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First ionization potentials of the heaviest actinides

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JAEA Tokai

The heaviest elements

Transuranium elements : $Z \geq 93$

Transactinide elements: $Z \geq 104$

The heaviest elements: The elements with $Z \geq 101$ that are produced only in heavy-ion-induced nuclear reactions. ⇒ **a few atoms at a time**

1																	18
1 H	2											13	14	15	16	17	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

Lanthanides	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Contents

JAEA Tandem Accelerator

1. Introduction

Objectives:

Chemical & atomic studies of the heaviest elements provide crucial & challenging opportunities

- to advance our understanding of properties of matter at the limits of existence
- to elucidate the influence of **relativistic effects** on atomic electrons
- to architect the Periodic Table at the farthest reach

The heaviest elements ($Z > 100$):

- available in quantities of only a few atoms or often **one atom-at-a-time**

Chemical & atomic characterization with an atom-at-a-time scale:

⇒ **Extreme Chemistry**

Complex formation abilities, oxidation states, redox potentials, valence electronic structure, *etc*.

⇒ **role of relativistic effects on valence electronic structure of heavy atoms**

Relativistic effects (1)

General: relativity - increase of the mass with increasing velocity

$$m = \frac{m_0}{\sqrt{1-(v/c)^2}}$$

At heavy elements: Increasing nuclear charge plays as the "accelerator" of the velocity of electrons.

⇒ Electrons near the nucleus are attracted closer to the nucleus and move there with high velocity.

⇒ mass increase of the inner electrons and the contraction of the inner electron orbitals (Bohr radius)

$$a_B = \frac{\hbar^2}{me^2} = \frac{\hbar^2}{m_0 e^2}\sqrt{1-(v/c)^2} = a_B^0\sqrt{1-(v/c)^2}$$

⇒ **1. Direct relativistic effects**

Relativistic effects (2)

⇒ Electrons further away from the nucleus are better screened from the nuclear charge by the inner electrons, and consequently the orbitals of the outer electrons expand.

⇒ **2. Indirect relativistic effects**

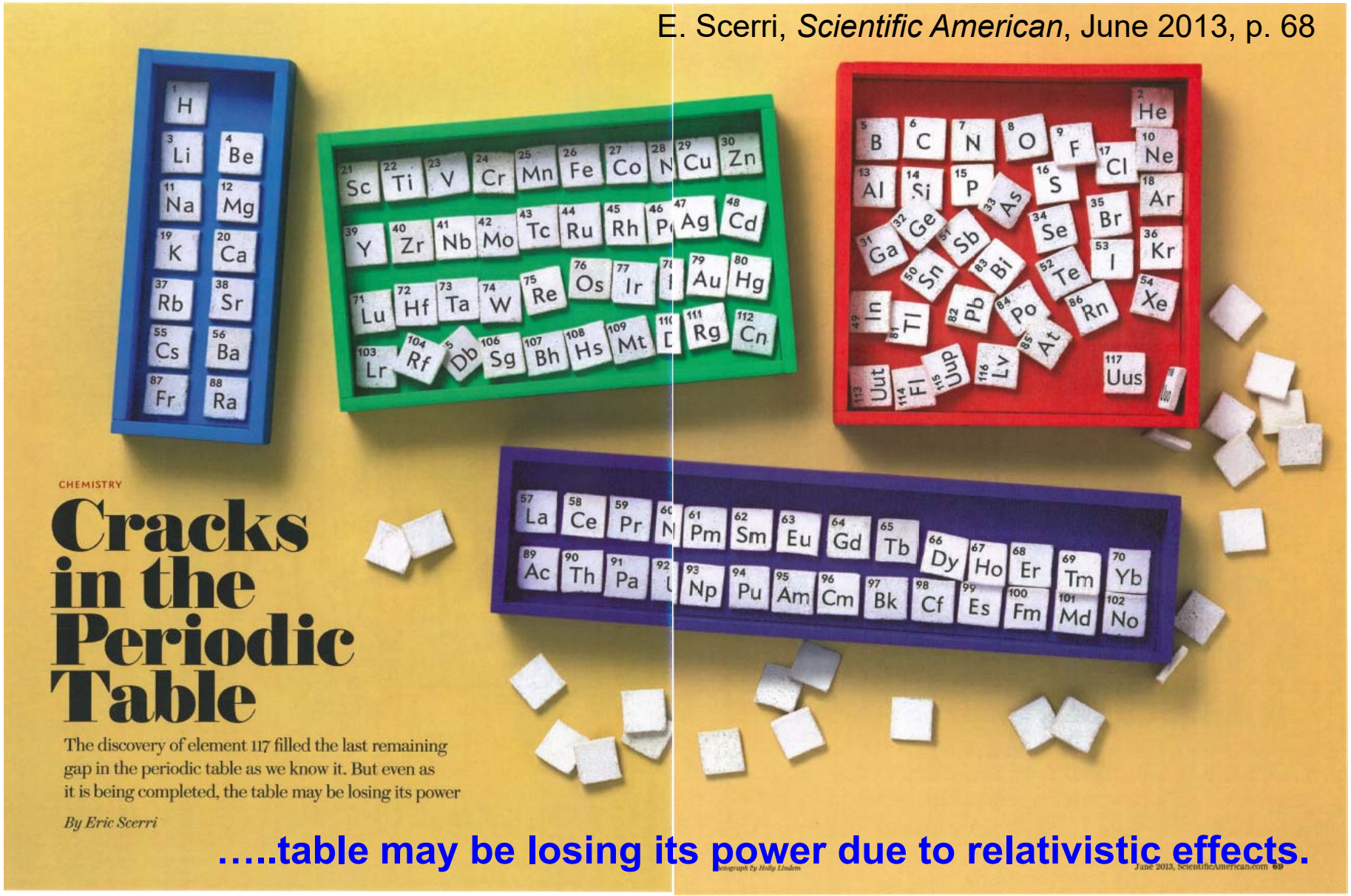
⇒ **3. Spin-orbit (SO) splitting of levels with $l > 0$ into two levels with $j = l \pm 1/2$**

