Lanthanide Ionization Energies and the Sub-Shell Break. Part 1. The Second Ionization Energies

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Lanthanide Ionization Energies and the Sub-Shell Break. Part 1. The Second 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 second ionization energies of the lanthanides have been obtained. In the early part of the series, between cerium and samarium, the revisions are significantly higher than currently accepted values. The revised values have been used to calculate the energy variation for the conversion of Ln(g, $4f^q6s^2$) to Ln^{2+}(g, $4f^q$) across the series Ba → Yb. The variation is smooth between lanthanum and ytterbium but the barium point at $q = 0$ is displaced downwards by more than 0.3 eV, thereby representing a significant sub-shell break. A case is also made for a substantial change to the second ionization energy of lutetium, the revised value being 14.13 ± 0.10 eV. *© 2017 AIP Publishing LLC for the National Institute of Standards and Technology.* [http://dx.doi.org/10.1063/1.4977958]

Key words: lanthanides; ionization energies; lutetium; thermochemical properties.

CONTENTS

List of Tables

List of Figures

1. Introduction

During an investigation of lanthanide thermodynamics, we had a need of sets of lanthanide ionization energies. The standard source is the excellent NIST Atomic Spectra

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Database.[1] This provides values of ionization potentials with assessed uncertainties, the detailed atomic spectra from which they were derived, and supporting bibliography that both precedes and postdates the recommended values. Unless otherwise stated, spectroscopic and ionization energy data used in this paper are taken from this website.[b] The first ionization energies of the lanthanides are well established, in most cases with small uncertainties of ≤0.0006 eV. However, many of the second and third ionization energies have larger uncertainties and were obtained by semi-empirical methods that involve interpolation of data within the lanthanide series. We noticed that the results of these methods were affected by the very question that we were investigating: should the interpolation process be applied to a series that runs from f^0 to f^{14}, or should f^0 be omitted and interpolation confined to the series f^1 to f^{14}? Our ligand field analyses of the thermodynamics of the first transition series[2–5] favour the second policy: removal of irregularly varying terms from quantities such as lattice enthalpies and hydration energies leaves a smooth variation between $3d^1$ and $3d^{10}$, but the value at $3d^0$ is usually displaced from it, sometimes by more than 60 kJ mol^{-1}. We have called this phenomenon the sub-shell break because the change in outer electronic configuration $3d^0 \rightarrow 3d^1$ is strictly $3p^6 \rightarrow 3d^1$.

In this paper, we look into the question by reassessing the interpolation methods that have been used to obtain second ionization energies of the lanthanides. Because of the complexity of the spectra of lanthanide ions, few of their ionization energies have been obtained from observations of long series in the atomic spectra. However, in 1965, a set of second ionization energies for the fourteen elements La → Yb were obtained in a ground-breaking paper by Sugar and Reader.[6] On the current NIST website, it is still cited as the source of twelve of those fourteen second ionization energies. The semi-empirical methods used by Sugar and Reader were later extended in a second paper that provided values for the third and fourth ionization energies.[7]

Here, we recalculate the second ionization energies with a revised version of their method. The revisions take advantage of the improvements and growth of the auxiliary data since 1965. As in the original paper, the method relies on a smooth variation in the energy difference, ΔT, between the unperturbed centres of gravity of those pairs of $4f^q6s$ and $4f^q7s$ levels that are based upon the lowest $4f^q$ parent level. Unknown values are obtained by interpolation of the smooth variation, which is 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 ΔT values are then expressed by a Rydberg–Ritz formula, which in this case takes the form

$$\Delta T = 4R\left\{[1/n^*(6s)]^2 - [1/(n^*(6s) + \Delta n^*)]^2\right\}. \qquad (1)$$

Here n^* is the effective principal quantum number and R the Rydberg constant. Sugar and Reader used the value $\Delta n^* = 1.050$ for the entire series of elements. Each value of ΔT then yields a value of $n^*(6s)$, which provides $T(4f^q6s)$, the amount by which the parent $4f^q$ level of $4f^q6s$ 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 lies below the ionization threshold and if that lowest level can be determined, the second ionization energy follows. In Secs. 2–6, 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 Δn^*

We begin this section by clarifying the meaning of the parameter q. In both this paper and its successor, we shall be concerned with the second, third, and fourth spectra, M II, M III, and M IV, of three series of atoms, M, in which the ion generated at the ionization limit can exist in the electronic configuration $\{Xe\}4f^q$. In nearly all cases, this is the ground state configuration of the generated ion; the exceptions occur in the spectra La II and Gd II. There, the ions La^{2+} and Gd^{2+} have ground state configurations $\{Xe\}5d^1$ and $\{Xe\}4f^75d^1$, respectively but levels arising from the configurations $\{Xe\}4f^1$ and $\{Xe\}4f^8$ can exist in the spectra and they occur as excited states, completing the definition of q. The definition sets up the M II series as Ba–Yb, the M III series as La → Lu, and the M IV series as Ce → Hf; all three begin at $q = 0$ and end when $q = 14$.

