

The Positions of Lanthanum (Actinium) and Lutetium (Lawrencium) in the Periodic Table

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The debate as to whether lanthanum and actinium or lutetium (and, more recently, lawrencium) should be placed in group IIIB of the periodic table along with scandium and yttrium (or equivalently, in electronic terms, which pair should be considered as the first members of the *d* block for periods 6 and 7) has a long, but poorly publicized, history. For quite some time it has been known that yttrium, and, to a lesser degree, scandium are closer in their chemical properties to lutetium and the other heavy rare earths than they are to lanthanum (1, 2) and on this basis alone a number of chemists in the 1920's and 1930's assigned lutetium rather than lanthanum to group IIIB (3). The current consensus, which places lanthanum and actinium in this position instead, appears to have evolved during the 1940's along with the use of periodic tables based on electronic configuration and the concept of the differentiating electron.

Early spectroscopic work on the rare earths seemed to indicate that the ground states of their atoms had, with few exceptions, an electronic configuration of the form [Noble Gas](*n* - 2)*f*^{*x*}(*n* - 1)*d*¹*ns*². Indeed, this was thought to conform to the "ideal" electronic configuration for the *f*-block elements in general (2). Thus, ytterbium was assigned the

ground state [Xe]4*f*¹³5*d*¹6*s*² and lutetium the ground state [Xe]4*f*¹⁴5*d*¹6*s*², resulting in a 4*f* differentiating electron for lutetium and firmly establishing it as the last member of the *f*-block for period 6. Barium, on the other hand, had the configuration [Xe]6*s*² and lanthanum the configuration [Xe]-5*d*¹6*s*², thus giving lanthanum a 5*d* differentiating electron and establishing it in group IIIB as the first member of the *d* block for period 6. This assignment for lanthanum appeared to be further justified by the analogy between its configuration and the configurations of the other members of group IIIB: Sc = [Ar]3*d*¹4*s*² and Y = [Kr]4*d*¹5*s*².

More recent spectroscopic work, however, has revised the earlier electronic configurations (4). Only three of the rare earths in period 6 (La, Gd, and Lu) are now known to have the ground state [Xe]4*f*^{*x*}-15*d*¹6*s*², all of the rest having the configuration [Xe]4*f*^{*x*}6*s*². In period 7 only six of the actinides (Ac, Pa, U, Np, Cm, and Lr) have the old configuration. Thorium has the configuration [Rn]6*d*²7*s*² and the remaining eight the configuration [Rn]5*f*^{*x*}7*s*². This strongly suggests [Noble Gas](*n* - 2)*f*^{*x*}*ns*² rather than [Noble Gas](*n* - 2)*f*^{*x*}-1(*n* - 1)*d*¹*ns*² as the ideal ground state configuration for the *f*-block elements in general. Ytterbium and nobelium now have the configu-

	I H 1.008																2 He 4.003							
	IA		IIA												IIIA	IVA	VA	VIA	VIIA					
PERIOD	3	4																	5	6	7	8	9	10
2	Li	Be																	B	C	N	O	F	Ne
	6.939	9.012																	10.811	12.011	14.007	15.999	18.998	20.183
PERIOD	11	12											VIII		IB		IIB		13	14	15	16	17	18
3	Na	Mg	IIIB	IVB	VB	VIB	VII B										Al	Si	P	S	Cl	Ar		
	22.990	24.312											26.982	28.086	30.974	32.064	35.453	39.948						
PERIOD	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36						
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
	39.102	40.08	44.956	47.90	50.942	51.996	54.938	55.847	58.933	58.71	63.54	65.37	69.72	72.59	74.922	78.95	79.909	83.80						
PERIOD	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54						
5	Rb	Sr	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
	85.47	87.62	88.905	91.22	92.906	95.94	[99]	101.07	102.91	106.4	107.870	112.40	114.82	118.69	121.75	127.60	126.90	131.30						
PERIOD	55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86						
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po*	At*	Rn*						
	132.91	137.3	174.97	178.49	180.95	183.85	186.2	190.2	192.2	195.09	196.97	200.59	204.37	207.19	208.98	210	[210]	222						
PERIOD	87	88	103	104																				
7	Fr*	Ra*	Lr*	Ku*																				
	[223]	226	[255]	[260]																				

LANTHANIDE SERIES	57	58	59	60	61	62	63	64	65	66	67	68	69	70
	La	Ce	Pr	Nd	Pm*	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
	138.91	140.12	140.91	144.24	[147]	150.35	151.96	157.25	158.92	162.50	164.93	167.27	168.93	173.04
ACTINIDE SERIES	89	90	91	92	93	94	95	96	97	98	99	100	101	102
	Ac*	Th*	Pa*	U*	Np*	Pu*	Am*	Cm*	Bk*	Cf*	Es*	Fm*	Md*	No*
	227	232.03	231	238.03	[237]	[242]	[243]	[247]	[247]	[251]	[254]	[257]	[258]	[255]

Revised version of the currently popular medium-length block form of the periodic table.

