# Lanthanide Ionization Energies and the Sub-Shell Break. Part 2. The Third and Fourth Ionization Energies

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# Lanthanide Ionization Energies and the Sub-Shell Break. Part 2. The Third and Fourth Ionization Energies

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By interpolating a $4f^q6s \rightarrow 4f^q7s$ transition within the sequence $f^1 \rightarrow f^{14}$ rather than between $f^0$ and $f^{14}$, revised third and fourth ionization energies of the lanthanides have been obtained. The revised values, together with the second ionization energies calculated in a previous paper, are used to calculate values of the standard enthalpies of formation of the gaseous tripositive ions, $\Delta_f H^{\ominus}(M^{3+},g)$, and of the lattice and hydration enthalpies of some lanthanide compounds and ions in the trivalent and tetravalent states. The displacements of $f^0$ values from nearly smooth $f^1 \rightarrow f^{14}$ variations exceed 30 kJ $mol^{-1}$ and indicate substantial subshell breaks. © *2017 AIP Publishing LLC for the National Institute of Standards and Technology.* [http://dx.doi.org/10.1063/1.4977959]

Key words: lanthanides; ionization energies; thermochemical properties; tetrad effect.

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## 1. Introduction

In a recent work,[1] we revised the second ionization energies obtained in a seminal paper by Sugar and Reader.[2] Improved accuracy was achieved in this revision by avoiding the influence of a possible subshell break and using more recent auxiliary data. Here we update, in a similar way, the third and fourth ionization energies obtained in a later paper[3] by the same authors. This later paper is the source of most recommended values of lanthanide third and fourth ionization energies on the invaluable NIST Atomic Spectra Database website.[4] Throughout, we shall be concerned with the third and fourth spectra, M III and M IV, of two series of atoms, M, in which the ion generated in the ionization limit has the ground state configuration $\{Xe\}4f^q$. This defines $q$ and sets up the M III series as La → Lu and the M IV series as Ce → Hf, which both begin at $q = 0$ and end when $q = 14$.

As in the first paper, the method relies on a smooth variation in the energy difference, $\Delta T$, between the unperturbed centers of gravity of the lowest pairs of levels of the $4f^q6s$ and $4f^q7s$ configurations. These lowest pairs arise from the same $4f^q$ parent state. Unknown values are obtained by interpolation of the smooth variation established by using the limited number of cases in which the necessary spectroscopic data are available for both the $4f^q6s$ and $4f^q7s$ levels. The $\Delta T$ values are then expressed by a Rydberg-Ritz formula

$$\Delta T = z^2 R\{[1/n^*(6s)]^2 - [1/(n^*(6s) + \Delta n^*)]^2\}, \quad (1)$$

where $z$ is the charge of the ion that is formed during ionization, $n^*$ is the effective principal quantum number, and $R$ the Rydberg constant. Sugar and Reader[3] used the value $\Delta n^* = 1.048$ for both series of elements with an estimated uncertainty of $\pm 0.002$. Each value of $\Delta T$ then yields a value of $n^*(6s)$ that provides $T(4f^q6s)$, the amount by which the unperturbed center of gravity of the lowest $4f^q6s$ pair lies below the ionization threshold. A small correction, denoted δ, converts this figure to the amount by which the lowest level of the $4f^q6s$ configuration (the lowest level of the lowest pair) lies below the ionization threshold and, if the excitation energy of that lowest level can be determined, the third and fourth ionization energies follow. In Secs. 2–9, we examine the steps in the calculation in more detail, paying attention to the way in which Sugar and Reader's method has been revised.

## 2. The Values of $\Delta n^*$

In Paper I,[1] we calculated and surveyed the available experimental data on $\Delta n^*$ for Ln II, Ln III, and Ln IV spectra and then used them to estimate unknown values for all three series. The values used here for the Ln III and Ln IV series appear in the fourth columns of Tables 1 and 2. They are the averages of the values provided by methods A and B in Table 2 of Paper I. As noted above, Sugar and Reader[3] took $\Delta n^* = 1.048 \pm 0.002$ for both these series; our estimated values for Ln III differ from this by less than 0.003 and in most cases by less than 0.001. In the Ln IV series, our values are lower than 1.048 but at most by 0.004.

In Paper I, we also derived an uncertainty in our estimated values of $\Delta n^*$ for all three series. This was $\pm 0.0052$ at the level of two standard deviations, a convention that is also used for uncertainties derived in the present paper. In the Ln III

TABLE 1. Calculation of $n^*$ and $T(4f^q6s)$ in Ln III spectra from estimated and experimental values of $\Delta T$ and $\Delta n^*$. Figures estimated by interpolation from Fig. 1 are in parentheses

| $q$ | Spectrum | $\Delta T/cm^{-1}$ | $\Delta n^*$ | $n^*$ | $T(4f^q6s)/cm^{-1}$ |
|---|---|---|---|---|---|
| 0 | La III | 68 756[a] | 1.049 45 | 2.6458 | 141 086 |
| 1 | Ce III | 70 245[a] | 1.048 18 | 2.6233 | 143 516 |
| 2 | Pr III | 71 601[b] | 1.047 02 | 2.6034 | 145 719 |
| 3 | Nd III | (72 833)[c] | 1.047 6 | 2.5867 | 147 606 |
| 4 | Pm III | (74 109)[c] | 1.047 7 | 2.5695 | 149 589 |
| 5 | Sm III | (75 381)[c] | 1.047 8 | 2.5527 | 151 564 |
| 6 | Eu III | (76 650)[c] | 1.047 9 | 2.5363 | 153 531 |
| 7 | Gd III | 77 883[a] | 1.048 0 | 2.5208 | 155 425 |
| 8 | Tb III | (79 180)[c] | 1.047 6 | 2.5045 | 157 454 |
| 9 | Dy III | (80 441)[c] | 1.047 2 | 2.4890 | 159 422 |
| 10 | Ho III | (81 699)[c] | 1.046 9 | 2.4739 | 161 374 |
| 11 | Er III | 82 977[a] | 1.046 5 | 2.4589 | 163 348 |
| 12 | Tm III | (84 211)[c] | 1.046 1 | 2.4446 | 165 265 |
| 13 | Yb III | 85 475[a] | 1.045 3 | 2.4301 | 167 243 |
| 14 | Lu III | 86 681[a] | 1.045 65 | 2.4171 | 169 047 |

[a]From Eq. (2) using experimental $\Delta E$ values[4–6] and $G_3$ from Tables 5 and 6.
[b]From Sugar and Reader's analysis[3] (see Sec. 7).
[c]By interpolation in Fig. 1.

TABLE 2. Calculation of $n^*$ and $T(4f^q6s)$ in Ln IV spectra from estimated and experimental values of $\Delta T$ and $\Delta n^*$. Figures estimated by interpolation from Fig. 2 are in parentheses

| $q$ | Spectrum | $\Delta T$/cm$^{-1}$ | $\Delta n^*$ | $n^*$ | $T(4f^q6s)$/cm$^{-1}$ |
|---|---|---|---|---|---|
| 0 | Ce IV | 96 900[a] | 1.03741 | 2.8842 | 211 069 |
| 1 | Pr IV | 99 240[a] | 1.0463 | 2.8638 | 214 086 |
| 2 | Nd IV | (100 983)[b] | 1.0456 | 2.8444 | 217 017 |
| 3 | Pm IV | (102 725)[b] | 1.0457 | 2.8260 | 219 852 |
| 4 | Sm IV | (104 466)[b] | 1.0458 | 2.8079 | 222 695 |
| 5 | Eu IV | (106 206)[b] | 1.0460 | 2.7904 | 225 497 |
| 6 | Gd IV | (107 945)[b] | 1.0461 | 2.7731 | 228 320 |
| 7 | Tb IV | (109 683)[b] | 1.0462 | 2.7563 | 231 111 |
| 8 | Dy IV | (111 420)[b] | 1.0458 | 2.7395 | 233 955 |
| 9 | Ho IV | (113 157)[b] | 1.0454 | 2.7230 | 236 799 |
| 10 | Er IV | (114 892)[b] | 1.0450 | 2.7069 | 239 624 |
| 11 | Tm IV | (116 626)[b] | 1.0446 | 2.6911 | 242 446 |
| 12 | Yb IV | 118 386[a] | 1.0443 | 2.6755 | 245 281 |
| 13 | Lu IV | 12 0045[a] | 1.0440 | 2.6611 | 247 943 |
| 14 | Hf IV | 12 1846[a] | 1.0443 | 2.6461 | 250 762 |

[a]From Eq. (2) using experimental $\Delta E$ values[4,7,19,20] and $G_3$ from Tables 5 and 6.
[b]By interpolation in Fig. 2.

series, it is equivalent to a contribution of $\pm 400$ cm$^{-1}$ to the uncertainty in the ionization energy. For the Ln IV series, the contribution is $\pm 600$ cm$^{-1}$.