It is expected that the heaviest elements would show a drastic rearrangement of electrons in their atomic ground states, and as the electron configuration is responsible for the chemical behavior of elements, such relativistic effects can lead to **surprising chemical properties**.

Increasing deviations from the periodicity of chemical properties based on extrapolation from lighter homologues in the Periodic Table are predicted.

Cracks in the Periodic Table

E. Scerri, *Scientific American*, June 2013, p. 68



…..table may be losing its power due to relativistic effects.

Typical production rates of the heaviest nuclides used for chemical studies

Z	Nuclide	$T_{1/2}$	Reaction	σ / nb	Production rate*
101	^{255}Md	27 min	^{248}Cm(^{11}B, 4n)	4000	1380 min^{-1}
102	^{255}No	3.5 min	^{248}Cm(^{12}C, 5*n*)	580	200 min^{-1}
103	^{256}Lr	27 s	^{249}Cf(^{11}B, 4*n*)	122	40 min^{-1}
104	^{261}Rf	68 s	^{248}Cm(^{18}O, 5*n*)	13	4 min^{-1}
105	^{262}Db	35 s	^{249}Bk(^{18}O, 5*n*)	6	2 min^{-1}
106	^{265}Sg	14 s/9 s	^{248}Cm(^{22}Ne, 5*n*)	0.38	6 h^{-1}
107	^{267}Bh	17 s	^{249}Bk(^{22}Ne, 4*n*)	0.07	2 h^{-1}
108	^{269}Hs	10 s	^{248}Cm(^{26}Mg, 5*n*)	0.007	3 d^{-1}
112	^{283}Cn	4 s	^{242}Pu(^{48}Ca, 3*n*)^{287}Fl $\rightarrow ^{283}$Cn	0.004	2 d^{-1}

* Assuming typical values of 0.8 mg/cm^2 for the target thickness and beam intensities of 3 x 10^{12} particles per second.

Atom-at-a-time chemistry

Because of the short half-lives and the low production rates of the heaviest nuclides, each atom produced decays before a new atom is synthesized.

Any chemistry to be performed must be done on an "**atom-at-a-time**" basis.

This imposes stringent limits on experimental procedures.

Rapid and very efficient nuclear & radiochemical procedures must be devised.

Strategy

Three experimental approaches:

1. Complex formation abilities

Chemical complex formation in liquid- & gas-phase chemical experiments

2. Oxidation states & redox potentials

Redox studies through electrochemical approaches

3. Valence electronic structure

First ionization potentials & electron affinities

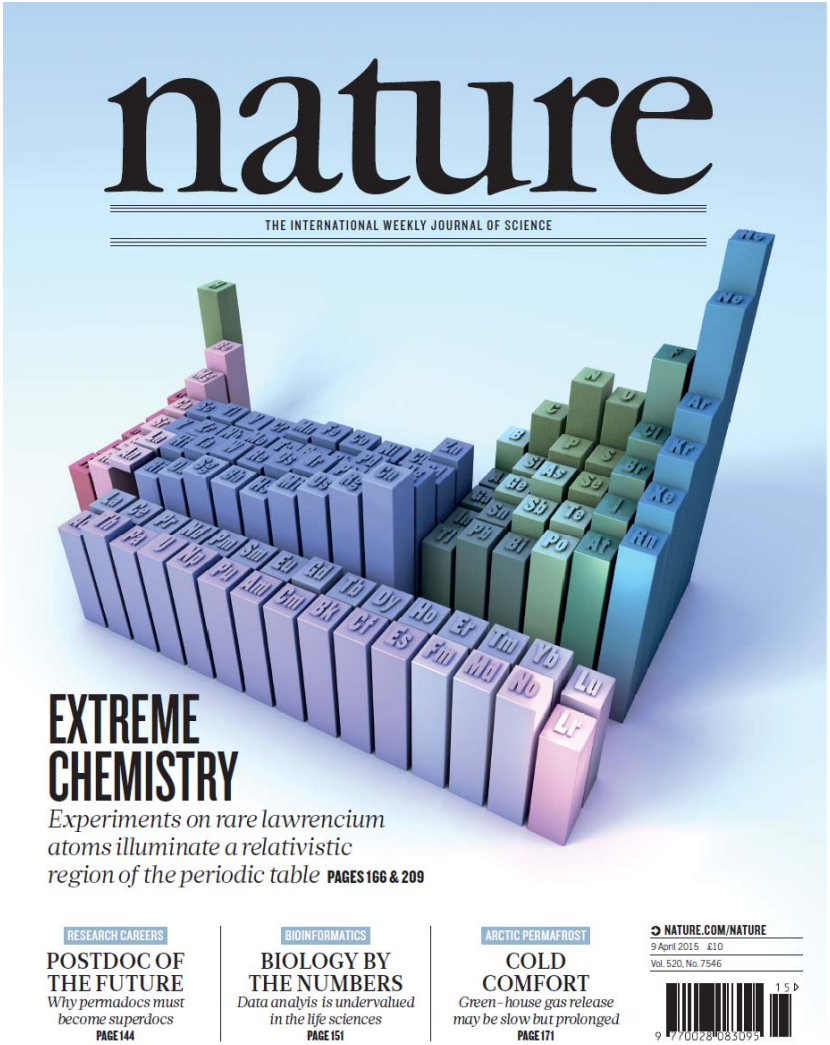
Spin configuration of valence electrons

1. First ionization potential (IP_1) of Lr

Cover of Nature : 9 April 2015

EXTREME CHEMISTRY

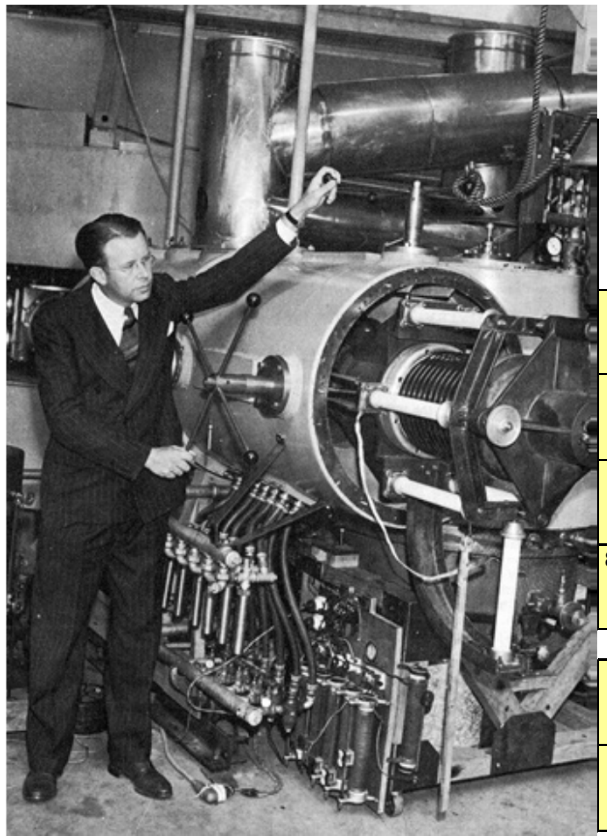
Experiments on rare lawrencium atoms illuminate a relativistic region of the periodic table



First ionization potential: IP_1

The first ionization potential (IP_1) is an atomic property which most sensitively reflects the outermost electronic configuration.

Precise and accurate determination of the IP_1 value provides significant information on the binding energy of the valence electrons and, thus, on increasingly strong relativistic effects.



Y. Nagame,
Nature Chem. **8**, 282 (2016).

3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
															2 He
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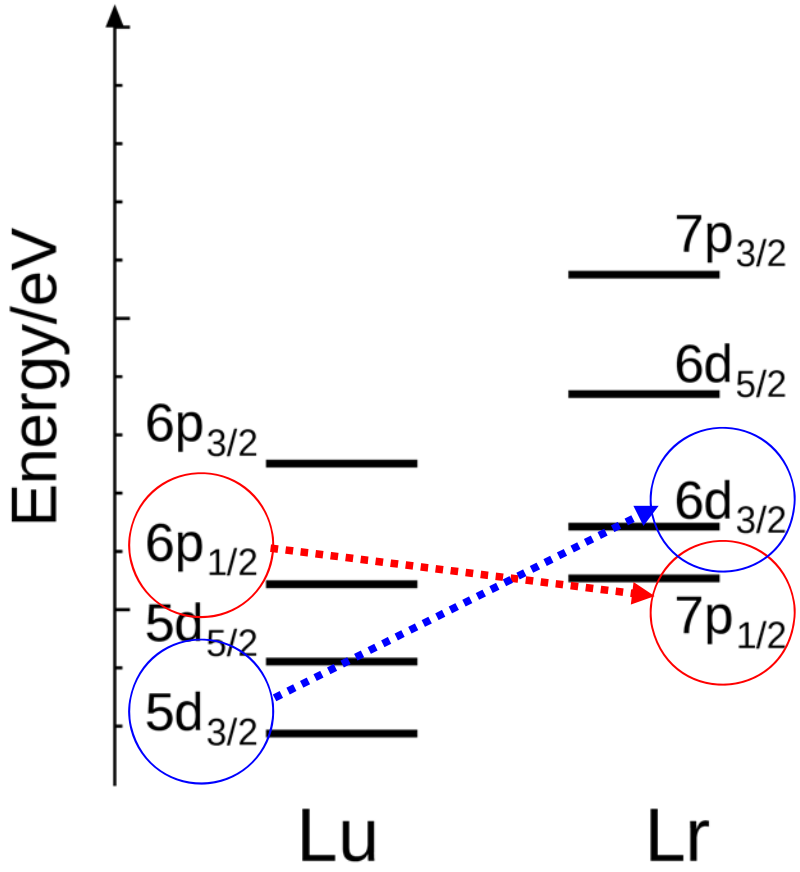
Valence electronic structure of Lr