To obtain experimental values of Δn^*, we require spectroscopic data on the $4f^q6s \rightarrow 4f^q7s$ transition and a value of the second ionization energy, I_2, which has been obtained by experimental methods that are independent of, and more accurate than, the one being used here. In the $f^0 \rightarrow f^{14}$ series, Ba–Yb, there are only three elements (Ba, Eu, Yb) that meet these criteria. In these three cases, each spectrum provides a value of ΔT and therefore of Δn^*.

The sparsity of experimental values makes it difficult to refine Sugar and Reader's use of a fixed value of Δn^*. Moreover, our concern about a possible sub-shell break prompted us to ignore the barium value so that our three values are reduced to just two. However, the number can be increased if one also includes Ln III and Ln IV spectra. We have therefore calculated as many experimental values of Δn^* as possible. Where δ values were required we used Judd's formulae.[8] We discuss δ values more fully later, but here we note only that our estimates are the same, or very nearly the same, as Sugar and Reader's.[6,7] The resulting values of Δn^* are obtained from the spectra of Eu II, Yb II, Ce III, Pr III, Yb III, Lu III, Lu IV, and Hf IV. They are set out in Table 1. The figures in square brackets are uncertainties that

Table 1. The reference values of Δn^* for the $4f^qns$ series obtained from experimental data using Eq. (1). The uncertainties were calculated from those in the ionization energies[1] and are given in square brackets in terms of the last decimal place

N_e	q	Ln II	Ln III	Ln IV
56	1		1.048 18[30]	
57	2		1.047 02[30]	
62	7	1.050 5[14]		
68	13		1.045 3[28]	1.0440[18]
69	14	1.047 22[1]	1.045 65[14]	1.0443[18]

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[b] It should be noted that in this work we assume that, unless stated otherwise, the assignments of spectral lines and energy levels in this and other relevant sources are correct.

TABLE 2. Values of Δn^* for the $4f^q ns$ series; the reference values of Table 1 appear in bold type. Estimates obtained by using two distinct methods, A and B, appear in normal type. In subsequent calculations we use estimates, which are the average obtained by the two methods

		Ln II		Ln III		Ln IV	
N_e	q	Method A	Method B	Method A	Method B	Method A	Method B
56	1	1.0497	1.0504	**1.048 18**	**1.048 18**	1.0469	1.0457
57	2	1.0485	1.0502	**1.047 02**	**1.047 02**	1.0457	1.0455
58	3	1.0489	1.0500	1.047 4	1.047 7	1.0461	1.0453
59	4	1.0493	1.0498	1.047 8	1.047 5	1.0465	1.0451
60	5	1.0497	1.0497	1.048 2	1.047 3	1.0469	1.0450
61	6	1.0501	1.0495	1.048 6	1.047 2	1.0473	1.0448
62	7	**1.0505**	**1.0505**	1.049 0	1.047 0	1.0477	1.0446
63	8	1.0499	1.0492	1.048 4	1.046 8	1.0471	1.0445
64	9	1.0493	1.0490	1.047 8	1.046 6	1.0465	1.0443
65	10	1.0487	1.0488	1.047 2	1.046 5	1.0459	1.0441
66	11	1.0481	1.0486	1.046 6	1.046 3	1.0453	1.0439
67	12	1.0475	1.0485	1.046	1.046 1	1.0447	1.0438
68	13	1.0469	1.0483	**1.045 3**	**1.045 3**	**1.0440**	**1.0440**
69	14	**1.0472**	**1.0472**	**1.045 65**	**1.045 65**	**1.0443**	**1.0443**

follow from those in the ionization energies and they are presented as multiples of the last quoted decimal place. The first column, N_e, shows the total number of electrons in the ion. The second gives the value of q that is equal to the number of 4f electrons in the $4f^q ns$ configuration of the Ln^+, Ln^{2+}, or Ln^{3+} ion. The rows with common values of N_e and q correspond to isoelectronic sequences.

The eight values are rather similar: they vary by less than 0.007 (<0.5%). The data for Ln II and Ln III suggest an *overall* decrease with the number of f electrons (q); those for $q = 13$ and 14 are consistent with a decrease with the charge of the ion (z) from which an electron is removed (z increases from 1 in Ln II to 3 in Ln IV). However, the detailed variation with q is irregular. The irregularities could be due, (a) to effects that are the same for each value of z, in which case, plots of Δn^* against q for each z value will tend to be parallel to each other. Such arguments were used by Brewer[9] in estimating spectroscopic transitions of the type $4f^q 6s \rightarrow 4f^q 5d$. On the other hand, the irregularities could be due, (b) to effects that are unique to each series (e.g., configuration interaction with another level, the position of which varies with z).

This leads to two ways, A and B, of estimating the missing values of Δn^*. The first, following (a), is to calculate the differences between the known values and use them to estimate unknown differences, thereby completing the values for $q = 1$, 2, 7, 13, and 14. The gaps between $q = 2$ and 7 and between $q = 7$ and 13 can then be bridged by dividing the overall differences equally.

