Lanthanide contraction

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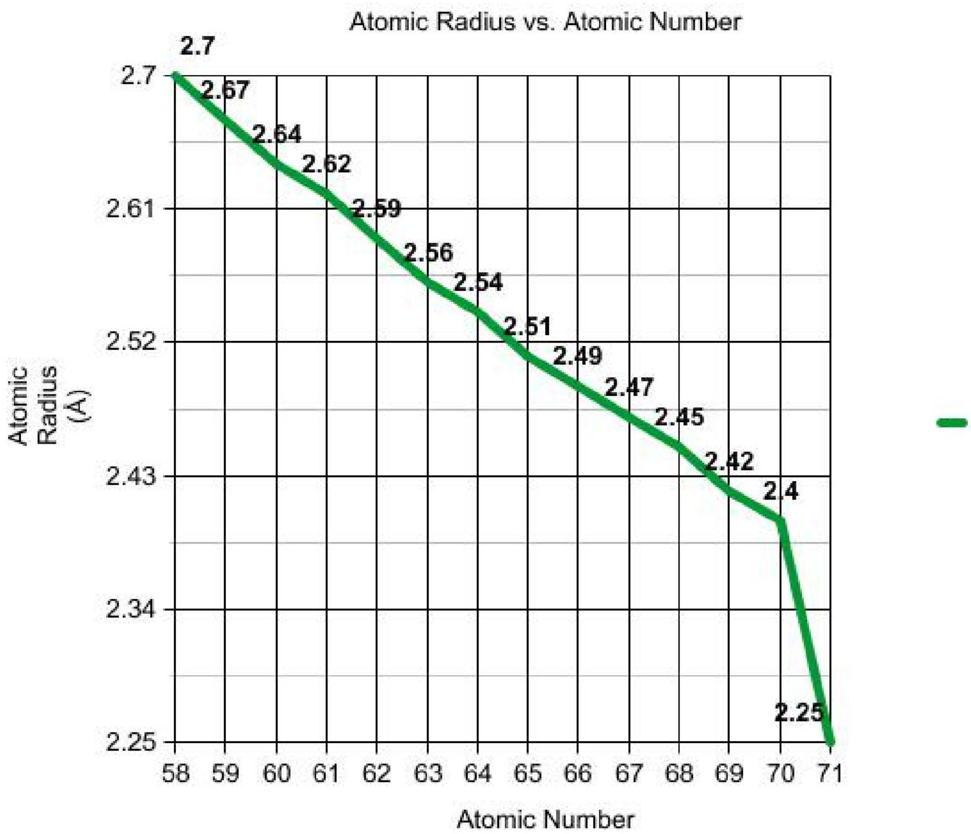
The lanthanides-or lanthanids, as they are sometimes called-are, strictly, the fourteen elements that follow lanthanum in the periodic table and in which the fourteen 4f electrons are successively added to the lanthanum configuration. Since these 4f relatively uninvolved in bonding, the main result is that all these highly electropositive elements have; as their prime oxidation state, the M^{+3} ion. The lanthanide series consist of the 14 elements, with atomic numbers 58 through 71……

Lanthanide contraction was used in discussing the elements of the third transition series, since it has certain important effects on their properties. It consists of a significant and steady decrease in the size of the atoms and ions with increasing atomic number, that is, La has the greatest, and Lu the smallest radius.