Lu 71 $[Xe]4f^{14}6s^{2}5d$

Lr 103 $[Rn]5f^{14}7s^{2}7p_{1/2}$

The ground-state electronic configuration of **Lr** is predicted to be **$[Rn]5f^{14}7s^{2}7p_{1/2}$**, in contrast to that of its lanthanide homolog **Lu**, **$[Xe]4f^{14}6s^{2}5d$**, as **the$7p_{1/2}$ orbital is expected to be stabilized below the 6d orbital in Lr by strong relativistic effects**.

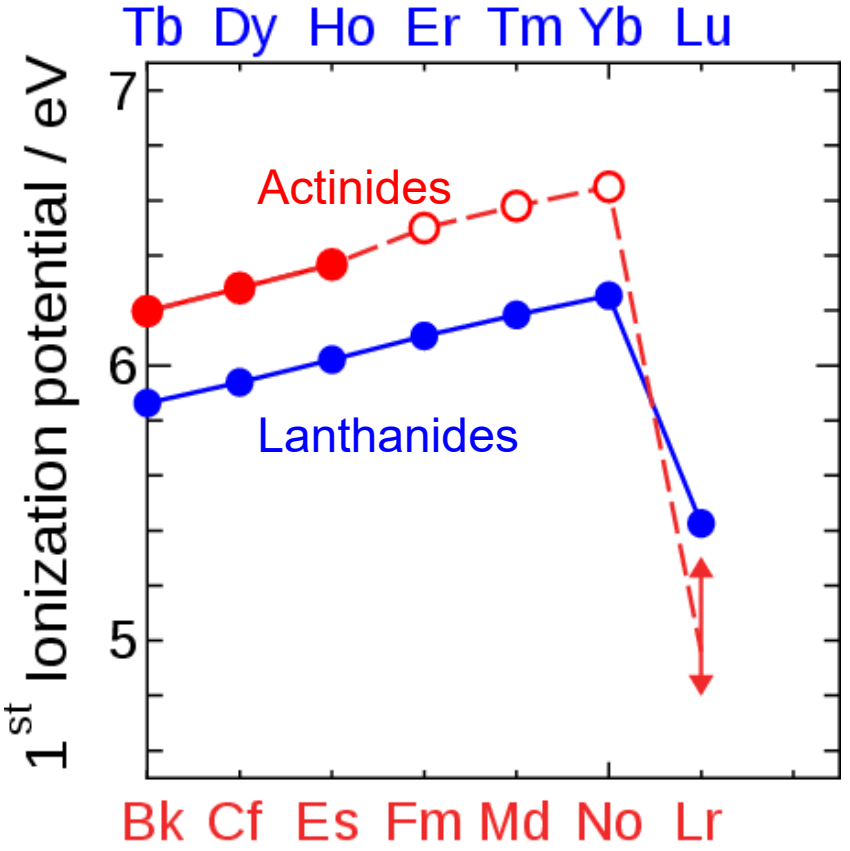


The determination of IP_1 of Lr sheds light on the important role of relativistic effects on the electronic structure of heavy elements.

IP_1 of heavy actinides

IP_1 values of heavy elements with $Z \geq 100$ could not be determined experimentally, because production rates drastically decrease for elements as their atomic number increases.

The study of these elements requires novel techniques on an atom-at-a-time scale.



First ionization potentials of Actinides & Lanthanides

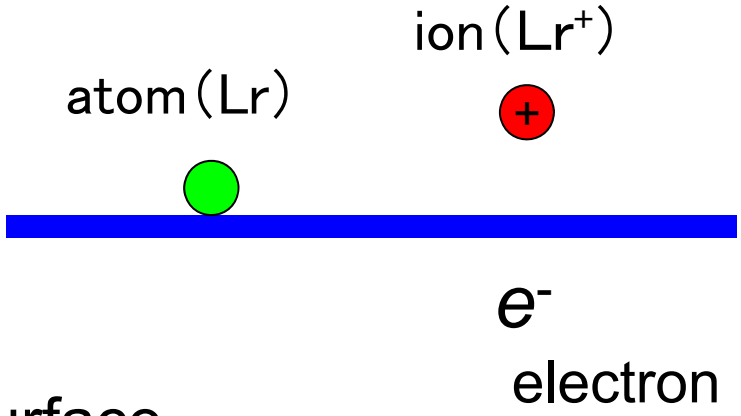
Surface ionization + mass separation

The surface ionization process takes place on a solid surface kept at high temperature and is expressed by the Saha-Langmuir equation.

