell, and on the chemical media in which the lanthanide and actinide ions are considered, give us information as to why some valence forms are stable and some are not, and what valence forms yet unobserved could be expected to exist.

The link between spectroscopic properties and stability is established with the use of thermodynamic cycles. Let us consider, for example, how $f^q \to f^{q-1}d$ transition energies affect the relative stabilities of the divalent and trivalent states of f-elements. The divalent and trivalent atomic configurations with the lowest energies are $f^q s^2$ and $f^{q-1}ds^2$ respectively, so that the thermodynamic cycle can be constructed as shown in figure 8. Here E_p is the promotion energy from the divalent atomic configuration to the trivalent one, ΔG_2^0 and ΔG_3^0 are the standard free energies of hydration when M means the aqua ion, or cohesive energies when M means the metal, leading to the divalent and trivalent valence states respectively and ΔG_{32}^0 is the standard free energy of transition from the trivalent valence state to the divalent one. If $\Delta G_{32}^0 > 0$ then M(III) is more stable than M(II). Since $\Delta G_{32}^0 = \Delta G_2^0 - \Delta G_3^0 - E_p$, an ion will prefer the state M(III) when $\Delta G_2^0 > E_p + \Delta G_3^0$. So relative stability of the valence states depends on the relationship between $f^q s^2 \to f^{q-1}ds^2$ promotion energies and the difference between the standard free energies of formation. The latter is approximately constant, and variation of relative stability along the series is due to changes in the promotion energies, which are of the type shown in figure 1. So figure 1 clearly indicates why there is no smooth valence state distribution along the series. Promotion energy analysis was applied by Johansson (1976) to investigate relative stability of the di-, tri- and tetra-valent metallic states and to show that $5f$-electrons in the earlier actinide metals, unlike $4f$-electrons in the lanthanide metals, are itinerant, i.e. participate in metallic binding. Appearance of the metal in a given valence state can be predicted if, besides the promotion energies, thermodynamic data on cohesive energies are available. Using general trends in cohesive energy behaviour in the left part of the Periodic Table, Johansson found that the cohesive energy difference between the tri- and di-valent states is about 55 kcal/mol for the lanthanides and 50 kcal/mol for the actinides. The difference for the tetra- and tri-valent states was assumed to be 45 kcal/mol for both series. Which state is stable—divalent or trivalent—is defined by the balance of the corresponding cohesive energy difference and the promotion energy from the divalent atomic state to the trivalent one. Hence if the promotion energy $f^q s^2 \to f^{q-1}ds^2$ is less than 55 kcal/mol for the lanthanides, or 50 kcal/mol for the actinides, the total energy gain is greater than zero,

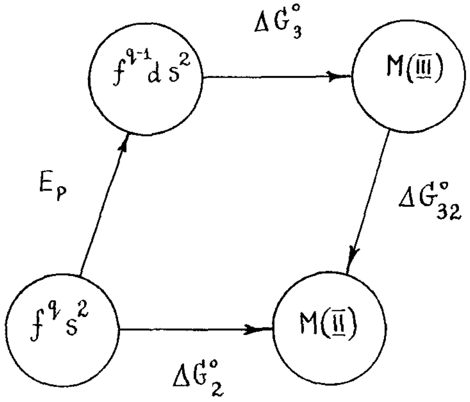

Figure 8. Thermodynamic cycle establishing relative stabilities of the divalent and trivalent states of the lanthanides and actinides.

and the corresponding metal must be trivalent. Analogously with the use of the promotion energies $f^{q-1}ds^2 \rightarrow f^{q-2}d^2s^2$, preference of the tri- and tetra-valent states was estimated. Figures 9 and 10 demonstrate the suggested valence-state distribution of the lanthanide and actinide metals. The plots in figure 9 show that, among the lanthanides, only europium and ytterbium are divalent metals, but, among the actinides, the divalent metallic state should prefer nobelium, mendelevium, fermium and einsteinium, demonstrating an increase in divalent-state stability with the atomic number in the second half of the actinide series. The result, stating an increase in relative stability of the divalent state for the heavier actinides, was also obtained by Nugent *et al.* (1973) and has gained experimental support (Mikheev *et al.* 1973, Mikheev and Spitsyn 1976). As seen in figure 9, californium presents a borderline case when both divalent and trivalent metals are possible. Experimental data show that californium can actually be found in a mixed valence state (Noè and Peterson 1976). On the other hand, figure 10 shows that neptunium and plutonium should prefer the trivalent metallic state, which contradicts experimental evidence (Johansson 1976). In particular the calculated cohesive energy of fictitious trivalent Pu metal (Johansson and Rosengren 1975) is less than the measured value by 12 kcal/mol. The failure of promotion-energy analysis, which relies heavily on the assumption about localized 5f-electrons, is apparently due to the fact that in the lighter actinide metals the assumption is not true. Johansson (1976) has stressed that the additional part of the cohesive energy is due to the