The second method, following (b), was suggested by a reviewer. This uses the eight values to calculate, first, an average linear variation with z and, second, an average linear variation with q. That procedure generates the following equation:

$$\Delta n^* = 1.052\,887 - 0.002\,350z - 1.7187 \times 10^{-4}q. \quad (2)$$

This approach effectively assumes that the departures from linearity are random. The results of both methods are shown in Table 2. Both schemes generate parallelisms in that there are similar constant differences between the Ln II, Ln III, and Ln IV series as q varies. However, method A tries to take account of irregularities by assuming they are a function of q; method B assumes a linear variation for each series.

TABLE 3. Results of the calculation of n^* and $T(4f^q 6s)$ from estimated and experimental values of ΔT and Δn^*. Figures estimated by interpolation in Fig. 1 are in parentheses

N_e	q	Spectrum	$\Delta T/\mathrm{cm}^{-1}$	Δn^*	$n^*(6s)$	$T(4f^q 6s)/\mathrm{cm}^{-1}$
55	0	Ba II	42 355	1.0516	2.3324	80 686
56	1	La II	43 986	1.0501	2.2975	83 158
57	2	Ce II	(44 743)	1.0494	2.2819	84 299
58	3	Pr II	(45 511)	1.0495	2.2668	85 426
59	4	Nd II	(46 286)	1.0496	2.2520	86 552
60	5	Pm II	(47 066)	1.0497	2.2373	87 693
61	6	Sm II	(47 852)	1.0498	2.2229	88 833
62	7	Eu II	48 625	**1.0505**	2.2093	89 930
63	8	Gd II	(49 443)	1.0496	2.1944	91 155
64	9	Tb II	(50 248)	1.0492	2.1804	92 330
65	10	Dy II	(51 058)	1.0488	2.1665	93 518
66	11	Ho II	(51 874)	1.0484	2.1529	94 704
67	12	Er II	(52 697)	1.0480	2.1394	95 903
68	13	Tm II	53 594	1.0476	2.1250	97 207
69	14	Yb II	54 304	**1.0472**	2.1139	98 230

Because the assumptions underlying the two methods are equally plausible, we have used average values in our subsequent calculations. For the Ln II series, Sugar and Reader[6] assumed a constant value $\Delta n^* = 1.050$; our chosen averaged values appear in column 5 of Table 3. Of the twelve estimated values, only four differ from 1.050 by more than 0.001.

The uncertainties in our estimated values of Δn^* arise partly from the uncertainties in the reference values and partly from the methods of estimation. The largest uncertainty in the reference values is ±0.0028. As a measure of those in the methods of estimation, we double the standard deviations[c)] of the pairs of values for which the largest value is 0.0022. Combining ±0.0044 with ±0.0028, we get a total uncertainty

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[c)] Throughout both parts of this paper, we set uncertainties based upon standard deviations at twice the standard deviation. For random uncertainties, this corresponds to a 95% confidence level.

of ±0.0052 in the values of Δn^*. In the Ln II series, this is equivalent to a contribution of ±200 cm^{-1} to the final uncertainty in the ionization energies.

3. The Values of ΔT

Sugar and Reader[6] established their variation in ΔT by drawing a smooth curve between the values for Ba II, Eu II, and Yb II. Vander Sluis and Nugent[10] later suggested that inclusion of the f^0 value might distort interpolation curves of this sort. Subsequent work suggests that, in this particular case, the inclusion of the f^0 point in the smooth curve does indeed lead, in the early part of the series, to estimates of ΔT that are significantly in error. Sugar and Reader's estimated value of 43 300 cm^{-1} for ΔT of La II led to a second ionization energy of lanthanum of 11.06 ± 0.08 eV. Subsequent work[11] on the Rydberg states of La$^+$ gave the value 11.184 96 ± 0.000 06 eV, a figure that is now recommended on the NIST website.[1] If Sugar and Reader's calculation is reversed and the new ionization energy is combined with our averaged estimate of 1.0501 in Table 3, ΔT becomes 43 986 cm^{-1}. We have constructed the ΔT variation by combining this last La II value with those of Eu II, Yb II and also that of Tm II, which can be calculated from data that have become available[1,12] since 1965.

ΔT is equal to the separation of the lowest levels of the 4f^{q}6s and 4f^{q}7s configurations after each lowest level has been corrected by the parameter δ. Judd's formulae[8] allow the calculation of δ in terms of an electronic repulsion parameter G_3, which can be derived by analysis of the atomic spectra. Wybourne[13] presents the formulae in a convenient form with helpful illustrative data. Cowan[14] provides useful information on the relationship between the different forms of the electronic repulsion parameter. Particularly relevant to the problem considered here is the relationship between G_3 and G^3 for fs interactions ($G^3 = 7G_3$).