$$I_{\mathrm{eff}} \propto \exp\left(\frac{\varphi - \mathrm{IP}^*}{kT}\right)$$

I_{eff} : ionization efficiency

IP* : effective ionization potential
φ : work function (Ta)
T : temperature of the ionizing surface
k : Boltzmann constant

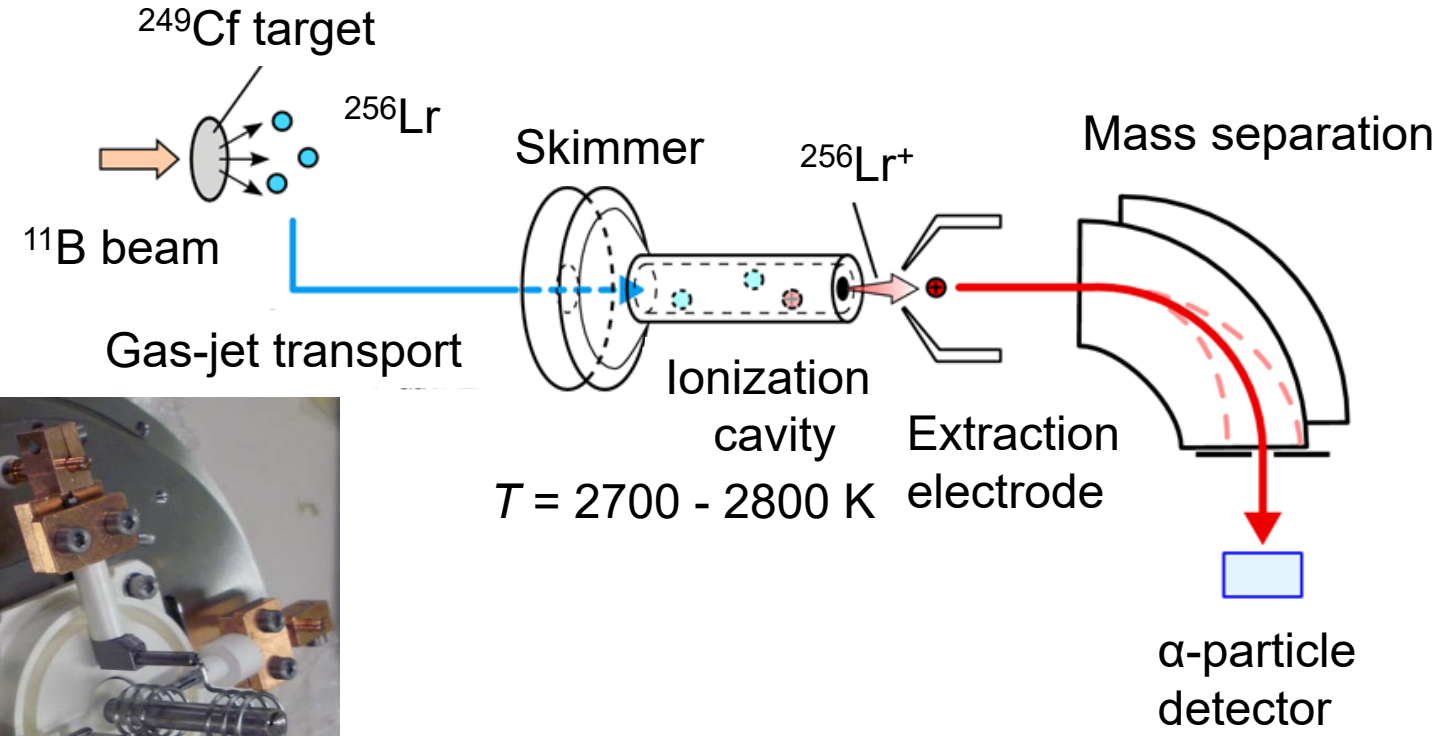


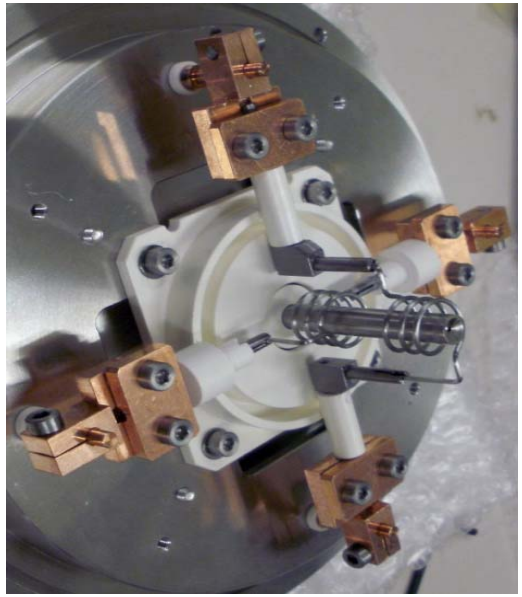
Experimental set-up

Measurement of I_{eff}

T. K. Sato *et al*. *Nature* **520**, 209 (2015)

^{249}Cf(^{11}B, 4*n*)^{256}Lr

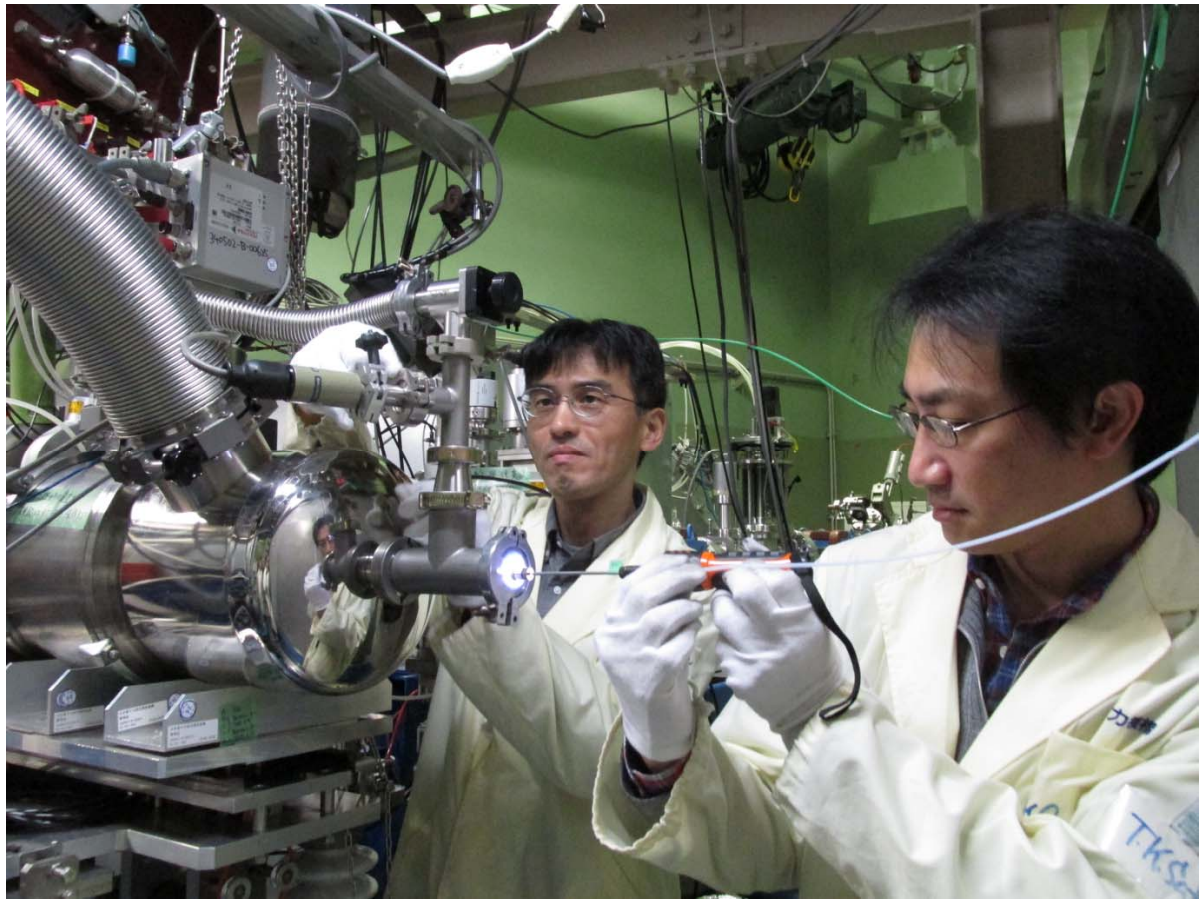