## 3. The Values of $\Delta T$

Since 1973, $4f^q6s$ and $4f^q7s$ levels in the spectra of Gd III,[5] Er III (Ref. 6), and Yb IV (Ref. 7) have become available. This means that, in the case of Ln III spectra, we have seven values of $\Delta T$ whereas Sugar and Reader had five; with Ln IV, there are now five rather than four. However, because of the possibility of a subshell break, we reject the La III and Ce IV values which visibly reduce the goodness of fit when $\Delta T$ is plotted against $q$.

$\Delta T$ is equal to the separation of the lowest levels of the $4f^q6s$ and $4f^q7s$ configurations after each lowest level has been corrected by the quantity, δ. As in Paper I, Judd's formulae[8,9] were used to calculate the values of δ, which depend on the parameter $G_3$. For non-zero values of $G_3(4f^q6s)$ in Ln III spectra, Sugar and Reader assumed $G_3 = 310$ cm$^{-1}$; for the Ln IV spectra they took $G_3 = 410$ cm$^{-1}$. We, however, have tried to calculate individual values where the available data permit. We give a full account of this in Sec. 7; here we merely direct attention to a useful result of Judd's formulae. If $\Delta E$ is the separation of the lowest levels of the configurations $4f^q6s$ and $4f^q7s$, and $S_1$ is the spin quantum number of the $4f^q$ core,

$$\Delta T = \Delta E - S_1\{G_3(4f^q6s) - G_3(4f^q7s)\}. \quad (2)$$

Our six selected experimental values for Ln III are plotted against $q$ in Fig. 1, and the four for Ln IV in Fig. 2. The values are among those shown in column 3 of Tables 1 and 2. None of the ten selected points deviate from the two fitted curves by more than 50 cm$^{-1}$. At $q = 0$, the displacement of the lanthanum III point from the curve is about 240 cm$^{-1}$; that of cerium IV by nearly 600 cm$^{-1}$. By using the interpolation equation for Ln III, estimated values of $\Delta T$ can be obtained for Nd III, Pm III, Sm III, Eu III, Tb III, Dy III, Ho III, and Tm III;

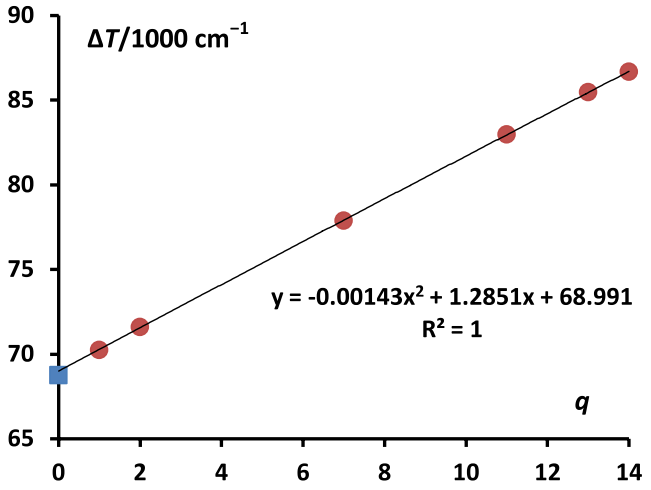


FIG. 1. The energy difference, $\Delta T$, between the $4f^q$ parent levels of the $4f^q6s$ and $4f^q7s$ configurations in lanthanide III spectra plotted against $q$. Points in the range $q = 1 \rightarrow 14$ are marked with dark red circles; the $q = 0$ point is marked with a blue square (a linear fit gives y = 1.2640x + 69.031).

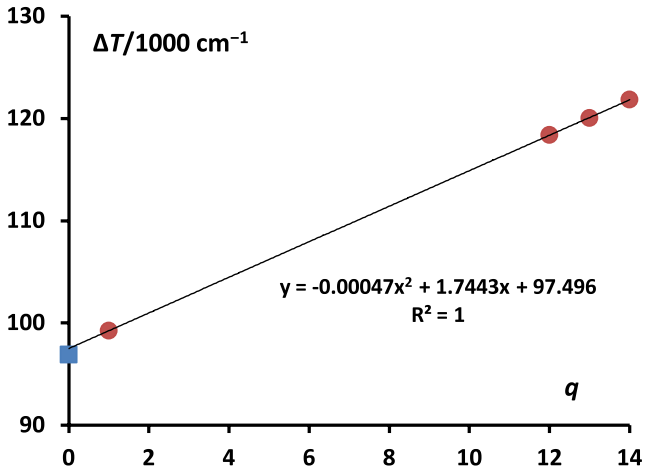


FIG. 2. The energy difference, $\Delta T$, between the $4f^q$ parent levels of the $4f^q6s$ and $4f^q7s$ configurations in lanthanide IV and Hf IV spectra plotted against $q$. Points in the range $q = 1 \rightarrow 14$ are marked with dark red circles; the $q = 0$ point is marked with a blue square (a linear fit gives y = 1.7376x + 97.504).

the equation for Ln IV provides estimates of $\Delta T$ for the sequence Nd IV–Tm IV. These too appear in column 3 of Tables 1 and 2. For the uncertainty in the $\Delta T$ values, we note that doubling the standard deviation of the separations of the fitted points from the curves in Figs. 1 and 2 gives $\pm 70$ cm$^{-1}$ in both cases. They transmit uncertainties of $\pm 110$ cm$^{-1}$ to both the third and the fourth ionization energies.

## 4. The values of $T(4f^q6s)$

When inserted into Eq. (1), the estimated and experimental values of $\Delta T$ and $\Delta n^*$ provide, first, values of $n^*(6s)$ for each element. The $n^*(6s)$ values in turn then yield $T(4f^q6s)$, the amount by which the unperturbed center of gravity of the lowest $4f^q6s$ pair lies below the ionization threshold of the sequence $4f^qns$. This threshold is the lowest level of the

configuration $4f^q$. The results of the calculations appear in Tables 1 and 2. In the Ln III spectra, the uncertainties in $\Delta n^*$ and $\Delta T$ that we have already discussed contribute a combined uncertainty of $\pm 420$ cm$^{-1}$ to $T(4f^q6s)$. In the Ln IV spectra, the figure is $\pm 620$ cm$^{-1}$.

We now consider the calculation of the values of $E(4f^q6s)$. Because the method used for Ln III spectra differs from that applied to Ln IV, we have separate sections on the two types of spectra.

## 5. The Values of $E(4f^q6s)$ in Ln III

$E(4f^q6s)$ is the energy of the lowest level of the $4f^q6s$ configuration relative to the ground state of the dipositive ion. It is one of a pair, there being a higher partner level arising from the same $4f^q$ parent. The amount by which the lower level lies below the ionization threshold can be found by adding δ, its separation from the unperturbed center of gravity of the pair, to $T(4f^q6s)$. Thus, if the lowest level of the $4f^q6s$ configuration has been located in the Ln III spectrum, the third ionization energy is obtained as the sum $\{E(4f^q6s) + T(4f^q6s) + \delta\}$.

In their paper in 1973, Sugar and Reader had available ten experimental values of $E(4f^q6s)$: the missing values were those of neodymium, promethium, samarium, europium, and dysprosium. Sugar and Reader obtained estimates of their five missing values by using what they called the system difference (SD), the difference between the lowest levels of the configurations $4f^q5d$ and $4f^{q+1}$. Estimates of this quantity for the third spectra, Ln III, made by Martin[10] allowed them to calculate ten values of the transition energy $4f^q5d \rightarrow 4f^q6s$ from their ten experimental values of $E(4f^q6s)$. They plotted these values against the atomic number and, by bridging the gaps with straight lines, obtained estimates for the energy of the $4f^q5d \rightarrow 4f^q6s$ transition in neodymium, promethium, samarium, europium, and dysprosium. Martin's SD estimates then allowed calculation of the five missing values of $E(4f^q6s)$.

Since 1973, experimental values of $E(4f^q6s)$ for europium[11] and dysprosium[12] have become available and there are now experimental data on the SD for all Ln III spectra except those of promethium and samarium. The twelve experimental values of $E(4f^q6s)$ are the figures without parentheses in column 5 of Table 7. The three values in parentheses have been obtained by a modification of the estimation method used by Sugar and Reader.

