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SUPERHEAVY ELEMENTS CHALLENGE EXPERIMENTAL AND THEORETICAL CHEMISTRY

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Dedicated to Adam Sobiczewski in honour of his 70th birthday

When reflecting on the story of superheavy elements, the author, an experimenter, acknowledges the role, which the predictions of nuclear and chemical theories have played in ongoing studies. Today, the problems of major interest for experimental chemistry are the studies of elements 112 and 114 including their chemical identification. Advanced quantum chemistry calculations of atoms and molecules would be of much help. First experiments with element 112 evidence that the metal is much more volatile and inert than mercury.

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1. New elements at Dubna in the 1960s

The standing problem of superheavy elements (SHEs) has greatly influenced my life in science. In 1960, I joined the Laboratory of Nuclear Reactions (LNR) headed by G.N. Flerov. An ambitious goal of this young Dubna laboratory equipped with the most powerful heavy ion cyclotron was the discovery of new chemical elements, with element 104 as the first candidate. By that time there were claims of researchers at Berkeley that they had discovered elements 102 and 103 in heavy ion induced reactions. Actually, it was an error as proved later by Dubna teams [1, 2].

The "planned" nuclide, $^{260}104$, was supposed to undergo, mostly, spontaneous fission (SF). The decay mode has no distinct spectral characteristics, and this hinders the assignment of the atomic and mass numbers, Z and A for the synthesized "suspected" nuclei by solely nuclear physical methods. Element 104 was expected to be the first "transactinoid", resembling in its properties hafnium, the first "translanthanoid"; *cf.* Table I. As such,

TABLE I

Mendeleev Periodic System of the Elements (with IUPAC recommended group notation). Ground state electronic configurations of atoms for elements 103 to 118 are calculated values.

3	4	5	6	7	8	9	10
Y $4d5s^2$	Zr $4d^25s^2$	Nb $4d^45s$	Mo $4d^55s$	Tc $4d^55s^2$	Ru $4d^75s$	Rh $4d^85s^2$	Pd $4d^{10}$
La-Lu $5d6s^2$	Hf $5d^26s^2$	Ta $5d^36s^2$	W $5d^46s^2$	Re $5d^56s^2$	Os $5d^66s^2$	Ir $5d^76s^2$	Pt $5d^96s$
Ac-Lr **103** $\boldsymbol{7s^2p}$	**Rf** **104** $\boldsymbol{6d7s^2p}$	**Db** **105** $\boldsymbol{6d^37s^2}$	**Sg** **106** $\boldsymbol{6d^47s^2}$	**Bh** **107** $\boldsymbol{6d^57s^2}$	**Hs** **108** $\boldsymbol{6d^67s^2}$	**Mt** **109** $\boldsymbol{6d^77s^2}$	— **110** $\boldsymbol{6d^87s^2}$

11	12	13	14	15	16	17	18
Ag $4d^{10}5s$	Cd $4d^{10}5s^2$	In $5s^2p$	Sn $5s^2p^2$	Sb $5s^2p^3$	Te $5s^2p^4$	J $5s^2p^5$	Xe $5s^2p^6$
Au $5d^{10}6s$	Hg $5d^{10}6s^2$	Tl $6s^2p$	Pb $6s^2p^2$	Bi $6s^2p^3$	Po $6s^2p^4$	At $6s^2p^5$	Rn $6s^2p^6$
111 $\boldsymbol{6d^97s^2}$	**112** $\boldsymbol{6d^{10}7s^2}$	**113** $\boldsymbol{7s^2p}$	**114** $\boldsymbol{7s^2p^2}$	**115** $\boldsymbol{7s^2p^3}$	**116** $\boldsymbol{7s^2p^4}$	**117** $\boldsymbol{7s^2p^7}$	**118** $\boldsymbol{7s^2p^6}$