In the Ln II series, values of G_3 have been derived for the 4f^{q}6s configuration in europium (209 cm^{-1}),[13] erbium (210 cm^{-1}),[15] and thulium (212 cm^{-1})[16] and the value 210 cm^{-1} seems to be a good approximation for the entire Ln II series.[15] That assumption was made by Sugar and Reader.[6] Judd's first formula then puts δ equal to S_1G_3 where S_1 is the total spin quantum number of the 4f^q core. This provides the δ value for La II, Eu II, and Tm II; for Yb II it is zero. In calculating the ΔT value for Tm II, we also need the small G_3 value for the 4f^{13}7s configuration. This is 85 cm^{-1}.[17]

The resulting values of ΔT for these four elements are those in column 4 of Table 3. They were used to construct the interpolation plot shown in Fig. 1. The Ba II point has also been included in the figure but not in the interpolation fit. It is displaced from the curve by over 800 cm^{-1} and we take this to be an indication of a sub-shell break. Figure 1 allows revised estimates of ΔT to be obtained for the elements in the lanthanum–europium and europium–thulium gaps. These also appear in column 3 of Table 3. For the uncertainty in the ΔT values, we note that doubling the standard deviation of the separations of the four points from the curve in Fig. 1 gives ±120 cm^{-1}. This transmits an uncertainty of ±170 cm^{-1} to the ionization energy.

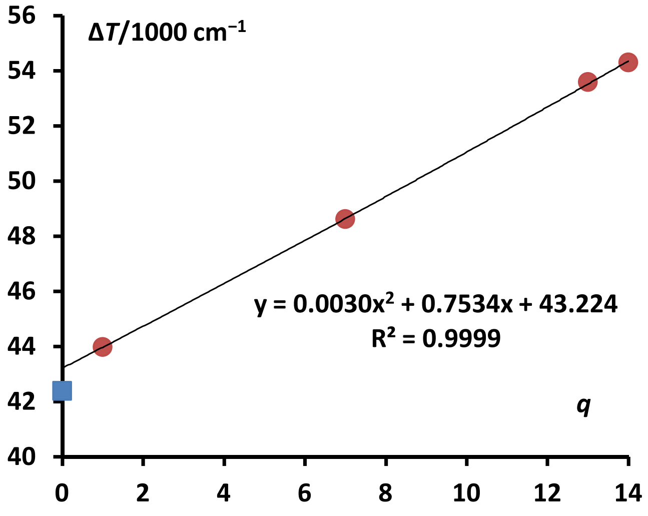

FIG. 1. The energy difference, ΔT, between the 4f^q parent levels of the 4f^{q}6s and 4f^{q}7s configurations plotted against q. The square symbol at $q = 0$, which has not been included in the fit, marks the value for barium (a linear fit gives y = 0.7989x + 43.136).

4. The Values of T(4f^{q}6s)

The estimated and experimental values of ΔT and Δn^* are inserted into Eq. (1), which is then solved for n^*(6s) by adjusting its value in an iterative procedure. The n^*(6s) values in turn yield T(4f^{q}6s), the amount by which the 4f^q parent of the lowest level of 4f^{q}6s lies below the ionization threshold for the sequence 4f^qns. This threshold is the lowest level of the configuration 4f^q. The results of the calculations are shown in Table 3.

5. The Second Ionization Energies

We write the energy of the lowest level of the 4f^{q}6s configuration, relative to the ground state of the singly charged positive ion, as E(4f^{q}6s). The amount by which it lies below the ionization threshold, 4f^q, can be found by adding δ, its separation from the parent 4f^q level, to T(4f^{q}6s). Now in most cases, the ground state configuration of the ion Ln$^+$ is 4f^{q}6s and that of Ln^{2+} is 4f^q. When this is so, the second ionization energy is simply $\{T(4f^q6s) + \delta\}$. Values of δ were calculated using Judd's first equation as described in Sec. 3. His second equation[8,13] is concerned with the interaction between 4f^qns levels with different 4f^q parent groups and the same value of J. The effect on δ is usually small.[18] However, in Sm II, the lowest level of the 4f^{6}6s configuration arises from the ^{7}F$_0$ level of the 4f^6 group and can be written as (^{7}F$_0$)6s with $J = 1/2$. It is close (~1300 cm^{-1}) to the upper of the two levels of (^{7}F$_1$)6s, which arises from ^{7}F$_1$ but also has $J = 1/2$. We have checked Sugar and Reader's calculation using Judd's second formula and find, as they did, $\delta = 518$ cm^{-1}.

In lanthanum and gadolinium, the ground state configurations of the dipositive ion are 4f^{q-1}5d rather than 4f^q and in lanthanum, cerium, and gadolinium, the ground state configurations of the singly charged ion are 5d^2, 4f^{1}5d^2, and 4f^{7}5d6s. So, in obtaining the second ionization energies of these three elements, the quantity $\{T(4f^q6s) + \delta\}$ must be adjusted to accommodate the five aberrant ground state configurations. The spectra[1] of La II, La III, Ce III, Gd II, and Gd III provide the necessary information and we can then write the ionization energies as $\{T(4f^q6s) + \delta + \mathrm{CC}\}$ where CC represents the correction for the aberrant configurations. The required data are supplied and the calculations are performed in Table 4. Column 6 shows our estimated values of the ionization energies in cm^{-1}. In column 7 these values have been converted to electron volts. We have used the conversion factor 1 eV = 8065.544 cm^{-1}.[19]

Combining the uncertainty in the ionization energy arising from that in Δn^* (± 200 cm^{-1}) with the contribution of ± 170 cm^{-1} transmitted by the uncertainty in ΔT gives a total uncertainty of slightly less than ± 270 cm^{-1}. Parameterizations of spectra[17,20] suggest uncertainties in G_3 of the order of ± 10 cm^{-1}, which translates to about ± 30 cm^{-1} in δ. The effect on the overall value is small. However, to allow for this and for possible systematic errors introduced by our interpolation methods, we take ± 300 cm^{-1} for the uncertainty in our estimated ionization energies. This is ± 0.04 eV to the nearest hundredth of an electron volt; hence the figure cited in Table 5.