The upper plot in Fig. 3 shows the twelve experimental values of the $4f^q5d \rightarrow 4f^q6s$ transition energy in lanthanide III spectra plotted against $q$. Following Sugar and Reader, the missing values in neodymium, promethium, and samarium could be estimated by bridging the gap with a straight line. However, we have used a different method. The lower plot in Fig. 3 shows the $4f^q5d \rightarrow 4f^q6s$ transition energy for the iso-electronic lanthanide II spectra. The latter comprise a complete set and, as noted by Brewer,[13] the two variations seem very similar. We have therefore estimated missing values in the lanthanide III spectra from the smooth curve obtained when the known Ln III values are plotted against their iso-electronic Ln II

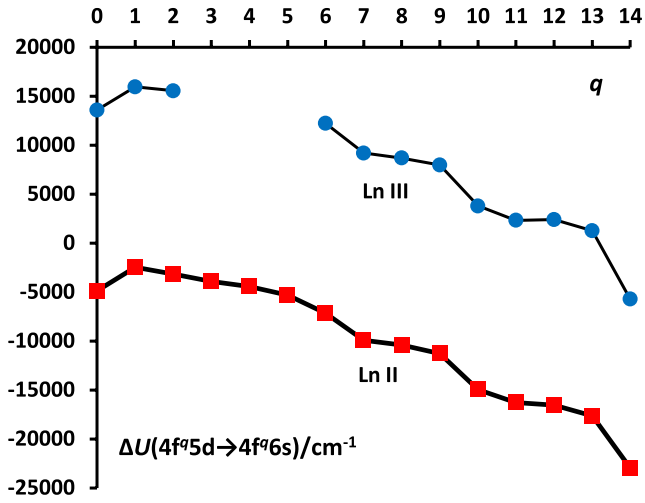


FIG. 3. Variations in the observed values of the transition between the lowest levels of the $4f^q5d$ and $4f^q6s$ configurations in lanthanide II and lanthanide III spectra plotted against $q$.

counterparts. The required transitions were chosen by first selecting those between the lowest levels of the two configurations. In all but two cases they then fulfilled a second requirement: that the spectroscopic designation of the initial and of the final states should be the same. The two cases in question were Gd II and Dy II, where $^8G_{13/2}$ in $4f^85d$ and $^6H_{15/2}$ in $4f^{10}5d$ were chosen so that they matched the lowest levels in Tb III and Ho III. The disruptions in level ordering are due to departures from $LS$ coupling but the matched levels have similar percentage compositions and the adjustments are small: 22 and 106 cm$^{-1}$, respectively.

The required data are shown in Table 3 and the plot appears in Fig. 4. The terminal point, Yb II/Lu III, has been omitted because it is so remote from the region within which we need to interpolate.

When inserted into the polynomial fit of Fig. 4, the Pr II, Nd II, and Pm II figures in Table 3 give 14 872, 14 394, and 13 598 cm$^{-1}$ for the $4f^q5d \rightarrow 4f^q6s$ transition energy in Nd III,

TABLE 3. Data used to estimate the $4f^q5d \rightarrow 4f^q6s$ transition energy in Nd III, Pm III, and Sm III

| | Ln II{$4f^q5d \rightarrow 4f^q6s$}[a] | Ln III{$4f^q5d \rightarrow 4f^q6s$}[a] |
|---|---|---|
| $q$ | cm$^{-1}$ | |
| 1 | −2 451 | 15 959 |
| 2 | −3 158 | 15 553 |
| 3 | −3 893 | |
| 4 | −4 438 | |
| 5 | −5 332 | |
| 6 | −7 135 | 12 240 |
| 7 | −9 923 | 9 195 |
| 8 | −10 397[b] | 8 704 |
| 9 | −11 262 | 7 980 |
| 10 | −14 952[b] | 3 791 |
| 11 | −16 282 | 2 340 |
| 12 | −16 553 | 2 405 |
| 13 | −17 625 | 1 270 |
| 14 | −22 961 | −5 708 |

[a]Unless otherwise stated, transitions occur between the lowest levels of the configurations; data are from Ref. 4.
[b]Includes small adjustments described in Sec. 5.

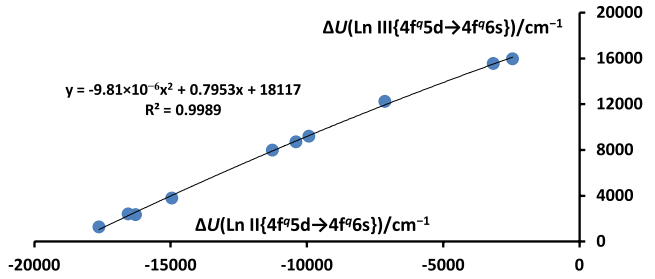


FIG. 4. Experimentally determined differences between the lowest levels of the $4f^q5d$ and $4f^q6s$ configurations in Ln III spectra plotted against their iso-electronic Ln II counterparts. The data appear in Table 3.

Pm III, and Sm III, respectively. The complete set of $4f^q5d \rightarrow 4f^q6s$ transition energies in lanthanide III spectra appears in column 4 of Table 7. The three values obtained from Fig. 4 are placed in parentheses to mark the fact that they are estimates. By doubling the standard deviation of the separations of the points from the curve in Fig. 4, we obtain an uncertainty in the three estimates of $\pm 370$ cm$^{-1}$.

Values of $E(4f^q6s)$ for Nd III, Pm III, and Sm III can now be obtained using the SD values in column 3 of Table 7. In Nd III the lowest *observed* level of the $4f^35d$ configuration is $^5K_5$ at 15 262 cm$^{-1}$ but in the isoelectronic spectrum Pr II, it is $^5L_6$ which lies about 200 cm$^{-1}$ below $^5K_5$ and has not yet been identified in Nd III. Ryabchikova *et al.*[14] give a parameterized treatment of the Nd III spectrum which estimates that $^5L_6$ will lie at about 15 300 cm$^{-1}$. The energy of the lowest level of the $4f^3$ 5d configuration cannot be very different from that of $^5K_5$ and we have placed it at 15 200 cm$^{-1}$ with an uncertainty of $\pm 200$ cm$^{-1}$. This is 800 cm$^{-1}$ below the estimate given by Martin.[10]

Values for Pm III and Sm III have been obtained by updating Martin's Table 1. This contains SD(I), the energy difference between the lowest levels of $4f^{q+1}6s^2$ and $4f^q5d6s^2$, and SD(III), the difference between the lowest levels of $4f^{q+1}$ and $4f^q5d$. When more recent, accurate values for praseodymium and gadolinium are added to Martin's Table 1, Δ(III, I), the difference {SD(III) − SD(I)} increases from 8400 cm$^{-1}$ in praseodymium to 8600 cm$^{-1}$ in gadolinium. We interpolate 8400 cm$^{-1}$ in promethium and 8500 cm$^{-1}$ in samarium. The resulting SD estimates for Pm III and Sm III then become our adopted values of 16 400 cm$^{-1}$ and 24 000 cm$^{-1}$, respectively. They are in only slight disagreement with the view[5] that the Sm III value lies "a little above 24 000 cm$^{-1}$."

The estimated values of $E(4f^q6s)$ for Nd III, Pm III, and Sm III in column 5 of Table 7 are then the sums of the figures in columns 3 and 4. The fact that they are estimates is marked by placing them in parentheses. The uncertainties in $E(4f^q6s)$ are obtained by combining the doubled standard deviation obtained from Fig. 4 ($\pm 370$ cm$^{-1}$) with the uncertainty in the SD. Earlier, we took $\pm 200$ cm$^{-1}$ as the uncertainty in the SD of Nd III. For Pm III and Sm III, the SD values are based on Martin's revised estimates.[3] In four cases, the standard deviation of their differences from subsequent experimental values was $\pm 530$ cm$^{-1}$. We double this figure and take $\pm 1060$ cm$^{-1}$ as the uncertainty of the SD for Pm III and Sm III. The uncertainties in $E(4f^q6s)$ are then $\pm 430$ cm$^{-1}$ for Nd III and $\pm 1200$ cm$^{-1}$ for Pm III and Sm III.

## 6. The Values of $E(4f^q6s)$ in Ln IV

In the lanthanide spectra Ln IV, $E(4f^q6s)$ is the energy of the lowest level of the $4f^q6s$ configuration relative to the $4f^{q+1}$ ground state of the tripositive ion.

In their paper in 1973, Sugar and Reader had available four experimental values of $E(4f^q6s)$: those of cerium, praseodymium, lutetium, and hafnium. As with the Ln III spectra, they obtained estimates of the eleven missing values by using the system difference (SD). However, in eleven of the fourteen spectra, experimental values of the SD were unavailable. The eleven values were therefore estimated by adding 57 300 [1000] cm$^{-1}$ to Martin's estimates[10] for the iso-electronic systems in Ln III.

With these Ln IV SDs, they were able to calculate four values of the transition $4f^q5d \rightarrow 4f^q6s$ from their four values of $E(4f^q6s)$. A nearly linear variation was observed when the four values in Ln IV were plotted against the values for the isoelectronic systems in Ln III. The missing values of the transition $4f^q5d \rightarrow 4f^q6s$ in Ln IV were then derived from this variation using the iso-electronic estimated/experimental values in Ln III. When added to the estimated SD values, an estimate of each missing value of $E(4f^q6s)$ was obtained.