An atom is ionized to the +1 charge state via the interaction with a solid metal surface at high temperature and is selectively mass-separated from nuclear reaction by-products.

Experimental set-up

Physics Today, June 2015



The white tube delivers Lr atoms, contained in a carrier gas, to the Ta ionizer inside the steel chamber.

Analysis: $I_{eff} \Rightarrow IP_1$

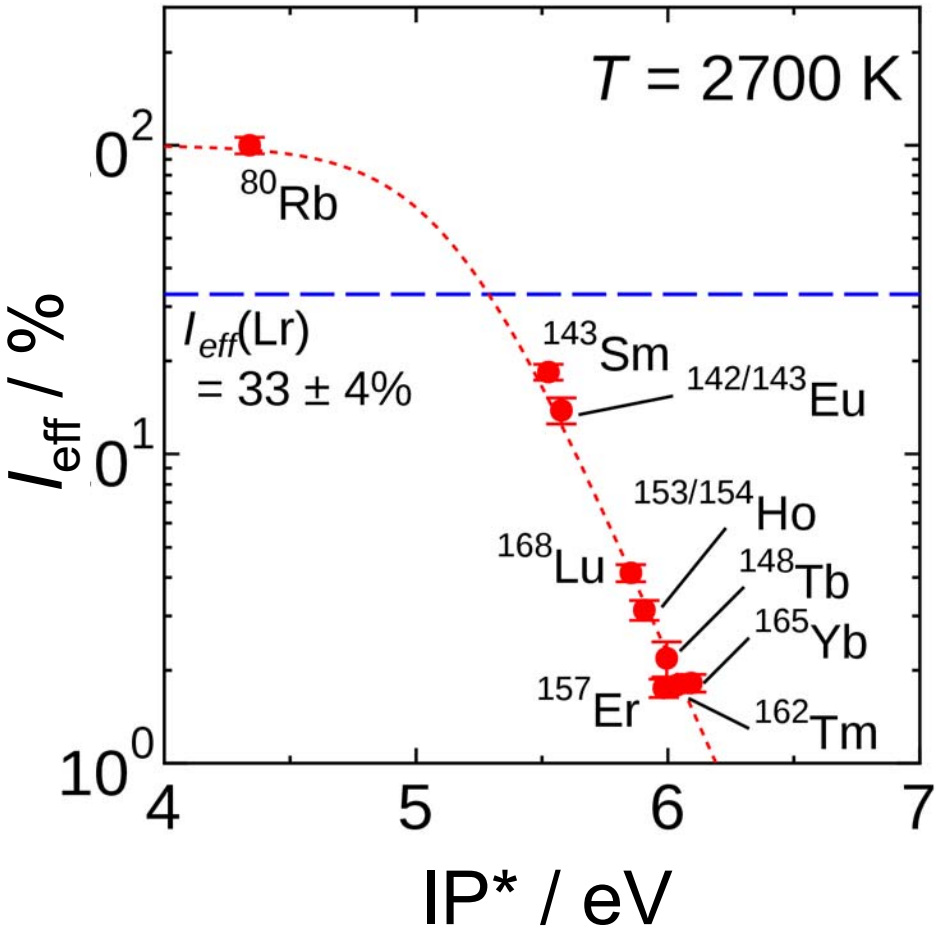
T. K. Sato *et al*. *Nature* **520**, 209 (2015)