TABLE 4. The calculation of the second ionization energies from the values of $T(4f^q6s)$ given in Table 3

Spectrum	q	$T(4f^q6s)/\mathrm{cm}^{-1}$	δ/cm^{-1}	$\mathrm{CC}/\mathrm{cm}^{-1}$	I_2/cm^{-1}	I_2/eV
La II	1	83 158	105	6953	90 216	11.185
Ce II	2	84 299	210	3854	88 363	10.956
Pr II	3	85 426	315	0	85 741	10.631
Nd II	4	86 552	420	0	86 972	10.783
Pm II	5	87 693	525	0	88 218	10.938
Sm II	6	88 833	518	0	89 351	11.078
Eu II	7	89 930	730	0	90 660	11.240
Gd II	8	91 155	630	5611	97 396	12.076
Tb II	9	92 330	525	0	92 855	11.513
Dy II	10	93 518	420	0	93 938	11.647
Ho II	11	94 704	315	0	95 019	11.781
Er II	12	95 903	210	0	96 113	11.916
Tm II	13	97 207	105	0	97 312	12.065
Yb II	14	98 230	0	0	98 230	12.179

TABLE 5. Second ionization energies of the elements La → Lu in electron volts: Column 2, Ref. 6; column 3, current NIST recommendations, Ref. 1; column 4, this work using our estimated Δn^* values; column 5, our recommended values drawn from columns 3 and 4. The figures in square brackets represent uncertainties in the last decimal place

Spectrum	Reference 6	NIST 2016	This work	Selected
La II	11.06	11.184 96[6]	11.185	11.184 96[6]
Ce II	10.85	10.85[7]	10.956	10.956[40]
Pr II	10.55	10.55[7]	10.631	10.631[40]
Nd II	10.73	10.72[7]	10.783	10.783[40]
Pm II	10.90	10.90[7]	10.938	10.938[40]
Sm II	11.07	11.07[7]	11.078	11.078[40]
Eu II	11.25	11.241[6]	11.240	11.240[6]
Gd II	12.1	12.09[7]	12.076	12.076[40]
Tb II	11.52	11.52[7]	11.513	11.513[40]
Dy II	11.67	11.67[7]	11.647	11.647[40]
Ho II	11.80	11.80[7]	11.781	11.781[40]
Er II	11.93	11.93[7]	11.916	11.916[40]
Tm II	12.05	12.05[7]	12.065	12.065[40]
Yb II	12.17	12.179 184[25]	12.179	12.179 184[25]
Lu II	13.9	13.9[4]	14.13	14.13[10]

Table 4 deals with the elements La → Yb but the second ionization energy of lutetium is also often needed in studies of lanthanide systematics. It cannot be accessed by the method used thus far in this paper. The current NIST recommendation[1] is 13.9 ± 0.4 eV. The Appendix investigates the origin of this figure and suggests a revised value of 14.13 ± 0.10 eV.

6. Discussion

In columns 2–4 of Table 5, our revised ionization energies are presented in electron volts and compared with the original values of Sugar and Reader[6] and with the current NIST recommendations.[1] For the eleven elements, Ce–Sm, Tb–Tm, and Lu, NIST gives figures that are identical to those of Ref. 6, which is cited as their source. Setting aside the case of lutetium, our selected values in column 5 combine our estimates in Table 4 with the NIST values for lanthanum, europium, and ytterbium that have small uncertainties of ≤ 0.006 eV. The uncertainties of ± 0.04 eV for Ce–Sm and Gd–Tm are lower than the NIST values of ± 0.07 eV and we justify this by the new auxiliary data that we were able to exploit.

In the second half of the La → Yb series, our values differ from the NIST values by ≤ 0.025 eV. Ignoring lanthanum, in the first half of the series the difference is ≤ 0.11 eV. Here our values are distinctly higher but the difference decreases from 0.11 eV in cerium to 0.01 eV in samarium. This is a consequence of our acknowledgement of the subshell break by removing barium from the ΔT plot and replacing it with a value for lanthanum computed by exploiting the very accurate value of the second ionization energy. The effect of this change is felt most strongly immediately after lanthanum and then diminishes gradually.