Here then, unknown values of $E(4f^q6s)$ are obtained by summation of two steps which are themselves usually estimates. This exposes the calculation to the compounding of uncertainties which, in the case of Ln IV spectra, are increased by the assumption that the SDs can be obtained by adding a constant difference to iso-electronic Ln III values. However, it is possible to eliminate the two-step summation. Inclusion of Hf IV now gives us nine experimental values of $E(4f^q6s)$: cerium,[4] praseodymium,[4] neodymium,[15] terbium,[16] erbium,[17] thulium,[18] ytterbium,[7] lutetium,[4] and hafnium.[19,20] In the Ln IV spectra, the ground state configuration is $4f^{q+1}$. In such cases, $E(4f^q6s)$ is identical to the energy difference between the lowest levels of the configurations $4f^{q+1}$ and $4f^q6s$. An estimation curve can therefore be established simply by plotting the experimental values of the transition $4f^{q+1} \rightarrow 4f^q6s$ in Ln IV against those of

TABLE 4. Experimental data used to estimate unknown values of $E(4f^q6s)$ in Ln IV spectra. In all but one case, the transition energies shown are equal to $E(4f^q6s)$ because the ground state configuration of the spectrum is $4f^{q+1}$. The exception is Gd III ($q = 7$) where $Gd^{2+}$ has a $4f^75d$ ground state and $E(4f^76s)$ is 9195 cm$^{-1}$

| | Ln III{$4f^{q+1} \rightarrow 4f^q6s$}[a] | Ln IV{$4f^{q+1} \rightarrow 4f^q6s$}[a] |
|---|---|---|
| $q$ | cm$^{-1}$ | |
| 1 | 19 236 | 100 259 |
| 2 | 28 399 | 110 056[b] |
| 7 | 6 814 | 84 955 |
| 10 | 21 824 | 10 1710[c] |
| 11 | 19 316 | 98 973[d] |
| 12 | 25 303 | 106 011[e] |
| 13 | 34 656 | 116 798 |

[a]Unless otherwise stated, transition energies occur between the lowest levels of the configurations and data are from Ref. 4.
[b]Reference 15.
[c]Reference 17.
[d]Reference 18.
[e]Reference 7.

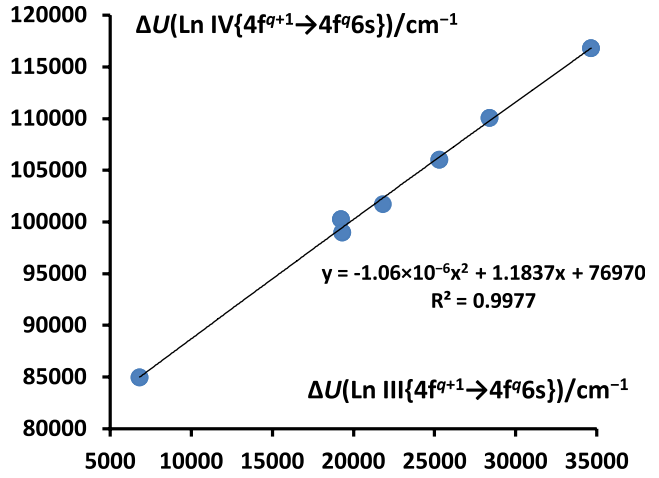


FIG. 5. Differences between the lowest levels of the $4f^{q+1}$ and $4f^q6s$ configurations in the Ln IV spectra plotted against their Ln III counterparts. The data appear in Table 4 (a linear fit gives y = 1.1434x + 77 312).

the iso-electronic Ln III spectra. The data are shown in Table 4. The plot appears in Fig. 5. By means of Fig. 5, missing values of Ln IV $\{E(4f^q6s)\}$ can be estimated from the energies of the transition $4f^{q+1} \rightarrow 4f^q6s$ in Ln III which, in all but two cases, have been determined experimentally. The results are shown in column 3 of Table 8 where the estimates are enclosed in parentheses. For Gd IV, Dy IV, and Ho IV, the uncertainties in $E(4f^q6s)$ are obtained by doubling the sample standard deviations of the points from the curve in Fig. 5. This gives $\pm 1100\ cm^{-1}$. For Pm IV, Sm IV, and Eu IV, we must include a contribution from the values for Nd III, Pm III, and Sm III that were determined in Sec. 5, and upon which they depend. The resulting uncertainties in $E(4f^q6s)$ are $\pm 1200\ cm^{-1}$, $\pm 1600\ cm^{-1}$, and $\pm 1600\ cm^{-1}$, respectively.

## 7. The Values of $G_3$ and δ

The lowest energy level arising from a configuration $4f^qns$ when $0 < q < 14$ is one of a pair; it has a partner level arising from the same $4f^q$ parent. The quantity δ is the separation of the lowest level of $4f^qns$ from the unperturbed center of gravity of the pair. In Paper I, Judd's formulae[8,9] were used to calculate values of δ, which depend on the Racah parameter $G_3$, and, with Sugar and Reader,[2] we found the constant value $G_3 = 210\ cm^{-1}$ to be a satisfactory approximation for $4f^q6s$ in Ln II spectra. When dealing with $4f^q6s$ in the Ln III spectra, Sugar and Reader[3] again assumed a constant value ($G_3 = 310\ cm^{-1}$); for the Ln IV spectra they took $G_3 = 410\ cm^{-1}$. However, subsequently parameterized analyses of the spectra suggest significant variation in the Ln III and Ln IV cases. In Table 5 we give values of $G_3$ obtained from experimental data by analyses of this kind. These appear without parentheses. For both Ln III and Ln IV, the terminal values are larger than the initial ones, but there is a minimum close to the middle of the series near the half-filled shell configuration $4f^76s$. To obtain estimates for the missing values, we have assumed linear changes between the experimental values and the resulting estimates appear in parentheses. With the exceptions of Pr III, Eu III, and Gd IV, values of δ for the lowest level of the $4f^q6s$ configuration are then given by Judd's first formula[8,9] which puts δ equal to $S_1G_3$. Here $S_1$ is the total spin quantum number of the $4f^q$ core. In Pr III, we accepted Sugar and Reader's analysis[3] based on $4f^2(^3H)ns$ centers of gravity. This implies $\delta = 292\ cm^{-1}$. In Eu III and Gd IV, the lowest level of the $4f^66s$ configuration with $J = 1/2$ is perturbed by interaction with a close but higher level that has the same value of $J$. In these two cases, we have simply modified Sugar and Reader's calculation by calculating δ with our revised estimates of $G_3$ in Table 5. For Eu III and Gd IV, we found $758\ cm^{-1}$ and $851\ cm^{-1}$, respectively. The complete sets of δ values for $4f^q6s$ appear in Tables 7 and 8. The sources for $G_3$ in Table 5 provide typical uncertainties of $\pm 20\ cm^{-1}$ in Ln III spectra and $\pm 30\ cm^{-1}$ in Ln IV. We multiply these figures by $S_1$ to get the consequent uncertainties in δ.

Finally, some values of $G_3(4f^q7s)$ are needed for the calculation of the $\Delta T$ values plotted in Figs. 1 and 2. The nonzero values appear in Table 6.

TABLE 6. Values of the Racah parameter $G_3(4f^q7s)$ that were used in calculating the $\Delta T$ values plotted in Figs. 1 and 2

| Spectrum | Ce III[a] | Gd III[b] | Er III[6] | Yb III[a] | Pr IV[c] | Yb IV[7] | Lu IV[27] |
|---|---|---|---|---|---|---|---|
| $G_3/cm^{-1}$ | 82 | 101 | 98 | 104 | (104) | 135 | 73 |

[a]Calculated from the $4f(^2F)7s$ levels using Judd's formulae.
[b]Calculated from the $4f^7(^8S)7s$ levels following Wybourne.[9]
[c]Estimated; see Sec. 8.2.

## 8. The Ionization Energies

Column 5 of Table 7 contains values of $E(4f^q6s)$ that were obtained in the way described in Sec. 5. The two subsequent columns in Table 7 provide the additional data needed to convert them into the third ionization energies that appear in the last two columns of the table, the first giving figures in $cm^{-1}$ and the second in eV. Table 8 gives the values of $E(4f^q6s)$ obtained in Sec. 6 and repeats the operations of Table 7 to give the fourth

TABLE 5. Values of the Racah parameter $G_3$ for the configuration $4f^q6s$ in Ln III and Ln IV spectra. Estimated values are in parentheses. The other values were obtained from analyses of experimentally determined spectra

| Ln III | Ce[a] | Pr[21] | Nd | Pm | Sm | Eu[22] | Gd[b] | Tb[23] | Dy[12] | Ho[24] | Er[6] | Tm[c] | Yb[25] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $G_3/cm^{-1}$ | 313 | 309 | (307) | (305) | (302) | 299 | 294 | 278 | 303 | 313 | 303 | 295 | 337 |
| Ln IV | Pr[26] | Nd[15] | Pm | Sm | Eu | Gd | Tb[b] | Dy | Ho | Er[17] | Tm[18] | Yb[7] | Lu[27] |
| $G_3/cm^{-1}$ | 384 | 390 | (378) | (365) | (352) | (339) | 327 | (348) | (369) | 391 | 409 | 419 | 437 |

[a]Calculated from the $4f(^2F)6s$ levels using Judd's formulae.
[b]Calculated from the $4f^7(^8S)6s$ levels following Wybourne.[9]
[c]Calculated from the $4f^{12}(^3H)6s$ levels using Judd's formulae.