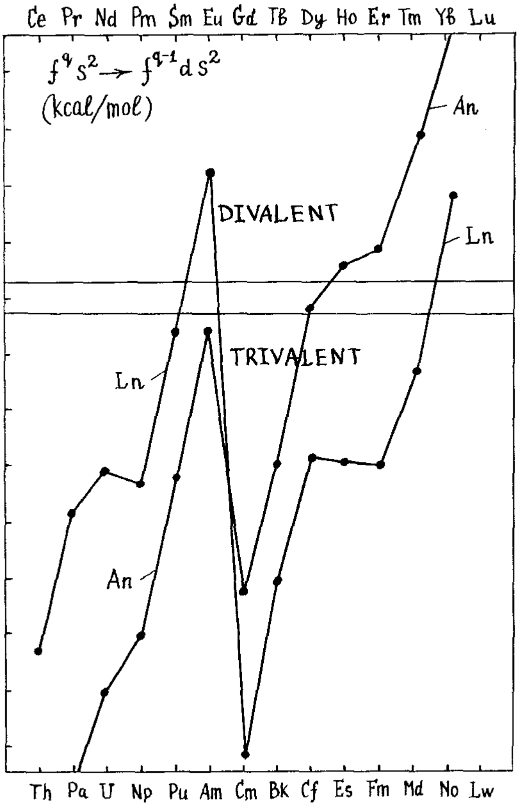

Figure 9. The energy differences between the lowest levels of the divalent $f^q s^2$ and the trivalent $f^{q-1}ds^2$ atomic configurations of the lanthanides and actinides.

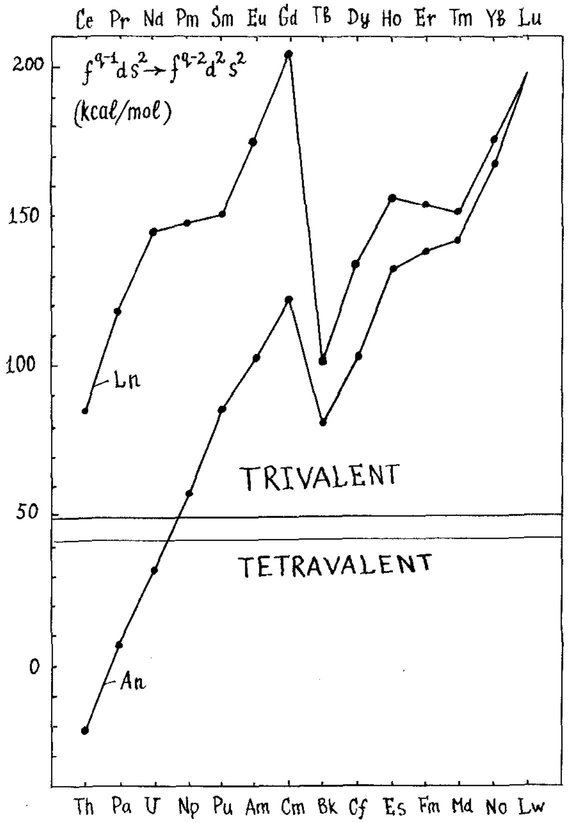

Figure 10. The energy differences between the lowest levels of the trivalent $f^{q-1}ds^2$ and the tetravalent $f^{q-2}d^2s^2$ atomic configurations of the lanthanides and actinides.

delocalized character of the 5*f*-electrons, i.e. to their significant contribution to metallic binding. The conclusion is confirmed by analysis of the actinide metallic radii (Johansson 1976) and by entropy investigations, showing an absence of magnetism in the lighter actinide metals (Ward and Hill 1976). In the study of relative stabilities of various oxidation states in solution, it is appropriate to use standard oxidation potentials, which can be directly measured for a reversible oxidation process. The standard oxidation potential

$$E^0(M^{z+1}/M^{z+})=W+q(E-A)+\Delta k_1(q)E^1+\Delta k_3(q)E^3+\Delta k_{\mathrm{so}}(q)\zeta_{nf} \qquad (28)$$