ration [Noble Gas]($n - 2$) $f^{14}ns^2$ and lutetium and lawrencium the configuration [Noble Gas]($n - 2$) $f^{14}(n - 1)d^1ns^2$, resulting in a d rather than an f differentiating electron for both lutetium and lawrencium and making them equally valid candidates for the first members of the d block in periods 6 and 7. On the other hand, the [Rn]6 d^27s^2 configuration for thorium, which no one doubts is an f -block element with an irregular configuration, strongly supports the supposition that both lanthanum and actinium should be considered as f -block elements with irregular configurations derived from the ideal configuration [Noble Gas]($n - 2$) $f^{14}ns^2$. In other words, lanthanum and actinium should be considered the first members of the f block (rather than Ce and Th), ytterbium and nobel-

ium should be considered the last members of the f block (rather than Lu and Lr), and lutetium and lawrencium (rather than La and Ac) should be considered the first members of the d block in periods 6 and 7 and assigned to Group IIIB along with scandium and yttrium.

The argument that the total (i.e., core plus valence) electronic configurations of lanthanum and actinium are closer to those of scandium and yttrium than are the configurations of lutetium and lawrencium (due to their filled ($n - 2$) f^{14} subshells) is misleading. One must consider intraperiod as well as intragroup analogies. Thus, the remaining nine d -block elements of period 6 (Hf - Hg) all have the complete [Xe]4 f^{14} core like lutetium and not just the [Xe] core of lanthanum.

Table 1. Periodic Trends in Various Properties for the First Part of the d -Block

Atomic Radii ^a (Å)	Sum of the First Two Ionization Potentials ^a (eV)	Melting Point ^b (°K)	Electronegativity ^b (Allred-Rochow) Scale
Sc 1.570 — Y 1.693 — La 1.915 versus Sc 1.570 — Y 1.693 — Lu 1.553	Sc 19.45 — Y 18.61 — La 17.04 versus Sc 19.45 — Y 18.61 — Lu 20.85	Sc 1812 — Y 1803 — La 1193 versus Sc 1812 — Y 1803 — Lu 1925	Sc 1.20 — Y 1.11 — La 1.08 versus Sc 1.20 — Y 1.11 — Lu 1.14
Ti 1.477 — Zr 1.593 — Hf 1.476	Ti 20.40 — Zr 19.76 — Hf 20.40	Ti 1940 — Zr 2130 — Hf 2495	Ti 1.32 — Zr 1.22 — Hf 1.23
V 1.401 — Nb 1.589 — Ta 1.413	V 20.94 — Nb 20.78 — Ta 23.90	V 2188 — Nb 2741 — Ta 3253	V 1.45 — Nb 1.23 — Ta 1.33
Cr 1.453 — Mo 1.520 — W 1.360	Cr 23.25 — Mo 22.85 — W 25.68	Cr 2173 — Mo 2893 — W 3653	Cr 1.56 — Mo 1.30 — W 1.40
Mn 1.278 — Tc 1.391 — Re 1.310	Mn 23.07 — Tc 22.10 — Re 24.47	Mn 1517 — Tc 2473 — Re 3453	Mn 1.70 — Tc 1.36 — Re 1.46
Fe 1.227 — Ru 1.410 — Os 1.266	Fe 24.08 — Ru 23.96 — Os 25.70	Fe 1809 — Ru 2700 — Os 3290	Fe 1.64 — Ru 1.42 — Os 1.52
		Co 1768 — Rh 2233 — Ir 2727	Co 1.70 — Rh 1.45 — Ir 1.55
		Ni 1728 — Pd 1825 — Pt 2042	Ni 1.75 — Pd 1.35 — Pt 1.44

^a From ref. (7). ^b Data from ref. (16)

Likewise, in passing down the columns of the *d* block from Ti-Zn one always encounters the addition of the $4f^{14}$ subshell on passing from period 5 to period 6. In short, if one wishes to use analogies based on trends in the configurations of the cores, eighteen of these analogies favor the assignment of lutetium and lawrencium to Group IIIB and only one favors the assignment of lanthanum and actinium.

Arguments of this nature were put forward by Luder in favor of the reassignment of lutetium and lawrencium over a decade ago but appear to have gone unnoticed (5, 6). Likewise, the Russian chemist Christyakov, using periodic trends in ionization potentials and atomic radii, arrived at the same conclusion (7, 8). One may also add to this list trends in ionic radii, redox potentials, and electronegatives, as well as the chemical behavior of scandium and yttrium mentioned earlier. The most compelling evidence, however, has been presented by the physicists (9-13). This includes comparisons of trends in the melting points of the elements (11, 12), their crystal structures at room temperature (11), the crystal structures of their oxides and various intermetallic compounds (11), the structures of their excited state spectra (11), their superconductivities (10, 11), and the structures of their conductivity bands as revealed by X-ray isochromats (13). All of these properties unanimously favor the placement of lutetium and lawrencium, rather than lanthanum and actinium, in group IIIB. Some example data are summarized in Tables 1 and 2.