TABLE 7. Calculation of $I_3$ using Fig. 4 for the estimation of unknown values of $E(4f^q6s)$

| | | SD[a] | $4f^q5d \rightarrow 4f^q6s$[a] | $E(4f^q6s)$[a] | δ | $T(4f^q6s)$ | $I_3$ | |
|---|---|---|---|---|---|---|---|---|
| $q$ | | | | $cm^{-1}$ | | | | $I_3$/eV |
| 0 | La | 0 | 13 591 | 13 591 | 0 | 141 086 | 154 677 | 19.178 |
| 1 | Ce | 3 277 | 15 959 | 19 236 | 157 | 143 516 | 162 909 | 20.198 |
| 2 | Pr | 12 847 | 15 553 | 28 399 | 292 | 145 719 | 174 410 | 21.624 |
| 3 | Nd | (15 200)[b] | (14 872)[b] | (30 072)[b] | 461 | 147 606 | 178 139 | 22.086 |
| 4 | Pm | (16 400)[b] | (14 394)[b] | (30 794)[b] | 610 | 149 589 | 180 993 | 22.440 |
| 5 | Sm | (24 000)[b] | (13 598)[b] | (37 598)[b] | 755 | 151 564 | 189 917 | 23.547 |
| 6 | Eu | 33 856 | 12 240 | 46 096 | 758 | 153 531 | 200 385 | 24.845 |
| 7 | Gd | 0 | 9 195 | 9 195 | 1029 | 155 425 | 165 649 | 20.538 |
| 8 | Tb | 8972 | 8 704 | 17 676 | 834 | 157 454 | 175 964 | 21.817 |
| 9 | Dy | 16 453[c] | 7 980[c] | 24 433[c] | 758 | 159 422 | 184 613 | 22.889 |
| 10 | Ho | 18 033 | 3 791 | 21 824 | 626 | 161 374 | 183 824 | 22.791 |
| 11 | Er | 16 976 | 2 340 | 19 316 | 455 | 163 348 | 183 159 | 22.704 |
| 12 | Tm | 22 897 | 2 405 | 25 303 | 295 | 165 265 | 190 863 | 23.664 |
| 13 | Yb | 33 386 | 1 270 | 34 656 | 169 | 167 243 | 202 068 | 25.053 |
| 14 | Lu | 5 708 | −5 708 | 0 | 0 | 169 047 | 169 047 | 20.959 |

[a]Unless otherwise stated, transitions occur between the lowest levels of the configurations; data are from Ref. 4.
[b]Estimated values, see text.
[c]Reference 12.

TABLE 8. Calculation of $I_4$ from the experimental values of $E(4f^q6s)$ and estimated values obtained using Fig. 5

| | | $E(4f^q6s)$[a] | δ | $T(4f^q6s)$ | $I_4$ | |
|---|---|---|---|---|---|---|
| $q$ | | | | $cm^{-1}$ | | $I_4$/eV |
| 0 | Ce | 86 602 | 0 | 211 069 | 297 671 | 36.907 |
| 1 | Pr | 100 259 | 192 | 214 086 | 314 537 | 38.998 |
| 2 | Nd | 110 056[b] | 390 | 217 017 | 327 463 | 40.600 |
| 3 | Pm | (111 604)[c] | 567 | 219 852 | 332 023 | 41.166 |
| 4 | Sm | (112 412)[c] | 730 | 222 695 | 335 837 | 41.639 |
| 5 | Eu | (119 970)[c] | 880 | 225 497 | 346 347 | 42.942 |
| 6 | Gd | (129 282)[c] | 851 | 228 320 | 358 453 | 44.443 |
| 7 | Tb | 84 955 | 1145 | 231 111 | 317 211 | 39.329 |
| 8 | Dy | (97 562)[c] | 1044 | 233 955 | 332 561 | 41.232 |
| 9 | Ho | (105 259)[c] | 923 | 236 799 | 342 981 | 42.524 |
| 10 | Er | 101 710[b] | 782 | 239 624 | 342 116 | 42.417 |
| 11 | Tm | 98 973[b] | 614 | 242 446 | 342 033 | 42.407 |
| 12 | Yb | 106 011[b] | 419 | 245 281 | 351 711 | 43.607 |
| 13 | Lu | 116 798 | 219 | 247 943 | 364 960 | 45.249 |
| 14 | Hf | 18 380[d] | 0 | 250 762 | 269 142 | 33.369 |

[a]Unless otherwise stated, data are from Ref. 4.
[b]See references in Table 4.
[c]Estimated from Fig. 5; see text.
[d]Reference 19.

ionization energies in its last two columns. In Table 9, our third and fourth ionization energies are compared with those estimated by Sugar and Reader (1973)[3] and with the current NIST recommendations.[4]

The uncertainties in our ionization energies were calculated by combining those in $T(4f^q6s)$, $E(4f^q6s)$, and δ in quadratic fashion. The figures for the three components appear in Secs. 2–7.

### 8.1. Third ionization energies

The NIST values for La, Ce, Pr, Yb, and Lu are identical to ours because they have small uncertainties and were used as basic data in our semiempirical scheme. In these cases, differences from Sugar and Reader[3] are due to subsequent improvements that are independent of the methods used both by them and in this paper.

For the five elements Gd, Tb, Ho, Er, and Tm, the NIST values are virtually identical to those of Sugar and Reader and, in these cases, NIST does indeed cite the 1973 paper as the source. The differences in europium and dysprosium are due to improved spectroscopic data obtained since 1973,[11,12] which allowed recalculations of $I_3$ using Sugar and Reader's method and auxiliary data. Until recently, the NIST database also recommended Sugar and Reader's third ionization energies for Nd, Pm, and Sm. However, during the preparation of this paper, it introduced the new figures in column 3 of Table 9.

The revised NIST values for neodymium and samarium are those of Morss[28] who derived them from thermo-chemical cycles. The method is exposed to uncertainties in auxiliary thermodynamic data, including those in the values of lanthanide second ionization energies for which Morss used the estimates of Sugar and Reader[2] that we have since recalculated. Nevertheless, his values for the third ionization energies of neodymium and samarium agree with ours within the range of uncertainties.

In promethium, the NIST database currently recommends the value obtained by Vander Sluis and Nugent.[29] This is 0.4 eV lower than ours and lies well outside our uncertainty range. In the middle region of the series, Vander Sluis and Nugent's linearization technique produces values of the third ionization energies that are lower than those found by other methods. In neodymium and samarium, their estimates are 0.2 and 0.36 eV lower than the current NIST values. Similar deficiencies of 0.13–0.26 eV occur in Eu, Gd, Tb, and Dy. Vander Sluis and Nugent suggested that this might be because the interpolations made by Sugar and Reader did not take account of what we have called the subshell break. However, our revision eliminates this problem, and the disparities with Vander Sluis and Nugent's method persist.

To summarize, if we ignore the case of promethium, our values differ from the NIST recommendations by less than 0.1 eV, being slightly lower from samarium onward.

TABLE 9. Three sets of third and fourth ionization energies: Columns 2 and 6, Sugar and Reader (1973); columns 3 and 7, current NIST recommendations; columns 4 and 8, this work

| Element | $I_3$/eV | | | Element | $I_4$/eV | | |
|---|---|---|---|---|---|---|---|
| | S&R 1973 | NIST 2016 | This work | | S&R 1973 | NIST 2016 | This work |
| La | 19.1774[6] | 19.1773[6] | 19.1773[6] | Ce | 36.758[5] | 36.906[9] | 36.906[9] |
| Ce | 20.198[3] | 20.1974[25] | 20.1974[25] | Pr | 38.98[2] | 38.981[25] | 39.00[8] |
| Pr | 21.624[3] | 21.6237[25] | 21.6237[25] | Nd | 40.41[20] | 40.4[4] | 40.60[8] |
| Nd | 22.14[30] | 22.05[11] | 22.09[8] | Pm | 41.09[32] | 41.0[6] | 41.17[17] |
| Pm | 22.32[36] | 22.04[13] | 22.44[15] | Sm | 41.37[38] | 41.4[7] | 41.64[21] |
| Sm | 23.43[30] | 23.56[11] | 23.55[15] | Eu | 42.65[32] | 42.7[6] | 42.94[21] |
| Eu | 24.70[32] | 24.92[10] | 24.84[6] | Gd | 44.01[35] | 44.0[7] | 44.44[16] |
| Gd | 20.63[10] | 20.63[10] | 20.54[6] | Tb | 39.79[20] | 39.36[10] | 39.33[8] |
| Tb | 21.91[10] | 21.91[10] | 21.82[6] | Dy | 41.47[20] | 41.4[4] | 41.23[16] |
| Dy | 22.79[30] | 22.93[10] | 22.89[6] | Ho | 42.48[32] | 42.5[6] | 42.52[16] |
| Ho | 22.84[10] | 22.84[10] | 22.79[6] | Er | 42.65[21] | 42.7[4] | 42.42[8] |
| Er | 22.74[10] | 22.74[10] | 22.70[6] | Tm | 42.69[20] | 42.7[4] | 42.41[8] |
| Tm | 23.68[10] | 23.68[10] | 23.66[6] | Yb | 43.74[20] | 43.56[10] | 43.61[8] |
| Yb | 25.03[2] | 25.053[25] | 25.053[25] | Lu | 45.19[2] | 45.249[25] | 45.249[25] |
| Lu | 20.9596[10] | 20.9594[12] | 20.9594[12] | Hf | 33.33[2] | 33.370[25] | 33.370[25] |

### 8.2. Fourth ionization energies

Again, the identity of the NIST values for Ce, Lu, and Hf with ours reflects their low uncertainties and their use in our fitting procedures.