where for the last three terms we have used the notation accepted in the present paper. The sum of the third and fourth terms in (28) presents the double–double component, which results from the difference between the tetrad terms corresponding to the states M^{z+1} and M^{z+} (see (7)); the fifth term is the analogous difference between the spin–orbit terms (see (12)); the first and second terms with parameters W and $(E-A)$ (the parameter E should not be confused with E in (20) and (21) take into account the influence of hydration energies, binding energies of *f*-electrons, the entropy part, and some other effects (Nugent *et al.* 1973). It should be noted that expression (28) has in fact an ionization energy form and follows from the expression for the ground term energy of an ion with a pure f^q-configuration. It was originally used by Jørgensen (1962 a, b) in his treatment of $4f^q \rightarrow 4f^{q-1}5d$ transitions. The results show that the expression (28), derived for ions with a pure f^q-configuration, which the lanthanides and actinides possess when they are in M^{3+} or higher oxidation states, is also applicable to the lanthanide ions in the M^{2+} state, as if the d-electron in the $5d$-shell may be considered as a $4f$-electron. Moreover (28) proves to be a good approximation also for the difference between the energies of the lowest levels of f^qs and $f^{q-1}ls$ configurations of the actinide M^+ ions, and of f^qs^2 and $f^{q-1}ls^2$ configurations of the neutral actinide atoms (see Vander Sluis and Nugent 1972 and references therein), where $l = d$ or p. Presence of the electron in an incomplete shell other than the f-shell can be taken into account by the use of corrections (Nugent *et al.* 1973). Application of (28) to the standard oxidation potentials of the lanthanides and actinides is based on the experimental facts of the existence of a linear correlation between $E^0(M^{z+1}/M^{z+})$ and the energies of the lowest electron-transfer bands (Barnes and Day 1964), and between $E^0(M^{z+1}/M^{z+})$ and the energies of the lowest $f \rightarrow d$ absorption bands (Miles 1965).

The values of the standard oxidation potentials $E^0(M^{3+}/M^{2+})$ and $E^0(M^{4+}/M^{3+})$ of the lanthanides and actinides calculated by Nugent *et al.* (1973) with the use of (28) are now widespread in the literature. In calculations, the parameters E^1 and E^3 were determined for each member of the series by fitting (28) to the experimental values of the energies of $f^q \rightarrow f^{q-1}d$ transitions (Vander Sluis and Nugent 1972), and for the s–o parameter ζ_{nf} its usual values, cited in the paper of Nugent *et al.* (1971), were taken. The values of the parameters W and $(E-A)$, which were assumed to be the same for the entire series, were obtained by fitting (28) to the experimentally known values of the oxidation potentials.

It is interesting to compare the general trend of the lanthanide and actinide potentials $E^0(M^{3+}/M^{2+})$. For this purpose expression (28) can conveniently be used. Transition from the lanthanides to the actinides decreases both E and A. The decrease in the parameter A, which originates mainly from the interelectronic repulsion parameter E^0 (Jørgensen 1962 b), reflects a considerable decrease of interelectronic repulsion of the $5f$-electrons in the actinides relative to that of the $4f$-electrons in the lanthanides. Since the decrease in A is greater than the decrease in E, the actinide parameter $(E-A)$ is greater than the lanthanide parameter (Nugent *et al.* 1973). The parameter $(E-A)$ defines the slope of the linear part in (28), so the increase of the parameter in the actinides explains why relative stability of the divalent state in the second half of the actinide series is much higher than that in the second half of the lanthanide series (see figure 9). On the other hand, an interesting analogy exists between the second half of the actinide series and the first half of the lanthanide series, where variation of the energies of the $f^{q-1}ds^2 \rightarrow f^{q-2}d^2s^2$ transitions versus z show a close similarity (see figure 10). The analogy, which holds also for ionization energies and oxidation potentials, is due to the fact that the contraction in the second half of the actinide series approaches that in the first half of the lanthanide series (Spitsyn 1976). This is clearly seen from the values of the parameters E^1 and E^3 in table 1, since the values reflect the degree of localization of f-electrons in the incomplete shells.

The plots in figures 9 and 10 show the degenerate double–double effect, where two plateaus appear instead of the intermediate maxima and minima as in figure 2. The plateaus, which are caused by the term $\Delta k_3(q)E^3$ in (28), are more pronounced in the second halves of both series than in the first halves of the corresponding series. This is due to an increase in the parameter E^3 with z (see table 1). In particular the increase in E^3 explains why for the lanthanides the plateau in the first half of the series in figure 10 goes up, indicating an increase in relative stability of the trivalent state in the region Nd–Pm–Sm, whereas in the second half there is a downward plateau, showing a local increase in relative stability of the tetravalent state in the region Ho–Er–Tm. The consequence of such a behaviour is a successful stabilization of tetravalent thulium in the double salt Cs_3TmF_7 (Martynenko *et al.* 1982).