The effect results from poor shielding of nuclear charge (nuclear attractive force on electrons) by 4f electrons; the 6s electrons are drawn towards the nucleus, thus resulting in a smaller atomic radius. In single-electron atoms, the average separation of an electron from the nucleus is determined by the subshell it belongs to, and decreases with increasing charge on the nucleus; this in turn leads to a decrease in atomic radius. In multi-electron atoms, the decrease in radius brought about by an increase in nuclear charge is partially offset by increasing electrostatic repulsion among electrons. In particular, a "shielding effect" operates: i.e., as electrons are added in outer shells, electrons already present shield the outer electrons from nuclear charge, making them experience a lower effective charge on the nucleus. The shielding effect exerted by the inner electrons decreases in the order $s > p > d > f$. Usually, as a particular subshell is filled in a period, atomic radius decreases. This effect is particularly pronounced in the case of lanthanides, as the 4*f* subshell which is filled across these elements is not very effective at shielding the outer shell (n=5 and n=6) electrons. Thus the shielding effect is less able to counter the decrease in radius caused by increasing nuclear charge. This leads to "lanthanide contraction". The ionic radius drops from 103 pm for lanthanum(III) to 86.1 pm for lutetium(III).

About 10% of the lanthanide contraction has been attributed to relativistic effects.



The graph shows the atomic radius decreasing as the atomic number is increasing, Lanthanide Contraction.

The elements following the lanthanides in the periodic table are influenced by the lanthanide contraction. The radii of the period-6 transition metals are smaller than would be expected if there were no lanthanides, and are in fact very similar to the radii of the period-5 transition metals, since the effect of the additional electron shell is almost entirely offset by the lanthanide contraction.

For example, the atomic radius of the metal zirconium, Zr, (a period-5 transition element) is 159 pm and that of hafnium, Hf, (the corresponding period-6 element) is 156 pm. The ionic radius of Zr^{4+} is 79 pm and that of Hf^{4+} is 78 pm. The radii are very similar even though the number of electrons increases from 40 to 72 and the atomic mass increases from 91.22 to 178.49 g/mol. The increase in mass and the unchanged radii lead to a steep increase in density from 6.51 to 13.35 g/cm^3.

Zirconium and hafnium therefore have very similar chemical behavior, having closely similar radii and electron configurations. Radius-dependent properties such as lattice energies, solvation energies, and stability constants of complexes are also similar. Because of this similarity hafnium is found only in association with zirconium, which is much more abundant, and was discovered as a separate element 134 years later (in 1923) than zirconium (discovered in 1789). Titanium, on the other hand, is in the same group but differs enough from those two metals that it is seldom found with them. As the proton number increases and the atomic radius decreases, the ionization energy increases. This is due to a more positively charged nucleus and a greater pull on the electrons by the nucleus. A greater pull is the result of an increased effective nuclear charge. Effective nuclear charge is caused by the nucleus having a more positive charge than the negative charge on the electron (net positive charge). The density, melting point, and hardness increase from left to right throughout the Lanthanide Series. The Lanthanide Contraction makes chemical separation of the Lanthanides easier. The Lanthanide Contraction, while making the chemical separation of Lanthanides easier, it makes the separation of elements following the series a bit more difficult.

Element	Atomic electron configuration (all begin with [Xe])	Ln^{3+} electron configuration	Ln^{3+} radius (pm) (6-coordinate)
La	$5d^1 6s^2$	$4f^0$	103
Ce	$4f^1 5d^1 6s^2$	$4f^1$	102
Pr	$4f^3 6s^2$	$4f^2$	99
Nd	$4f^4 6s^2$	$4f^3$	98.3
Pm	$4f^5 6s^2$	$4f^4$	97
Sm	$4f^6 6s^2$	$4f^5$	95.8
Eu	$4f^7 6s^2$	$4f^6$	94.7
Gd	$4f^7 5d^1 6s^2$	$4f^7$	93.8
Tb	$4f^9 6s^2$	$4f^8$	92.3
Dy	$4f^{10} 6s^2$	$4f^9$	91.2
Ho	$4f^{11} 6s^2$	$4f^{10}$	90.1
Er	$4f^{12} 6s^2$	$4f^{11}$	89
Tm	$4f^{13} 6s^2$	$4f^{12}$	88
Yb	$4f^{14} 6s^2$	$4f^{13}$	86.8
Lu	$4f^{14} 5d^1 6s^2$	$4f^{14}$	86.1