For the 11 elements Pr–Gd and Dy–Yb, the NIST database again cites Sugar and Reader (1973)[3] as the source. In terbium, the difference of 0.43 eV between Sugar and Reader's value and that cited by NIST is important because it arises from subsequent work[16] that identified $E(4f^q6s)$ at 84 955 $cm^{-1}$, compared with the estimate of 88 100 $cm^{-1}$ in the 1973 paper. The chief source of the error was the $4f^n \rightarrow 4f^q5d$ system difference which was found at 51 404 $cm^{-1}$ rather than 54 900 $cm^{-1}$. Our value for terbium differs from the revised NIST estimate by only 0.03 eV.

In the first half of the series, between neodymium and gadolinium, our estimated values exceed the NIST recommendations by 0.17–0.44 eV. In the second half of the series, between dysprosium and thulium, our values tend to be lower, but by less than 0.3 eV. One effect of these last differences is that the three-quarter shell effect, the downward break in $I_4$ between holmium and thulium, is more pronounced. The NIST data suggest that the value in thulium is 0.2 eV greater than in holmium; our values imply that it is 0.1 eV less. It may be that an important contribution to the differences arises from Sugar and Reader's use of a constant difference in the SDs of Ln III and Ln IV spectra. Spector and Sugar's later revision in terbium,[16] which reduced the ionization energy by 0.4 eV, suggested that this was the case. It also led them to recommend a doubling of the uncertainties proposed by Sugar and Reader for the nine elements Nd–Gd and Dy–Tm. This recommendation seems to have been accepted by NIST. Our estimation method avoids the use of SD and has an improved auxiliary database. Consequently, throughout the series the uncertainties in our estimated values are smaller than those proposed by NIST, except at praseodymium. This exception is chiefly due to our uncertainty in $\Delta n^*$ ($\pm 0.005$) which is more than double that proposed by Sugar and Reader.[3]

A recent paper[30] has drawn attention to the discrepancy of 3000 $cm^{-1}$ between the NIST value for the fourth ionization energy of praseodymium (38.98 eV) and the quantum mechanical value of Eliav *et al.* (38.61 eV).[31] It suggests that Sugar and Reader's semi-empirical value might be at fault because of an aberrant value of $\Delta n^*$ brought on by configuration interaction between 4f7s and 5d6p levels. The same suggestion automatically applies to our retracing of Sugar and Reader's method which has yielded a value close to theirs (39.00 eV).

Unfortunately, most of the 4f7s and 5d6p levels in Pr IV have not been experimentally observed. This makes the assessment of configuration interaction difficult. The upper level of $4f(^2F_{5/2})7s$ ($J = 3$) occurs at 199 728 $cm^{-1}$ but the lower level ($J = 2$) is missing. We have used the estimate, $G_3 = 104$ $cm^{-1}$, taken from Yb IV and Lu IV, to place it at 199640 $cm^{-1}$. Of the 11 levels of 5d6p, only two have been observed: $^3F_4$ at 195 917 $cm^{-1}$ and $^1F_3$ at 202 487 $cm^{-1}$. However, these estimates and observations do suggest that the full set spans the two relevant levels of 4f7s and this supports the possibility of a strong configuration interaction.

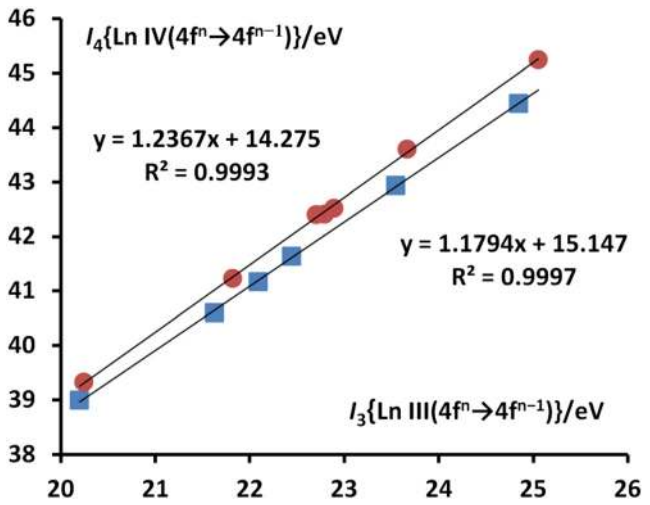


FIG. 6. The fourth ionization energies of the lanthanides plotted against the third ionization energies for isoelectronic transitions of the type $\{Xe\}4f^n \rightarrow \{Xe\}4f^{n-1}$. The lower plot shows the sequence Ce III/Pr IV → Eu III/Gd IV; the upper plot shows Gd III/Tb IV → Yb III/Lu IV.

The proximity of the levels of the two configurations depends on the charge of the ion, and in the isoelectronic Ce III, the 5d6p levels all lie above those of 4f7s. For example, there are separations of 3000 $cm^{-1}$ between 4f($^2F_{5/2}$)7s ($J = 2$) and 5d6p($^3F_2$), and 6400 $cm^{-1}$ between 4f($^2F_{5/2}$)7s ($J = 3$) and 5d6p($^3F_3$). In this case, larger separations would weaken any configuration interaction but if it occurs, it should have suppressed $\Delta T$ and, in its absence, the ionization energy would be higher. There is, however, no obvious sign of this. As Fig. 6 shows, plots of our values of $I_4$ against the isoelectronic values for $I_3$ (corrected in $Gd^{2+}$ to a $4f^n$ ground state) show excellent linearity for the sequences Ce III/Pr IV → Eu III/Gd IV and Gd III/Tb IV → Yb III/Lu IV. The $R^2$ values are 0.9997 and 0.9993, respectively. There is therefore no indication that the value for Pr(IV) is markedly aberrant in the context of the other semiempirical values.

Finally we note that, since the work of Eliav *et al.*, other quantum mechanical calculations have been made. Those of Cao and Dolg[32] treated the lanthanide series as a whole and this less specific approach by two slightly different methods gave values of 38.84 and 39.04 eV, which closely span those given by NIST and by us. Clearly there is a need for further work on the problem and especially on the spectrum of Pr IV.

### 8.3. The standard enthalpies of formation of gaseous tripositive ions

This quantity is needed for the calculation of the lattice enthalpies of lanthanide compounds and the hydration enthalpies of ions. It can also be used to explore the possibility of a subshell break and to check the overall reliability of our estimates. It can be calculated from the equation

$$\Delta_f H^{\ominus}(M^{3+},g) = \Delta_f H^{\ominus}(M,g) + I_1 + I_2 + I_3 + (15/2)RT. \quad (3)$$

Here we use the familiar ideal gas standard state at a pressure of 1 bar for gaseous ions and electrons. There are two recent reviews of the values of $\Delta_f H^{\ominus}$(M,g) for the lanthanide elements.[33,34] We have used the averages of the two sets, and they appear in column 3 of Table 10. Promethium has been omitted because of the absence of an experimental value. When combined with the NIST values of $I_1$, which have small uncertainties,[4] and our revised values of $I_2$ and $I_3$, Eq. (3) gives the values of $\Delta_f H^{\ominus}(M^{3+},g)$ in column 4. $\Delta_f H^{\ominus}(M^{3+},g)$ refers to the reaction

$$M(s) \rightarrow M^{3+}(g) + 3e^-(g). \quad (4)$$

Most lanthanide metals have some form of hexagonal close-packed structure[33] with three bonding electrons per metal atom outside an inner $4f^q$ sub-shell.[35] Reaction (4) is then one in which the 4f electrons are conserved. The energies of this kind of reaction usually vary nearly smoothly across the lanthanide series. This is because coupling between the outer bonding and inner 4f electrons is weak. There may be perturbations of the smooth variation caused by structural variations or a tetrad effect[36–38] but these are usually small (≤4 kJ $mol^{-1}$).