It is interesting to compare the current NIST values for Ba → Yb with our selection by calculating the internal energy change, ΔU, of the process

$$\mathrm{M}\left(\mathrm{g},4\mathrm{f}^q6\mathrm{s}^2\right) \rightarrow \mathrm{M}^{2+}\left(\mathrm{g},4\mathrm{f}^q\right) + 2\mathrm{e}^-(\mathrm{g}). \qquad (3)$$

If we use the lowest levels of the two configurations, ΔU is equal to $\{(I_1 + I_2) + \mathrm{CC}\}$. In this case, CC is a correction needed in lanthanum, cerium, and gadolinium where the configurations required in Eq. (3) differ from the ground states in the spectra of La I, La III, Ce I, Gd I, and Gd III. In total it amounts to -8002, -4763, and -8566 cm^{-1} in lanthanum, cerium, and gadolinium, respectively.

Equation (3) is a process in which the 4f electrons are conserved and in which the two 6s electrons that are lost are only weakly coupled to the $4f^q$ core. Like the ΔT variation in Fig. 1, we expect it to vary nearly smoothly as q changes from 1 to 14. Figure 2(A) shows the variation in ΔU calculated from the current NIST recommendations[1] for I_1 and I_2; Fig. 2(B) is obtained using the NIST recommendations for I_1 and our selected values of I_2. The I_1 values that are common to both plots have uncertainties of 0.01 eV in praseodymium and promethium; in other cases the uncertainties are ≤ 0.0006 eV.

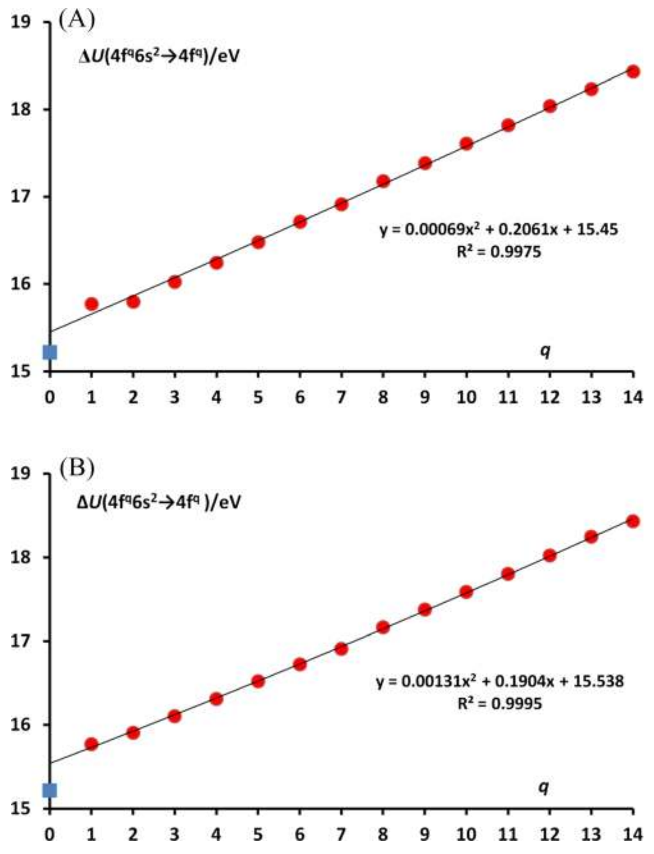

FIG. 2. The values of ΔU for Eq. (3) plotted against q, the number of 4f electrons: (A) using the current recommendations of Ref. 1 for I_1 and I_2; (B) using the current recommendations of Ref. 1 for values of I_1 and our selected values of I_2. The square symbol at $q = 0$, which has not been included in the fit, marks the value for barium.

In Fig. 2(A), the second order polynomial fit to the values at $q = 1$–14 is considerably less good in the first half of the series than in the second, the lanthanum point lying well above the curve and the points with $q = 2$–4 below it. As noted earlier, we believe this arises from a failure to take account of the subshell break revealed in Fig. 1. When we move to Fig. 2(B), these aberrations are much diminished and the improvement in the fit is registered by an increase in the R^2 value from 0.9975 to 0.9995. If the barium ($q = 0$) point is included in Fig. 2(B) correlation, R^2 drops to 0.9954. If it is included in Fig. 2(A), $R^2 = 0.9959$. A subshell break is apparent in both plots but in Fig. 2(B) it is larger (0.322 eV) and more clearly developed. Our investigation of the second ionization energies was prompted by the possibility of a subshell break. We regard the improved fit in Fig. 2(B) and the marked displacement of the point at $q = 0$ as evidence of the existence of such a break and as support for the method that has led us to revised values of the second ionization energies.

In Paper II[33] of this project, we shall carry out a similar revision of the third and fourth ionization energies. By combining this with the revised second ionization energies calculated here, we can then investigate the possible presence of subshell breaks in the lattice and hydration enthalpies of trivalent and tetravalent lanthanide compounds and ions.

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7. Appendix: The Second Ionization Energy of Lutetium

The second ionization energy of lutetium cannot be accessed by the method used elsewhere in this paper. It is also poorly established; the current NIST value[1] (13.9 eV) has an uncertainty of ±0.4 eV and is an average derived by Sugar and Reader[6] using two different methods.