Now we shall give a brief review of up to-date experimental and theoretical data on stability of various valence states of the lanthanides and actinides, paying the main attention to the extreme states.

8. The extreme valence states of the lanthanides and actinides

Several experiments, which proved to be successful, are known where attempts have been made to obtain monovalent lanthanides. Fong *et al.* (1966) studied lanthanide reduction to the monovalent state in crystal lattices. The wide absorption band in thermoluminescence spectra of Sm in KCl was identified as the $4f^6 6s \rightarrow 4f^5 6s^2$ transition corresponding to reduction of Sm^{2+} to Sm^+. Similar experiments were made by Sastry *et al.* (1975). Later Fong *et al.* (1970) reported stabilization of Eu^+. Unique experiments in synthesis of the monovalent lanthanides were made by Simon (1970, 1981), Mattausch *et al.* (1980), and by Araujo and Corbett (1981), who obtained the monovalent lanthanide compounds LnX, where Ln = La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu and X = Cl, Br. There are no reports of stabilization of the monovalent lanthanides in solution. Stabilization of the monovalent state in the actinides is still in question. It is of interest to consider the ways the lanthanides can achieve the monovalent state. The same arguments may be applied to predict possible candidates for the monovalent state among the actinides.

Most of the lanthanide and actinide neutral atoms have in the ground state the electron configuration $f^q s^2$, so that the monovalent state can be achieved when one of the s-electrons participates in chemical bonding and another is localized as in the monovalent alkali–earth halogenides. The latter compounds, which were obtained in the gas phase, are unstable in the solid phase and in solution. But unlike alkali–earth halogenides, the monovalent lanthanides and actinides can have electron transitions to another configuration, which stabilize the monovalent state. Ionova *et al.* (1976) estimated the role of the two most probable transitions: $M^+(f^q s) \rightarrow M^+(f^{q+1})$ and $M^+(f^q s) \rightarrow M^+(f^{q-1} s^2)$, where M = Ln, An, in stabilizing the monovalent lanthanides and actinides. The energy of the first transition in the actinide series has minima at plutonium and mendelevium. The corresponding minima in the lanthanide series are achieved at samarium and thulium. The energy of the second transition is, with the exception of that for mendelevium, much less in value than the energy of the first one and for the lanthanides shows a maximum in the samarium–europium region. This allows us to think that the monohalogenides obtained by Simon (1970, 1981), Mattausch *et al.* (1980) and by Araujo and Corbett (1981) use the transition of the second type. The conclusion is confirmed by the fact that these compounds have the distorted structure of CdI_2 or $Mg(OH)_2$, where the central atoms have localized s^2 pairs. At the same time, samarium and europium differ from the rest of the lanthanides: the ability to form the stable f^q configuration implies the first-type transition in stabilization of the monovalent state of samarium, and europium in the monovalent state is most probably analogous to the monovalent alkali–earth halogenides. Comparison of the energies of the second-type transition in the actinides and lanthanides shows the possibility of obtaining for the actinides the same class of monovalent compounds as were produced by Simon and others (*vide supra*) for the lanthanides.