In Fig. 7, $\Delta_f H^{\ominus}(M^{3+},g)$ has been plotted against $q$, the number of 4f electrons in the gaseous tripositive ion. The cerium value has been increased by 2 kJ $mol^{-1}$ to place it in the β hexagonally close packed form.[33,34] Eleven of the fourteen values vary nearly smoothly with $q$, any deviations from the curve being ≤8 kJ $mol^{-1}$ and less than the experimental uncertainties cited in Table 10. Two of the three

TABLE 10. Thermodynamic data on lanthanide compounds and ions at 298.15 K; $q$ is the number of 4f electrons in the gaseous tripositive ion

| | | $\Delta_f H^{\ominus}$(M,g)[a] | $\Delta_f H^{\ominus}(M^{3+},g)$[b] | $\Delta_f H^{\ominus}(MCl_3,s)$[c] | $\Delta_f H^{\ominus}(M^{3+},aq)$[d] | $\Delta_f H^{\ominus}(M_2O_3,s)$[e] |
|---|---|---|---|---|---|---|
| $q$ | Element | kJ $mol^{-1}$ | | | | |
| 0 | La | 432.3[40] | 3918[4] | −1071.6[15] | −707.6[25] | −1791.6[20] |
| 1 | Ce | 428.4[30] | 3987[5] | −1059.9[15] | −702.4[20] | −1799.8[10] |
| 2 | Pr | 356.2[30] | 4015[5] | −1058.1[15] | −705.7[20] | −1809.9[30] |
| 3 | Nd | 326.5[20] | 4050[9] | −1041.0[10] | −694.8[20] | −1806.9[30] |
| 5 | Sm | 206.7[20] | 4111[15] | −1025.3[20] | −690.0[20] | −1826.8[50] |
| 6 | Eu | 178.0[20] | 4227[7][f] | −935.4[30] | −605.4[40] | −1662.5[60] |
| 7 | Gd | 401.5[50] | 4160[9] | −1020.8[30] | −698.4[20] | −1819.7[40] |
| 8 | Tb | 389.7[30] | 4190[8] | −1010.6[30] | −699.8[40] | −1865.2[60] |
| 9 | Dy | 286.9[30] | 4211[8] | −992.8[30] | −700.2[30] | −1863.4[50] |
| 10 | Ho | 302.9[40] | 4238[8] | −997.6[25] | −707.7[30] | −1883.3[80] |
| 11 | Er | 313.6[40] | 4262[8] | −995.0[20] | −708.2[30] | −1900.1[70] |
| 12 | Tm | 232.8[30] | 4295[8] | −996.3[25] | −711.1[30] | −1889.3[60] |
| 13 | Yb | 152.1[20] | 4366[4] | −959.4[30] | −676.3[30] | −1814.5[60] |
| 14 | Lu | 427.6[30] | 4355[10] | −985.7[25] | −703.3[30] | −1877.0[80] |

[a]Averages of the sets of values recommended in Refs. 33 and 34.
[b]Calculated from Eq. (3) with first ionization energies from Ref. 4 and the recommended second and third ionization energies from Parts 1 and 2 of this work.
[c]Average of the set of values recommended in Refs. 40 and 41.
[d]Reference 43.
[e]Reference 42.
[f]Includes an electronic contribution to $(H^{\ominus}_{298} - H^{\ominus}_0)$ for $Eu^{3+}$(g) of 1.7 kJ $mol^{-1}$.

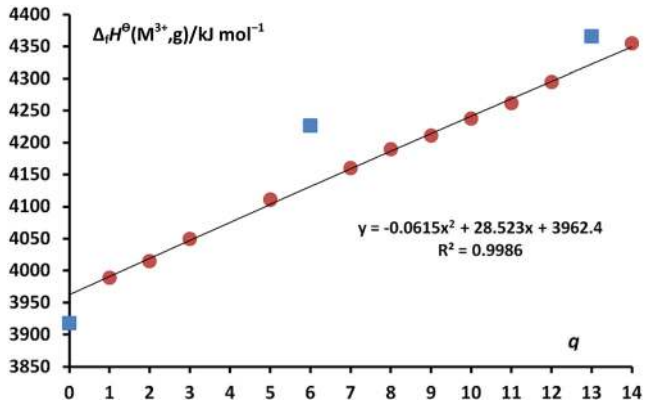


FIG. 7. Plot of $\Delta_f H^\ominus(M^{3+},g)$ for lanthanide elements against $q$ where $q$ is the number of 4f electrons in the gaseous tripositive ion. The polynomial fit covers only the dark red circular points. The square points represent lanthanum, europium, and ytterbium; promethium has been omitted.

exceptions, those in europium and ytterbium, are displaced upward by 96 and 43 kJ mol$^{-1}$, respectively. This is because in these two metals, there are two bonding electrons, rather than three, outside an inner 4f$^{q+1}$ subshell.[35] The displacements represent the amounts by which the two-electron divalent metals are stabilized with respect to the three-electron trivalent state. The third exception is in lanthanum which is displaced downward by 45 kJ mol$^{-1}$. We regard the good fit observed for eleven trivalent metals in Fig. 7 and the large displacement at $q = 0$ as support for both our revised ionization energies and a substantial subshell break.

### 8.4. Irregularities in the 4f$^q$5d → 4f$^q$6s transition in Ln III

In Sec. 5, we required values of the differences between the lowest levels of this transition for Nd III, Pm III, and Sm III. We obtained them by plotting known values for Ln III spectra against their isoelectronic Ln II counterparts. Figure 3 plots the data that we used and it includes the complete variation for Ln II with an incomplete one for Ln III. In Fig. 8 we have added our estimated values and plotted a complete variation for Ln III.

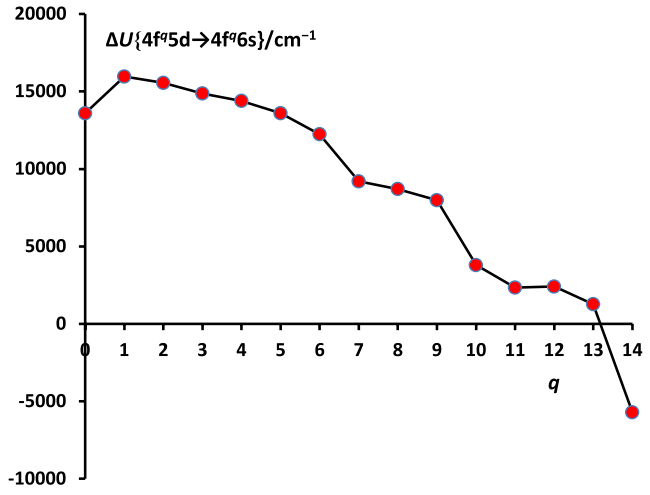


FIG. 8. Variations in the energy of the transition between the lowest levels of the 4f$^q$5d and 4f$^q$6s configurations in lanthanide III spectra plotted against $q$. The values at $q = 3$, 4, and 5 have been estimated from Fig. 4.

In this transition, the 4f electrons are conserved but unlike other changes of this type (Figures 1, 2, and 7) the transition energy does not vary nearly smoothly between 4f$^1$ and 4f$^{14}$. It seems that the 5d electron couples much more strongly with the inner 4f$^q$ subshell than do the s electrons in Figs. 1 and 2 or the bonding electrons in lanthanide metals. It is noticeable that the pattern of the irregularities in Fig. 8 is that of a tetrad effect, which, while only slightly evident in the first half of the series, is prominent from $q = 6$ onward: the values at f$^7$, f$^{10}$, and f$^{11}$ are depressed with respect to their immediate neighbors. This suggests that a substantial contribution to the irregularities is made by an increase in the interelectronic repulsion energy within the 4f subshell when the outer electron moves out of the 5d and into the 6s orbital.[36–38] According to the theory of the tetrad effect, this increase varies irregularly across the series and generates downward breaks at f$^3$/f$^4$, f$^7$, and f$^{10}$/f$^{11}$. However, in this case, the irregularities are an order of magnitude greater than those found in familiar examples of the effect which involve conventional chemical reactions.[39]

### 8.5. Lattice enthalpies and hydration enthalpies of trivalent compounds and ions

Here we find out if the subshell break in our values of $\Delta_f H^\ominus(M^{3+},g)$ is transmitted to lattice enthalpies and hydration energies. Reviews of the enthalpies of formation of lanthanide trichlorides,[40,41] sesquioxides,[42] and aqueous ions[43] give the values shown in Table 10. The figures for the trichlorides are the averages of those in Refs. 40 and 41. We take the lattice enthalpy of a solid lanthanide trichloride, $L^\ominus(LnCl_3)$, to be the standard enthalpy change, at 298.15 K, of the reaction

$$Ln^{3+}(g) + 3Cl^-(g) \rightarrow LnCl_3(s). \quad (5)$$

Thus, $L^\ominus(LnCl_3,s)$ is given by

$$L^\ominus(LnCl_3,s) = \Delta_f H^\ominus(LnCl_3,s) - \Delta_f H^\ominus(Ln^{3+},g) - 3\Delta_f H^\ominus(Cl^-,g). \quad (6)$$

Demonstrations of a subshell break are more convincing if they avoid possible irregularities introduced by structural change. We can do this by using the seven trichlorides, $LaCl_3$ → $GdCl_3$, which all have the hexagonal $UCl_3$ structure[40] ($PmCl_3$ has been omitted). With data from columns 4 and 5 of Table 10, and the value[44] $\Delta_f H^\ominus(Cl^-,g) = -233.95$ kJ mol$^{-1}$, Eq. (6) yields the values of $L^\ominus(LnCl_3)$ plotted in Fig. 9(A). The subshell break is 36 kJ mol$^{-1}$.

