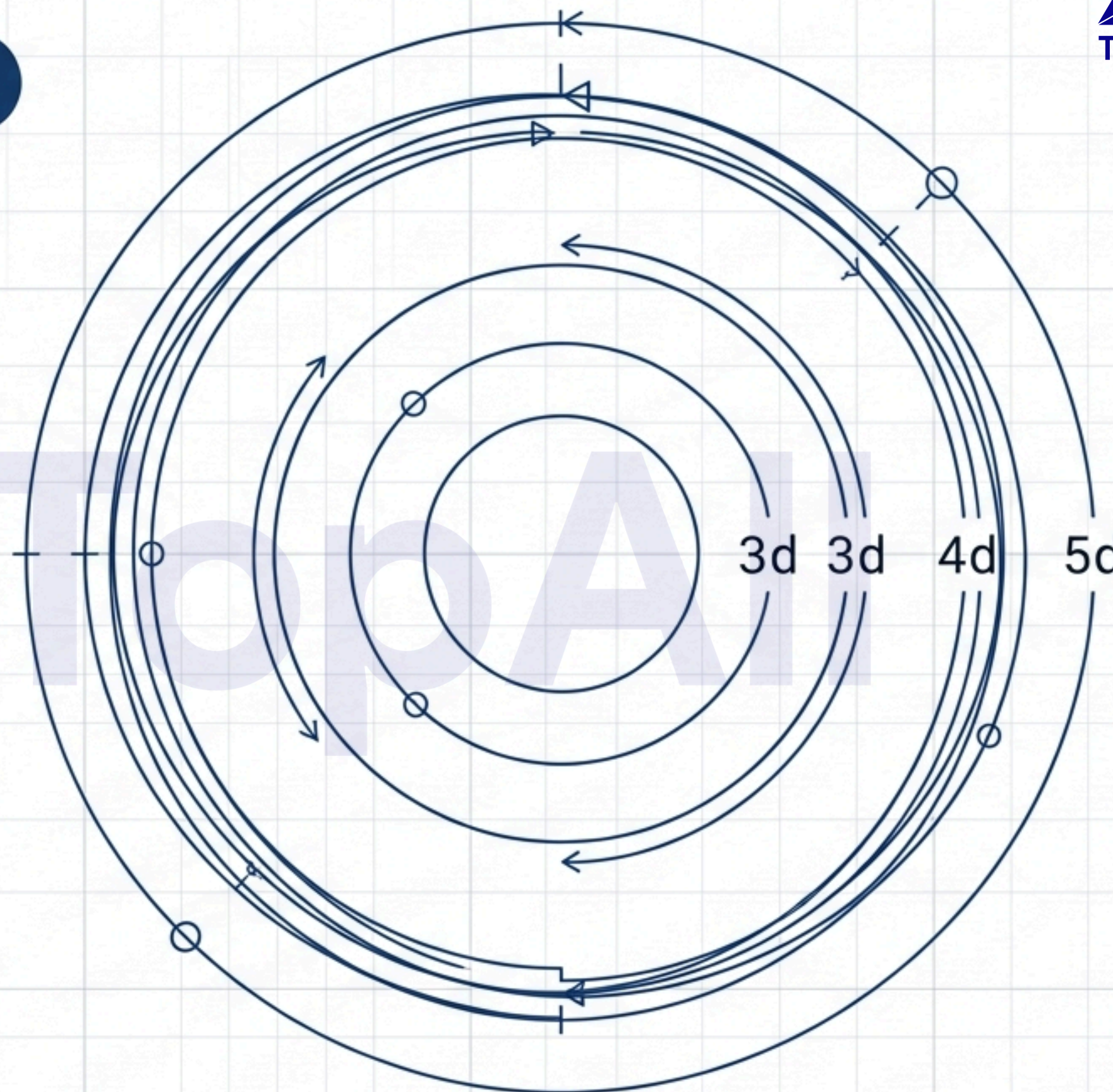


UNIT 4 • *d*- AND *f*-BLOCK ELEMENTS

Variation in Atomic and Ionic Sizes

The 5d Size Anomaly
and the Physics of
Lanthanoid Contraction



Vocabulary 1

Lanthanoid Contraction

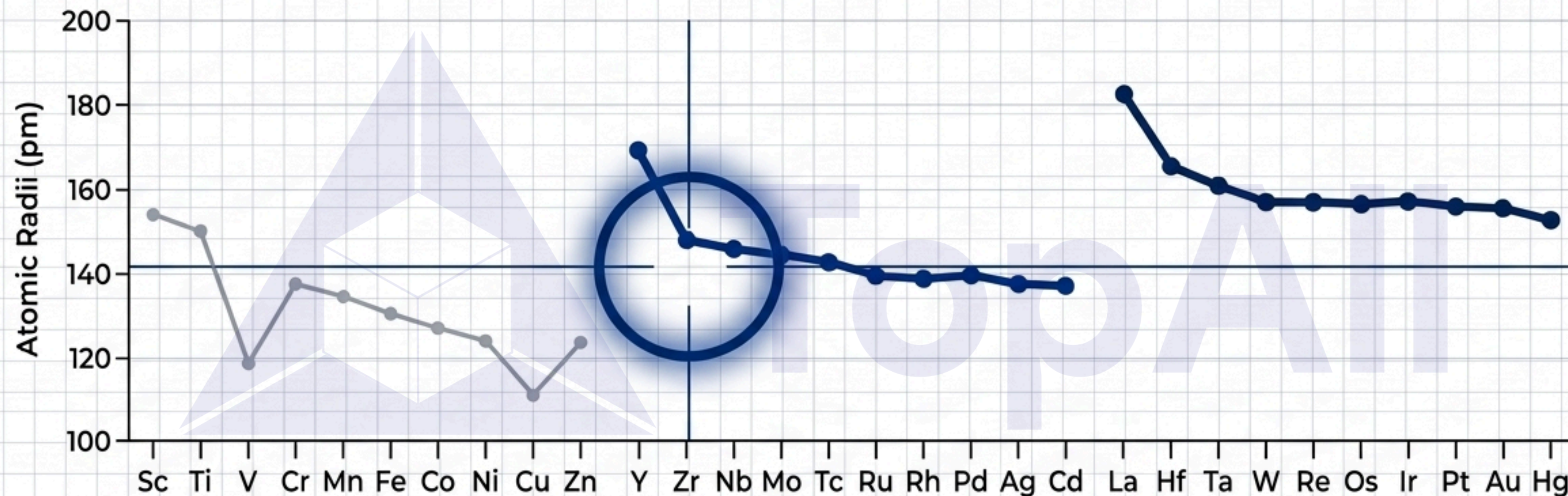
The regular, unavoidable decrease in atomic and ionic radii across the f-block that actively cancels out expected periodic expansion.

Vocabulary 2

Shielding Effect

The ability of inner electrons to block the nucleus's positive pull. (Note: 4f electrons are exceptionally poor at this).

The 4d/5d Size Anomaly



Moving down a group usually means a larger radius. But here, the 5d series is virtually identical in size to the 4d series.



You've Learned the Theory. Let's Test Them Now.

$$E=mc^2$$



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The Mechanism of Contraction

[4f FILLING]