Relative stabilities of the di, tri- and tetra-valent states of the lanthanides and actinides in aqua solutions were estimated by Nugent *et al.* (1973), who calculated the standard oxidation potentials $E^0(M^{3+}/M^{2+})$ and $E^0(M^{4+}/M^{3+})$ for all members of the lanthanide and actinide series. As discussed previously, from the calculations of Nugent *et al.* (1973), and other investigations (Johansson 1976, Mikheev and Spitsyn 1976), it follows that stability of the divalent state is quickly rising in the second half of the actinide series, whereas for the heavier lanthanides, with the exception of ytterbium, it remains low. For this reason No^{2+} is stable in aqua solutions, but Yb^{2+} is not, Es, Fm, Md and No are divalent metals, whereas among the lanthanides only Eu and Yb have the divalent metallic state. With the use of calculated values of $E^0(M^{4+}/M^{3+})$, the possibility of stabilization of Cf^{4+}, Es^{4+}, Pm^{4+}, Sm^{4+}, Fm^{4+} and Md^{4+} was predicted (Nugent *et al.* 1971). It was suggested that tetravalent promethium, samarium, einsteinium, fermium and mendelevium can be stabilized in the double salts Cs_3PmF_7, Cs_3SmF_7, Cs_3EsF_7, Cs_3FmF_7, Cs_3MdF_7, and tetravalent californium may have some stability in aqueous concentrated Cs_3F_7 solution or prepared in the mixed salt $7NaF \cdot 6CfF_4$. The possibility of obtaining tetravalent thulium was indicated in the paper of Ionova *et al.* (1981), where the energies of the transitions $f^q \rightarrow f^{q-1}d, f^{q-1}s$ and $f^{q-1}p$ were considered. Some of these theoretical prognoses have proved to be true. Tetravalent californium was stabilized in aqua solution by Kosyakov *et al.* (1977). Bouissières *et al.* (1980) reported obtaining Cf^{4+} in the gas phase. A recent report about stabilization of thulium in the double salt Cs_3TmF_7 (Martynenko *et al.* 1982) confirmed the stability of Tm^{4+} suggested by Ionova *et al.* (1981).

David *et al.* (1976) suggested that Cf^{5+} must be stable in aqua solution, but Bk^{5+} is likely to be unstable. Earlier, the possibility of obtaining Cf^{5+} was suggested in the work of Nugent (1975), where the standard oxidation potentials $E^0(M^{5+}/M^{3+})$ and $E^0(M^{6+}/M^{3+})$ were presented. Nugent pointed out that Cf^{5+}, Bk^{5+} and possibly Cm^{5+} can be stabilized, and that the possibility of ever obtaining the pentavalent actinides following californium is very low. In the same paper, stability of Cm^{6+}, Bk^{6+}, Cf^{6+} and Es^{6+} was discussed. Einsteinium was proposed to be the last element among the heavier actinides for which the hexavalent state can be expected. Pentavalent californium in the form CfO_2^+ was obtained by Kosyakov *et al.* (1982) with the use of ^{249}Bk β-decay. Earlier, hexavalent curium in the form CmO_2^{2+} was stabilized in an analogous way by the use of Am^{5+} β-decay (Peretrukhin *et al.* 1978). Substantial time has passed since Np^{7+}, Pu^{7+} (Krot *et al.* 1967) and Am^{7+} (Krot *et al.* 1974) were discovered. Until now these remain the highest valence forms known for the actinides. As the most probable candidate for the octovalent state, plutonium might be considered, yet attempts to obtain Pu^{8+}, either by electrochemical oxidation or by the use of strong oxidants, have been unsuccessful (Krot *et al.* 1972).

9. Summary

In the present paper we have made an attempt to outline the general trends in variations of the lanthanide and actinide properties along the series. In accordance with this purpose, *f*-element properties can be divided into two classes. One of the classes comprises the properties which have, by Peppard's terminology, a tetrad variation, and another includes the properties with the double–double variation, to use the term proposed by Fidelis and Siekierski. The characteristics which show the tetrad effect, for instance the standard free energies of extraction, distribution factors, and unit cell volumes, depend only on a single valence state of the lanthanide or actinide element, and the properties showing the double–double effect, for example, ionization energies, the standard oxidation potentials, and the energies of $f^q \rightarrow f^{q-1}d$ transitions, depend on two different valence states. It should be stressed that actually the two types of regularities appear when all members of the series are considered in the same conditions, i.e. when they are in the same valence state and enter the same chemical compound with the same type of crystal structure. Obviously such rigid conditions cannot always be fulfilled. For instance, the actinides do not have a valence state which would be stable for all members of the series. Thus the tetrad effect in the actinide distribution factor can be observed only for a fragment of the series, as shown in figure 4.

Both types of regularities in *f*-element properties are due to fourfold *f*-shell factorization, which is reflected in symmetry of the quantum numbers of the total spin *S* and the total orbital angular momentum *L*. It is noteworthy that although there is considerable departure from the Russell–Saunders coupling scheme in the lanthanides and actinides, because of substantial relativistic and interconfiguration energy-level mixing, nevertheless it 'works' sufficiently well when used to characterize the link between the lowest-energy levels of different members of the series. This is why elementary mathematical techniques based on the Russell–Saunders approximation, which was used above, allow us to depict successfully the general trends in *f*-element properties, and in particular in the valence-state distribution. The technique is suitable for interpretation of the results that follow from accurate atomic calculations, and on the other hand serves as a basis for semiempirical calculations.

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