The first method applied Eq. (1) to the first two levels of the 5dns series in La II and the $4f^{14}5dns$ series in Lu II. The $^2D_{3/2}$ parent levels were used as series members. The positioning of this parent for 5d6s required a value of the Slater parameter G_2, and Sugar and Reader used the value 1650 cm^{-1} for both La II and Lu II. More extensive parameterizations of the second spectra now suggest that G_2 increases across the series: values for the $4f^{q-1}5d6s$ configuration increase from Nd II (1574 cm^{-1})[21] through Gd II (2083 cm^{-1})[22] and Er II (2356 cm^{-1})[20] to Yb II (2437 cm^{-1}).[23] We have used this drift to estimate values of 1350 and 2500 cm^{-1} for La II and Lu II, respectively. Sugar and Reader used the lanthanum value to estimate the second ionization energy but, as noted earlier in this paper, a subsequent determination[11] gave a more accurate value of 11.185 eV. So we have reversed their calculation, using the revised value of G_2, to obtain $\Delta n^* = 1.0589$ for the 5dns series in La II.

We now require a value of Δn^* for the $4f^{14}5dns$ series in Lu II. Sugar and Reader assumed that it was equal to 1.085, the value obtained from the Ba I spectrum. Our La II figure is significantly lower and we believe it provides a better basis for estimating the value for Lu II. If we use the centres of gravity of the configurations to calculate Δn^* values for the ns series in Ba II (ns), Yb II ($4f^{14}ns$), and Hg II ($4f^{14}5d^{10}ns$), we obtain 1.052, 1.047, and 1.107, respectively. The difference between the Ba II value and our recalculated La II (5dns) figure is 0.007 and if this same increment is applied to Yb II and Lu II ($4f^{14}5dns$), then $\Delta n^*(\text{Lu II}) = 1.054$. If we assume a linear increase between Yb II and Hg II, we get 1.053. We have therefore repeated Sugar and Reader's calculation with $\Delta n^* = 1.054$ and our revised value of G_2; the second ionization energy is then 114 500 cm^{-1} or 14.20 eV. The Δn^* values for the ns series in Ba II, La II, Sc II, Y II, and Yb II lie between 1.036 and 1.059 with a standard deviation of 0.0082. We double this and take ±0.0164 as the uncertainty in Δn^*(Lu II), which is equivalent to ±0.09 eV.

In the method just described, the lower parent level is calculated using an estimated interelectronic repulsion parameter, G_2; the higher is taken as the centre of gravity of the $J = 1$ and 2 levels. It should be noted that the ionization energy is relatively insensitive to the chosen value of G_2: a change of 500 cm^{-1} alters the calculated ionization energy by only about 100 cm^{-1}. However, we can avoid the need for G_2 by using the centre of gravity for both parent levels. The La II value of Δn^* then becomes 1.062. Now the Ba II/La II difference is 0.010, which when added to Δn^* (Yb II) gives Δn^* (Lu II) = 1.057. The resulting ionization energy is 114 700 cm^{-1} or 14.22 eV. Thus, these two ways of conducting the 5dns calculation give similar values with a common uncertainty of ±0.09 eV.

Sugar and Reader's second figure was derived from the first two levels of the $4f^{14}6snd$ series in Lu II. In this case they used the centres of gravity of configurations as series members. That of 6s5d lies at 14 181 cm^{-1}. In 6s6d, the $^1D_2$ level has not been observed but they used the positions of the $^3D_1$, $^3D_2$, and $^3D_3$ levels to place the centre of gravity of the configuration at 72 444 cm^{-1}. This gives $\Delta T = 58\,263$ cm^{-1}.

Again, the choice of Δn^* is crucial. Sugar and Reader used $\Delta n^* = 1.288$ obtained from the 6s*n*d series in Ba I. Using the centres of gravity of the configurations in Ba I, we find $\Delta n^* = 1.256$. However, other spectra now provide more convincing estimates. There are data on Yb I, which is iso-electronic with Lu II. This gives $\Delta n^* = 1.129$. We can also obtain a figure for La II by combining Sugar and Reader's method of calculating the centres of gravity in this spectrum with the accurate second ionization energy[11] and our revised value of G_2. This puts the unperturbed centre of gravity of 6s5d at 3383 cm^{-1} and gives $\Delta T = 61\,283$ cm^{-1} with $\Delta n^* = 1.258$.

For pairs of cases in which the transition is of the type $\{ns(n-1)d \rightarrow nsnd\}$, the second spectrum seems usually to have a slightly higher Δn^* value than the first. For Ca I/Sc II the increase is 0.19; for Sr I/Y II it is 0.13. However, for Ba I/La II it is only 0.002 suggesting a similar value for Yb I/Lu II and Δn^*(Lu II) = 1.13. Alternatively, if we calculate Δn^* from 5d → 6d transitions in the Ba II spectrum and from {6s5d → 6s6d} transitions in La II we get 1.147 and 1.258, respectively: insertion of the 6s electron increases Δn^* by 0.11. As the value for Yb II is 1.072, this suggests that Δn^*(Lu II) is 1.18. We take Δn^*(Lu II) = 1.16 ± 0.04. This yields an ionization energy of 113 754 cm^{-1} or 14.10 ± 0.16 eV.