$$I_{\mathrm{eff}} = \frac{N\exp\left(\frac{\varphi - \mathrm{IP}_1^*}{kT}\right)}{1 + N\exp\left(\frac{\varphi - \mathrm{IP}_1^*}{kT}\right)}$$

$$\mathrm{IP}_1^* = \mathrm{IP}_1 - kT\left(\frac{Q_\mathrm{i}}{Q_0}\right)$$

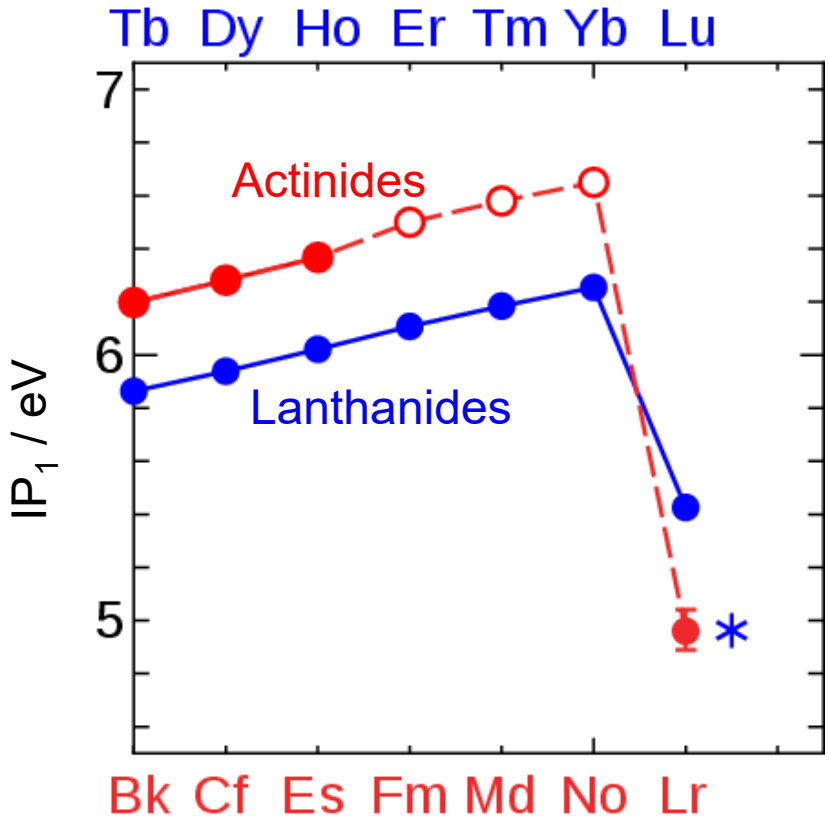
$$Q_\mathrm{i} = \sum_j g_\mathrm{i}^j \exp\left(-\frac{E_\mathrm{i}^j}{kT}\right)$$