it would strongly differ in chemical properties from all the lighter transuranium elements, and this might enhance its chemical identification. Thus, this independent (of physics) and reliable method of determination of Z, became very desirable. It was the first task I got involved in. To identify element 104, the chemical procedure had to be continuous and capable of immediate isolating the new atom created in average once an hour or so. It had to be as fast as possible, and to allow detection of SF events. Some of the requirements were unique, like the short separation time: then only batch-wise isolation techniques existed for hafnium and most other metallic elements, and they took at least minutes. Also the expected production rate was by orders of magnitude lower than ever before. The more unusual was the combination of these musts. After a few years, we did come with a technique operating down to a second. It consisted in thermalizing the recoils in a gas flow, producing gaseous compounds of the element under study by adding appropriate gaseous reagents, and separating the mixture of nuclear interaction products by a sort of gas phase chromatography. Since then, similar approach has been extensively used in many laboratories in searching for SHEs, and for identification and studies of fundamental chemistry of transactinoids, including SHEs; for review, see recent Refs. [3,4]. Almost every heaviest elements is expected to form some characteristic volatile compound(s) or be relatively volatile metal (see below).

Identification of a new short-lived nuclide is feasible and the efficiency of each concrete experimental technique is high enough only in a limited range of half-lives. These were discussed at many seminars held regularly in LNR. In the early 1960s, the expectation of SHEs was not yet there and the available data about the SF half-lives gave little indication how to obtain a credible estimate for $^{260}104$ by extrapolation. Pessimists expected 1 μs; such value would completely prevent chemical identification and disable the physical techniques which had performed so well [1] for elements 102 and 103 living seconds or longer. Optimists hoped for a second (fortunately, they got closer to the truth). Remember that the general trend predicted by the liquid drop model of nuclei and observed in the actinoid elements was ever shorter SF lifetime with larger Z; this would soon put limit on the possible atomic number because of prompt fission of nuclei.

2. Superheavy elements in Nature

Right in those years, a principal breakthrough happened in the problem of how nuclear shells affect SF half-lives thanks to the pioneering works published in 1966–1968 by Swiatecki, Strutinski, Sobiczewski, Nilsson and others. Inspired by the, then newly, predicted proton magic number 114, which (unlike the "trivial" 126) seemed experimentally in reach, they outlined how to proceed from qualitative ideas to quantitative description of the fission barriers. We got certain that one would eventually understand the SF half-lives reasonably accurately, though there was obviously yet a long way ahead. And we got very excited by the chance that the nuclides around $^{298}114$ live long, maybe even enough to survive in Nature.

Though busy with the synthesis of elements 102 to 105, the LNR started searches for superheavy elements in Nature. This did not require accelerators and many groups all over the world got involved in the problem. Of course, the instrumental methods of detecting SF events have limits of sensitivity, which, in general, can be effectively made much lower by (radio) chemical enrichment prior to the measurements. One has to outline the chemical homologs of the SHE among the known elements, estimate the possible differences in properties of the homologs, and design enrichment procedures to treat the promising materials. Thus, the research was essentially similar to the works of M. Curie and other classics of radiochemistry.

The theory could not firmly point to the SHE nuclide with the longest *total* half-life. Hence, necessarily, chemists had to look whether the SHE around $Z = 114$ have some common distinct properties which would enhance their concentration. Indeed, though the nearest homologs of the individual SHEs are different (see Table I), elements 112 to 118 have a specific common property — they must be quite volatile in the elemental state in the absolute sense and mostly more volatile that their lighter congeners, Hg to Rn. This became a popular guideline in selecting natural samples in which geochemical (and/or cosmochemical) processes as well as possible subsequent industrial treatment might have already done some enrichment work. Less often, the searches in Nature followed the indications that the longest total half-lives are to occur for isotopes of elements around $Z \approx 110$, because at higher Z's the faster alpha-decay takes over SF. The elements 108 to 110 are to be homologs of noble metals Os, Ir, and Pt.