In 1965, Sugar and Reader obtained 14.06 eV by their first method and 13.60 eV by the second. As shown above, newer data have brought the two methods into closer agreement at a higher figure of 14.18 ± 0.08 eV.

Our revised value has some support from thermo-chemical calculations of the kind that provided the first complete sets of third ionization energies of the lanthanides.[24,25] They combined Born–Haber cycles with the assumption of a smooth variation in the lattice energies of trivalent lanthanide compounds consistent with the lanthanide contraction. In later studies, Morss[26] pointed out that these methods indicated that the second ionization energy for lutetium was 14.14 eV. That value was accepted by subsequent workers[27] in similar calculations. Here we apply a modified version of Morss' method.

The oxides $Sm_2O_3 \rightarrow Lu_2O_3$ all have the cubic C-type M_2O_3 structure in which the lanthanide ions are in distorted octahedral coordination.[28] Their lattice enthalpies, $L^{\ominus}(M_2O_3,s)$, are the standard enthalpy change, at 298.15 K, of the reaction,

$$2M^{3+}(g) + 3O^{2-}(g) \rightarrow M_2O_3(s). \qquad (A1)$$

In Fig. 3, the values of $1/2L^{\ominus}(M_2O_3,s)$ for the sequence $Sm_2O_3 \rightarrow Yb_2O_3$, obtained from data in Paper II[33] of this series, are plotted against the reciprocal of $\{r(M^{3+}) + r(O^{2-})\}$. Here, $r(M^{3+})$ is the Shannon radius[29] in six coordination and $r(O^{2-}) = 1.38$ Å. The fit is superior to that obtained by a plot against q, is linear within the experimental uncertainties, and in linear form is more suited to extrapolation. The Shannon radii provide a lutetium ordinate of 0.4462 Å^{-1} which gives $1/2L^{\ominus}(Lu_2O_3,s) = -6689$ kJ mol^{-1}. If that is combined with $\Delta_fH^{\ominus}$(Lu,g), $\Delta_fH^{\ominus}(O^{2-},g)$, and the first and third ionization energies of lutetium in Paper II,[33] we get 14.13 eV for the second ionization energy. To obtain an uncertainty, we double the standard deviation of the points from the fitted curve in Fig. 3; this gives 14.13 ± 0.10 eV and is very close to the value obtained by Morss.[26]

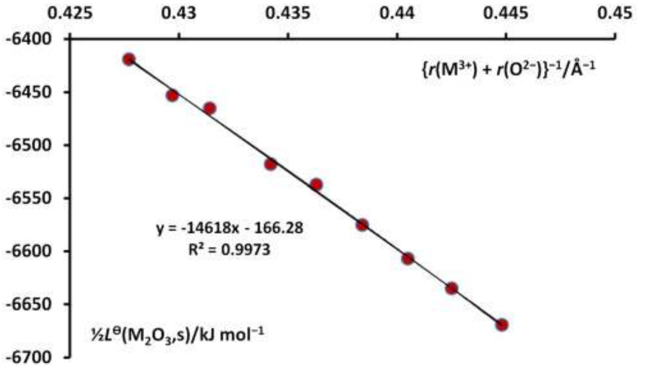

FIG. 3. Values of the lattice enthalpies, $1/2L^{\ominus}(M_2O_3,s)$, for the sequence samarium to ytterbium plotted against the reciprocal of $\{r(M^{3+}) + r(O^{2-})\}$, where $r(M^{3+})$ and $r(O^{2-})$ are Shannon radii[29] in six and four coordination, respectively.

Finally, there are two recent relativistic quantum mechanical calculations, the first being 14.05 eV,[30] which was subsequently revised to 13.98 ± 0.04 eV.[31] The uncertainty in the latter value was the root mean square of a sample of differences between experimental values and the authors' calculated values. We include this in our assessment by making the uncertainty consistent with our conservative policy through a doubling of the sample standard deviation of the differences for the five experimental values for which the uncertainty is less than 100 cm^{-1}. This gives 13.98 ± 0.13 eV. If that is combined with the value derived from spectroscopic data (14.18 ± 0.08 eV) and the thermo-chemical figure (14.13 ± 0.10 eV), the outcome is 14.13 ± 0.06 eV. However, this range does not span that of the three components (0.20 eV) which raises the possibility of systematic errors in at least one of the three. An allowance can be made for this at the one standard deviation level by supplementing the usual method of combining uncertainties with an additional contribution that depends upon the deviations of the individual values from the weighted mean.[32] This method converts the standard deviations of our three values (0.065, 0.05, and 0.04 eV) into a combined uncertainty of ±0.05 eV and two standard deviations become ±0.10 eV. Our final recommended value is therefore 14.13 ± 0.10 eV.

Our proposed uncertainty is more than double that in the second ionization energies of the other lanthanide elements. In addition, the position of lutetium just beyond the end of the lanthanide series makes thermodynamic data on this element especially important in lanthanide systematics. Further study of Lu II is therefore more desirable than that of any of the other second spectra that we have considered in this paper.

8. References

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