$$Q_0 = \sum_j g_0^j \exp\left(-\frac{E_0^j}{kT}\right)$$



I_{eff} = 33% ⇒ IP^*_1 = 5.29 eV ⇒ **IP_1 = 4.96 eV**

IP_1 of Lr



First ionization potentials of Actinides & Lanthanides

	IP / eV
Exp.	4.96 ± 0.08
Cal.	4.963*

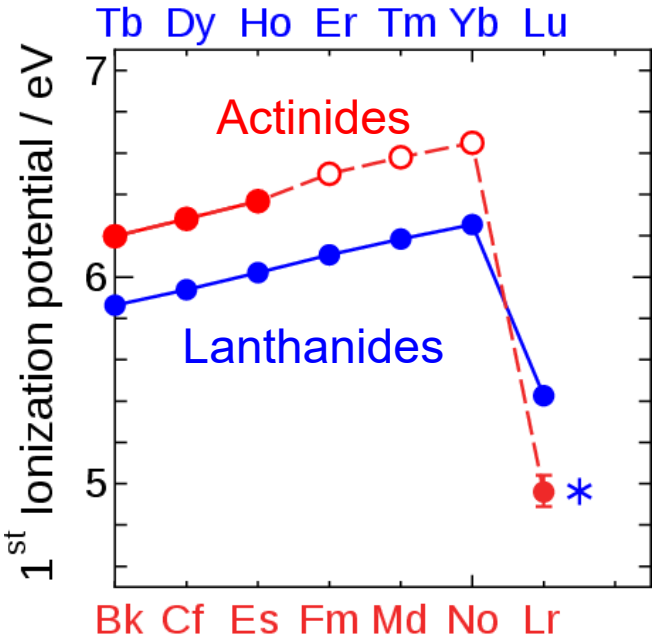
The good agreement with theoretical prediction obtained using relativistic calculations, which favor a **$7s^2 7p_{1/2}$** configuration in the Lr atom, supports this ground state configuration.

This quantitatively reflects and confirms the theoretically predicted situation of closed $5f^{14}$ and $7s^2$ shells with an additional weakly-bound electron in the valence orbital.

IP_1 of heavy actinides: Fm - No

In contrast to Lr, No is expected to have the highest IP_1 among the actinide elements due to its fully-filled 5f and 7s orbitals: $[Rn]5f^{14}7s^2$.

The IP_1 value of heavy actinides up to No is anticipated to increase with filling electrons up in the 5f orbital in analogy to heavy lanthanides.



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55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
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アクチノイド	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

4. Summary & perspectives

We report the determination of the first ionization potentials (IP_1) of the heavy actinides, fermium (Fm, Z = 100) through lawrencium (Lr, Z = 103), by using the novel technique based on the surface ionization process.

The measured ionization potentials are in excellent agreement with the values predicted by state-of-the-art relativistic calculations, and for nobelium (No, Z = 102) also with the recent result from the laser spectroscopy experiments.

The present work provides a reliable benchmark for theoretical calculations.

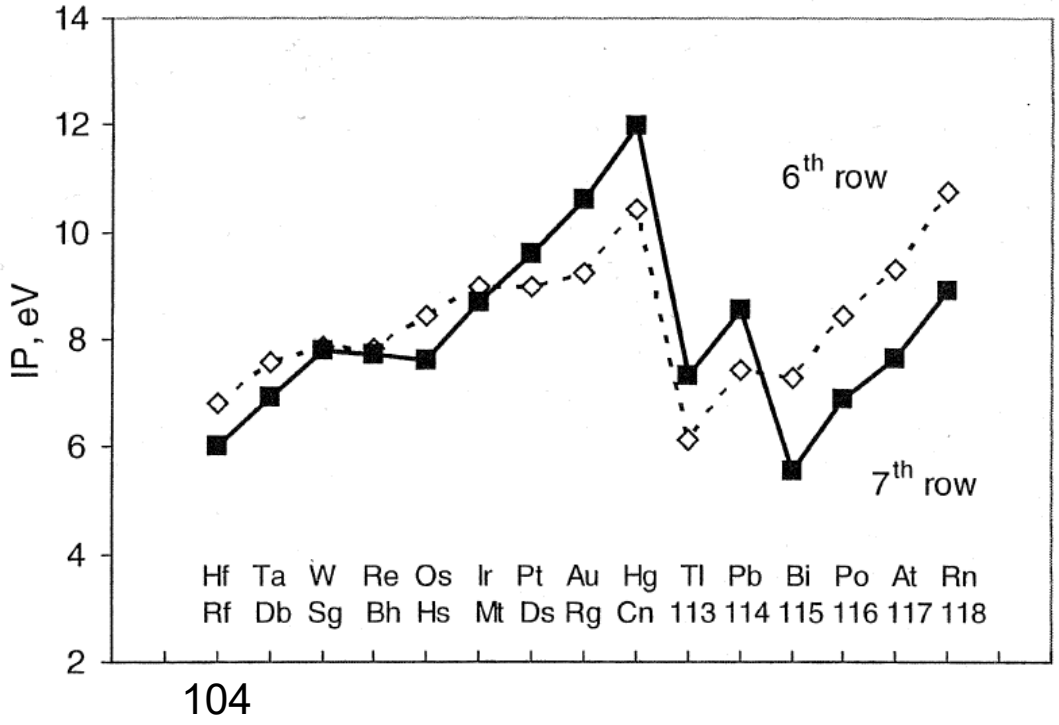
Development of the effective production method of superheavy element (ion) beams using the surface ionization technique coupled to the ISOL

⇒ **New challenge to Extreme Chemistry**

Perspectives

Valence electronic structure

1. IP_1: successive measurement of transactinides
   Development of a new technique
   to measure IP_1 of refractory
   super heavy elements



V. Pershina, In "*The Chemistry of Superheavy Elements* 3rd ed.", ed.
by M. Schädel & D. Schaughnessy

2. Spin state of a valence electron: Lr: $7s^2 7p_{1/2}$ or $7s^2 6d$
   Development of an atomic beam experiment

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