In fact, so overwhelming is the evidence for this assignment that Mazurs adopted it in the 1974 edition of his classic monograph on the periodic table (14). However, a quick examination of over fifteen freshman chemistry texts and four popular inorganic texts published since 1975 revealed that none of them had revised their periodic tables (15). Indeed, in talking with his fellow chemists, the author discovered that none of them was aware of the evidence favoring the reassignment of lutetium and lawrencium or indeed that there ever was any question about their placements (a category in which the author must include himself until very recently). As chemists, the periodic table is presumed to be our special province; surely its about time we pay attention to what the physicists have to tell us about its arrangement. A revised version of the currently popular medium-length block form of the table is shown above.

Literature Cited

- (1) In the classic chemical methods for separating the rare earths Sc, Y, and Lu occur together in what is called the yttrium group, whereas La and Ac occur together in what is called the cerium group. See, for example, Levi, S. L., "The Rare Earths," Longmans, Green and Co., London, 1915, Chap. IX.
- (2) Moeller, T., in "The Rare Earths," Spedding, F. H., and Daane, A. H., (Editors), Wiley, New York, 1961, Chap. 2.
- (3) See, for example, Shemyakin, F. M., *Zh. Obshch. Khim.*, 2, 62 (1932) and Bury, C. R., *J. Amer. Chem. Soc.*, 43, 1602 (1921). Further examples can be found in reference (14).

Table 2. A Comparison of Various Properties of Sc and Y versus those of Lu and La

Property	Sc	Y	Lu	La
Highest common oxidation state	3+	3+	3+	3+
Precipitation of sulfate in fractional crystallization ^a	Y group	Y group	Y group	Ce group
Structure of metal at room temperature ^b	hcp	hcp	hcp	special double hcp
Structure of oxide (M ₂ O ₃) ^{b,f}	$\frac{3}{\infty}[\text{AB}_{6/4}]c$	$\frac{3}{\infty}[\text{AB}_{6/4}]c$	$\frac{3}{\infty}[\text{AB}_{6/4}]c$	special hex. CN-7 A-M ₂ O ₃ struct.
Structure of chloride (MX ₃) ^{b,f}	$\frac{2}{\infty}[\text{AB}_{6/2}]m$	$\frac{2}{\infty}[\text{AB}_{6/2}]m$	$\frac{2}{\infty}[\text{AB}_{6/2}]m$	$\frac{3}{\infty}[\text{AB}_{9/3}]h$
Presence of low-lying nonhydrogenic <i>f</i> -orbitals ^c	No	No	No	Yes
<i>d</i> -Block-like structure for conduction band ^d	Yes	Yes	Yes	No
Superconductivity ^{c,e}	No	No	No	Yes (4.9°K)

^a Ref. (1)

^b Ref. (17)

^c Ref. (11)

^d Ref. (13)

^e Ref. (10)

^f Machatschki-Niggli coordination formulas

- (4) Consultation of various inorganic textbooks revealed a number of discrepancies with respect to Ce and Bk. The count given here is based on Mazurs (14). His count for the actinides is the same as that given in Seaborg, G. T., *Ann. Rev. Nucl. Sci.*, 18, 53 (1968). His count for the lanthanides, however, differs with regard to Ce from that in Moore, I. C., "Inorganic Potentials and Ionization Limits Derived from the Analyses of Optical Spectra," NSRDS-NBS 34, National Bureau of Standards, Washington, DC, 1970.
- (5) Luder, W. F., "The Electron-Repulsion Theory of the Chemical Bond," Reinhold, New York, 1967, Chap. 2.
- (6) Luder, W. F., *Can. Chem. Educ.*, 5(3), 13 (1970).
- (7) Christyakov, V. M., *Zh. Obshch. Khim.*, 38(2), 209 (1968); *Engl. Ed.*, 38(2), 213 (1968).
- (8) Christyakov, V. M., *Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk*, (3), 50 (1968); *Chem. Abst.*, 70, 61016b (1970).
- (9) Landau, L. D., and Lifshitz, E. M., "Quantum Mechanics," Pergamon, London, 1959, p. 245, footnote.
- (10) Hamilton, D. C., and Jensen, M. A., *Phys. Rev. Letters*, 11, 205 (1963).
- (11) Hamilton, D. C., *Amer. J. Phys.*, 33, 637 (1965).
- (12) Matthias, B. T., Zacharisen, W. H., Webb, G. W., and Engelhardt, J. J., *Phys. Rev. Letters*, 18, 781 (1967).
- (13) Merz, H., and Ulmer, K., *Phys. Letters*, 26A, 6 (1967).
- (14) Mazurs, E. G., "Graphic Representations of the Periodic System During One Hundred Years" Univ. Alabama Press, University, Alabama, 1974.
- (15) One exception to this list is the inorganic text by Lagowski, which, however, was published before 1975. He uses the long form of the periodic table proposed by Werner and places both Lu and Lr in group IIIB. See Lagowski, J. J., "Modern Inorganic Chemistry," Dekker, New York, 1973, p. 38 and pp. 602-605.
- (16) Ball, M. C., and Norburg, A. H., "Physical Data for Inorganic Chemists," Longman, London, 1974.
- (17) Wells, A. F., "Structural Inorganic Chemistry," 4th Ed., Clarendon Press, Oxford, 1975.