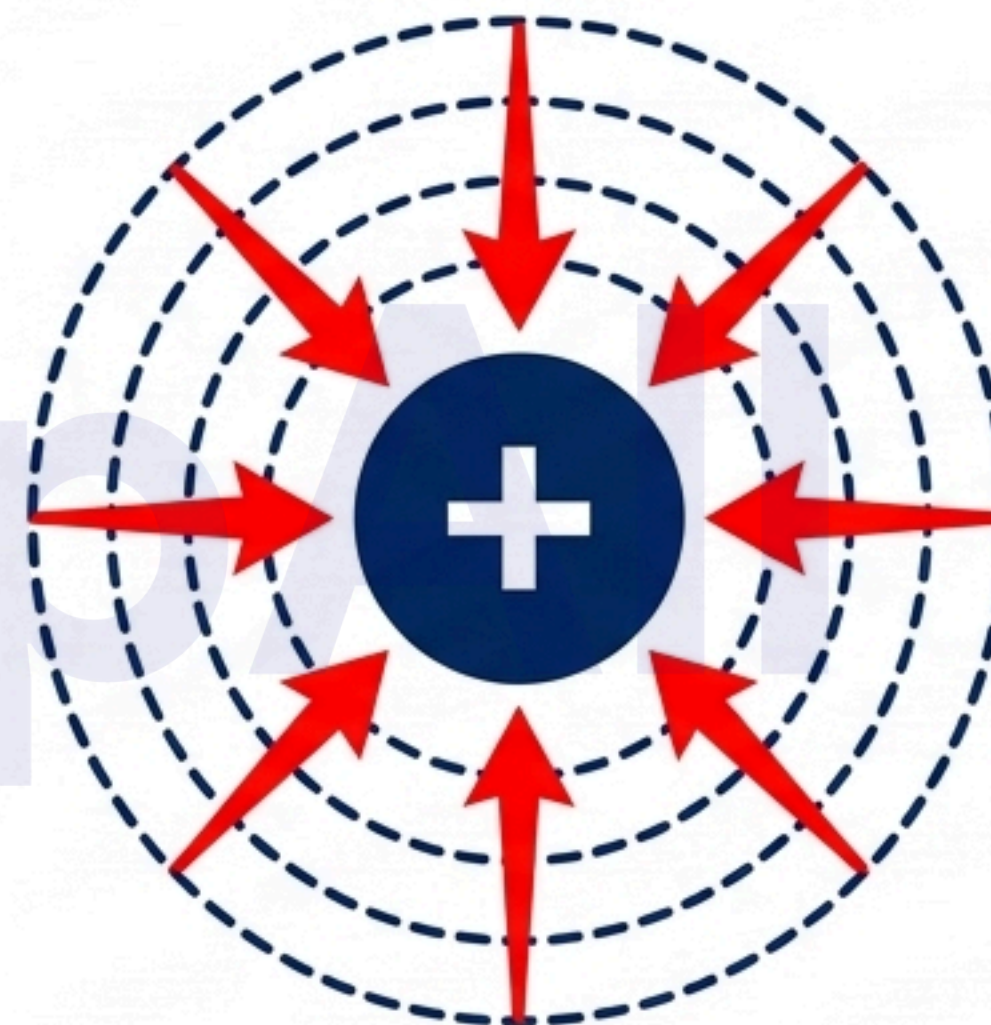
14 electrons must fill the 4f orbital before the 5d series begins.

[POOR SHIELDING]

The dispersed shape of the 4f orbital allows the increasing positive nuclear charge to leak through.

[INWARD PULL]

The unshielded nucleus exerts a massive inward pull on the outer electrons, shrinking the entire atom.



Case Study: Zirconium vs. Hafnium

Zirconium (Zr)

Period 5 | 4d series | Atomic No: 40

160 pm

Hafnium (Hf)

Period 6 | 5d series | Atomic No: 72

159 pm

Despite having 32 more protons and an entirely new electron shell, Hafnium is fundamentally the same size as Zirconium.

Watch for this assumption

~~Going down Group 4 (Ti $\rightarrow$ Zr $\rightarrow$ Hf), the atomic size must strictly increase because a new electron shell is added each time.~~

Size increases from Ti (3d) to Zr (4d), but remains constant from Zr (4d) to Hf (5d). The Lanthanoid Contraction perfectly cancels the expected periodic expansion.

RULE: Never assume a 5d element is larger than its 4d counterpart.

Why do Zirconium (Zr) and Hafnium (Hf) have almost identical atomic radii (160 pm and 159 pm respectively)?

A. They belong to the same period.

B. Diagonal relationship.



C. Lanthanoid contraction.

D. Actinoid contraction.

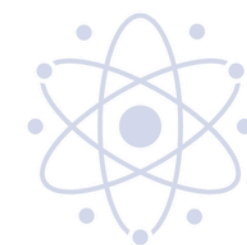
Key Takeaways

- The **4d** and **5d** transition series exhibit nearly identical atomic radii (e.g., $\text{Zr} \approx \text{Hf}$) despite the addition of a new electron shell.
- This anomaly is driven by the **Lanthanoid Contraction**—the filling of 4f orbitals before the 5d series, which offer highly imperfect shielding and allow the nucleus to pull outer electrons tightly inward.



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