There is evidence that in the early part of the lanthanide series, the four aqueous ions, $La^{3+}(aq)$, $Ce^{3+}(aq)$, $Pr^{3+}(aq)$, and $Nd^{3+}(aq)$, all have nine-fold trigonal tri-prismatic coordination.[45] We can reproduce the *variations* in the hydration enthalpies of these ions by using the quantity $\{\Delta_f H^\ominus(M^{3+},aq) - \Delta_f H^\ominus(M^{3+},g)/kJ\ mol^{-1}\}$ calculated from columns 4 and 6 of Table 10. This has been done in Fig. 9(B). The subshell break is 33 kJ mol$^{-1}$.

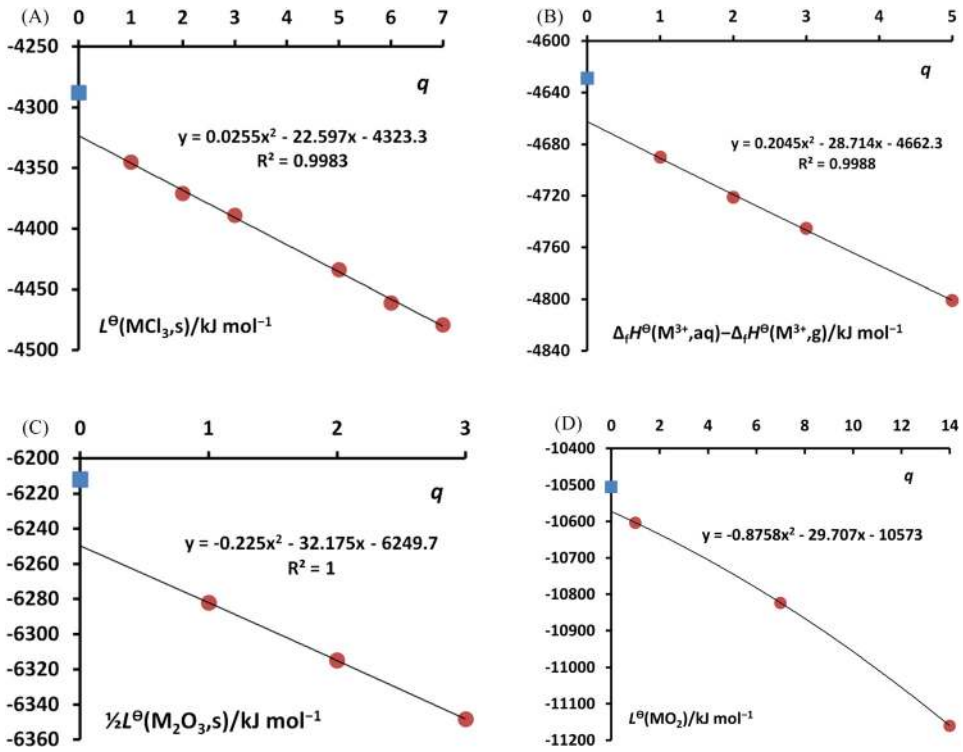


FIG. 9. The lattice and hydration enthalpies of some isostructural trivalent and tetravalent lanthanide compounds and ions plotted against $q$, the number of 4f electrons in the free ion. (A) The lattice enthalpies of trichlorides; (B) the variation in the hydration enthalpies of tripositive ions; (C) the lattice enthalpies of sesquioxides; (D) the lattice enthalpies of dioxides. Points in the range $q = 1 \rightarrow 14$ are marked with dark red circles; the $q = 0$ point is marked with a blue square.

TABLE 11. Calculation of the lattice enthalpies of lanthanide and hafnium dioxides with the fluorite structure; $q$ is the number of 4f electrons in the gaseous tetrapositive ion

| $q$ | Element | $\Delta_f H^{\ominus}(M,g)$ kJ mol$^{-1}$ | $\Delta_f H^{\ominus}(M^{4+},g)$ kJ mol$^{-1}$ | $\Delta_f H^{\ominus}(MO_2,s)$ kJ mol$^{-1}$ | $L^{\ominus}(MO_2,s)$[a] kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| 0 | Ce | 428.4[30][b] | 7554[6][c] | −1090.4[10][d] | −10 505 |
| 1 | Pr | 356.2[30][b] | 7784[10][c] | −959.1[20][d] | −10 603 |
| 7 | Tb | 389.7[30][b] | 7991[12][c] | −972.2[50][d] | −10 823 |
| 14 | Hf | 618.4[60][e] | 8207[60][f] | −1093[11][g] | −11 160 |

[a]Calculated using Eq. (8) with $\Delta_f H^{\ominus}(O^{2-},g) = 930$ kJ mol$^{-1}$.
[b]See Table 10.
[c]Calculated from Eq. (7) with first ionization energies from Ref. 4 and the recommended second, third, and fourth ionization energies from Parts 1 and 2 of this work.
[d]Reference 42.
[e]Reference 44.
[f]Calculated from Eq. (7) with ionization energies from Ref. 4.
[g]Reference 57 with an adjustment for conversion to a fluorite structure; see text.

The sequioxides of the series $La_2O_3 \rightarrow Nd_2O_3$ all have the hexagonal A-type $M_2O_3$ structure.[42] The values of $1/2L^{\ominus}(Ln_2O_3)$ can be calculated from columns 4 and 7 of Table 10 and the estimated value $\Delta_f H^{\ominus}(O^{2-},g) = 930$ kJ mol$^{-1}$.[46] Since this estimate is a constant for each lattice enthalpy, it does not affect the variation, or the subshell break of 38 kJ mol$^{-1}$ revealed by Fig. 9(C).

### 8.6. Lattice enthalpies of tetravalent lanthanide oxides

Past investigations of the first transition series have found that the subshell break tends to increase with the oxidation state of the transition element.[47–50] Does this also occur in the lanthanide series? The experimental data are very limited but seem sufficient to answer this question. In the series Ce → Hf, there are just four known dioxides: those of cerium, praseodymium, terbium, and hafnium. The dioxides of the first three elements have the eight-coordinate fluorite structure.[42] At room temperature, hafnium dioxide has a monoclinic structure in which the hafnium atom is seven-coordinate. However, the cubic fluorite form is stable above 2870 K and there is an experimental value of 5.08 Å for its unit cell parameter[51] (internuclear distance 2.20 Å). Theoretical calculations[52–56] indicate that, at 298.15 K, the standard enthalpy of the change from the monoclinic to the fluorite structure is approximately 25 ± 10 kJ mol$^{-1}$. The value

of $\Delta_f H^{\ominus}(HfO_2$, monoclinic)[57] is $-1117.5 \pm 2$ kJ mol$^{-1}$ so we use the figure $\Delta_f H^{\ominus}(HfO_2$,fluorite) $= -1093 \pm 11$ kJ mol$^{-1}$.

Table 11 contains the enthalpies of formation of the other three dioxides.[42] The quantity $\Delta H_f^{\ominus}(M^{4+},g)$ and the lattice enthalpy, $L^{\ominus}(MO_2,s)$, can be calculated from the equations

$$\Delta_f H^{\ominus}(M^{4+},g) = \Delta_f H^{\ominus}(M,g) + I_1 + I_2 + I_3 + I_4 + 10RT, \quad (7)$$

$$L^{\ominus}(MO_2,s) = \Delta_f H^{\ominus}(MO_2,s) - \Delta_f H^{\ominus}(M^{4+},g) - 2\Delta_f H^{\ominus}(O^{2-},g). \quad (8)$$

For the three lanthanide elements, we have used our revised ionization energies and the $\Delta_f H^{\ominus}$(M,g) values given earlier in this paper. The ionization energies of hafnium and its enthalpy of atomization are taken from Refs. 4 and 44. The lattice enthalpies were again calculated using $\Delta_f H^{\ominus}(O^{2-},g)$ = 930 kJ mol$^{-1}$ and, in Fig. 9(D), they are plotted against $q$. The subshell break amounts to 68 kJ mol$^{-1}$, approximately double that observed for the oxides $1/2M_2O_3$. It can be seen from Fig. 9(D) that the relative positions of the $CeO_2$, $PrO_2$, and $TbO_2$ points are such that the size of the break is relatively insensitive to the large uncertainties in the hafnium data.

## 9. Conclusion

The improvements in the auxiliary data, and the modifications that we have made to earlier estimation methods, justify the revised ionization energies and uncertainties listed in Table 9. The ionization energies with higher uncertainties mark the absence of desirable information from the observed spectra, notably the missing energies of the lowest levels of $4f^q6s$ for Nd III → Sm III, Nd IV → Gd IV, Dy IV, and Ho IV. In Pm III and Sm III, the uncertainties are further enhanced by the absence of values for the SD. Thus, further work on all these spectra could improve the estimation scheme. Finally two specific ionization energies, along with their associated spectra, merit further experimental investigation. First, the fourth ionization energy of praseodymium, obtained through the estimation scheme used by both us and Sugar and Reader, has been questioned from a theoretical standpoint. Second, we take this opportunity to reaffirm the point made in Paper I: the study of lanthanide systematics would be especially helped by a more accurate experimental value of the second ionization energy of lutetium.

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