SHEs were sought in hundreds of samples. What else might be a reasonable guideline? It does not seem completely logical to look mostly for the samples of homologs as concentrated as possible. For example, at a laboratory, to look for element 108 to 110, they assayed massive samples of platinum and naturally occurring osmiridium alloy. A piece of such very rare element can result only from some unique and extremely selective geochemical process. But let us perform an imaginary chemical or geochemical "experiment": take a material with some content of a particular SHE and its expected homolog, and gradually enrich the sample in the homolog. Now, plotting the specific activity of the SHE in the sample *versus* the concentration of the homolog, *cf.* Fig. 1, we may encounter different situations. If the SHE does not behave in the concrete processing as the homolog, its activity will soon drop practically to zero. If it behaves similar to the homolog, the specific activity of the concentrate will first increase but then drop when the homolog becomes very pure. Finally, if the separation technology better suits the SHE rather than the homolog, again the very concentrated homolog will not have the highest specific activity. One certainly cannot know the differences in properties and behavior in all reasonable separation processes. Hence, assaying not too pure samples of homologs seems more reasonable than taking very rich concentrates.

Many researchers had an unconscious, poorly justified idea that such exotic elements occur most probably in exotic media and exotic places on the Earth. On the other hand, certain exotic materials *were* reasonably prospective. If our prediction of SHE chemical properties is wrong, the geochemical and/or industrial processing will deplete rather than enrich the element. Hence, it was logical to assay specimens, whose composition would be as close as possible to the primordial matter of the solar system. Luckily enough, a meteorite of the very rare carbonaceous chondrite type, several tons in weight, fell in 1969 near Pueblito de Allende, Mexico. Just these meteorites are the least differentiated matter available on the Earth; the abundances of all volatile and noble metals in Allende are much higher than

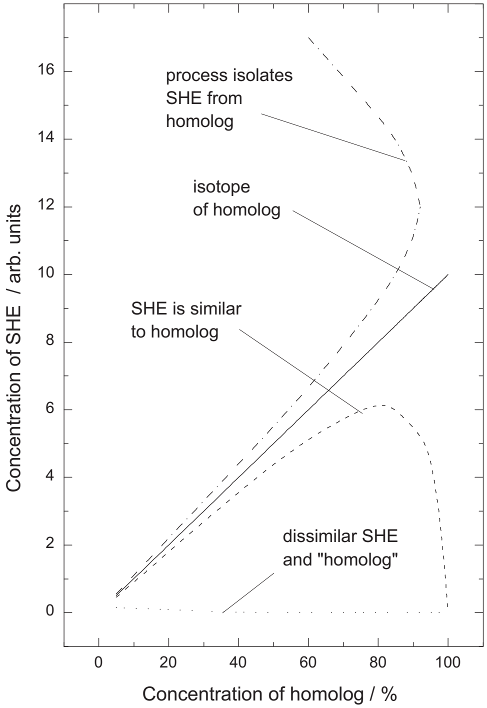

Fig. 1. Highly enriched samples of SHE homologs may not be the most prospective; see text.

in any Earth rocks. The Smithsonian Institution in Washington DC, which holds large portion of the found fragments kindly provided for G.N. Flerov's research 30 kg of pieces for nondestructive testing (to be returned) and later also 10 kg more for destructive chemical enrichment experiments. (At present, the Allende meteorite specimens are offered on Web for about $10 a gram.) In 1973, when I took the first sample to Dubna, the security guards in the Washington airport watched my handling that heavy box of strange stones with concern and confusion.

Another objects selected for research were the so-called ferro-manganese nodules from remote deep regions of the Pacific Ocean. The potato-like and -sized nodules grow extremely slowly (millimeters per thousand to million years) at the ocean floor mostly from hydroxides of Fe and Mn and contain so much of Cu, Ni, Co and other metals as to be prospective poly-metallic ore. We believed that the nodules might concentrate nuclei from the cosmic rays and dust, as the inflow of matter by the ocean streams and atmospheric precipitation is relatively very low. A dedicated expedition of the Soviet Academy of Sciences research ship Vitiaz dragged some nodules in Fiji islands region for our investigations.

In addition, a spying and detective story happened concerning the nodules. From an American popular science journal we learned that by 1973, in the USA, they built a special ship Glomar Explorer (185 m long, 51 000 t) for "deep ocean mining" the nodules on an industrial scale. Mentioned were airlift transportation and a sophisticated *accurate and stable positioning system* of the ship. One could hope that soon a pilot or full-scale plant would treat the ore producing also a number of technological fractions enriched in different groups of elements. However, the story of the ship proved to be a fake. It covered a top-secret project of lifting from a depth of 5000 m an armed Soviet nuclear submarine, which was lost in 1968 some 600 miles of Hawaii. In 1974, the ship did indeed lift a part of the submarine, no nodules.

In 1969, when Dubna was the most active laboratory searching for SHE, I presented a summary of the laboratory results at one of the first international scientific meetings with the subject on program. Of historical interest is undoubtedly the following passage about SHE from the conference summary by de-Shalit [5]:

> "There is, however, another aspect to this (SHE) problem which makes it necessary, to my mind, for all of us to stop for a minute and think more thoroughly about where we are heading and what we are preparing for humanity. (These SHE)... may undergo induced fission with the emission of a substantial number of neutrons. Since the size of critical assemblies is inversely proportional to the number ... minus one, it is not hard to imagine what could be the outcome of the existence of such SHE with such a value of around 12 ... It is not quite clear to me whether we as physicists can do anything at this stage to prevent catastrophic results that may come out of mass production of such superheavy nuclei. But I think that all of us want to know that we have given the matter the most serious thought and consideration before we proceed full speed on this new venture."

Actually, in speaking, his words were even more anxious. Obviously, the national security agencies in the USA and USSR did not learn about this warning as the research was not made classified.

A variety of instrumental techniques were used to search for SHEs in Nature; see Ref. [6] for review. The most efficient and universal was a counter of prompt neutrons from spontaneous fission built in LNR [7], in which prompt gamma rays from SF triggered measurement of neutrons, which were moderated in polyethylene and registered within a $\approx 100\ \mu$s coincidence time window by an assembly of dozens of ^{3}He-filled proportional detectors. Samples up to several liters in volume and some 30 kg in mass could be measured. The somewhat modified counter is now in use in FLNR for studies of the synthetic element 112 (see below) because of its negligible background and large volume.

Unfortunately, all the then reported positive results of searches for SHE were at the limit of sensitivity of the detectors and the attempts to chemically enrich such samples failed. The best limit expressed as the SHE half-life divided by the content (fraction) of SHE in the sample was 10^{24} years. It is not possible to measure the two quantities separately but if the half-life were 10^9 years, one would have to treat billions of tons of raw material to obtain the critical mass of SHE (see above the worries of de-Shalit).

The search for SHEs has been an interesting multidisciplinary undertaking. Flerov and Ilyinov described it vividly in a small popular book [8], which could well bring the title "Physics as Cognitive Adventure" like the well-known book by A. Einstein, L. Infeld. The story is by no means over. The ever more credible values of half-lives of SHE by Sobiczewski *et al.*, [9–12] may bring revitalization of the efforts [13], as the range of most prospective nuclides gets narrower. I did not mention the yet occasional attempts to detect SHEs (not necessarily the longest-lived) provided that they were produced by some more recent astrophysical processes and mechanisms and steadily come to the Earth from outer space.

3. Man-made superheavy elements — status

From the mid-1970s to mid-1980s, in parallel with the search in Nature, the laboratories possessing heavy ion accelerators also attempted synthesis of short-lived SHE isotopes. They put many efforts in bombarding actinoid targets with heavy ions. The most "popular" was ^{248}Cm + ^{48}Ca but ^{254}Es + ^{48}Ca, ^{238}U + ^{238}U, and other combinations were also tried. It meant jumping over several still unknown elements on the way to the SHE region. In many cases, radiochemical methods including those based on the expected volatility of metallic SHE were used for separation. Again, there were no conclusively positive results. Fig. 3 [14], sums up the results with the ^{248}Cm target obtained by joint efforts till 1985 in terms of the upper limits for the production cross section. In flight separation of the recoiling bombardment products by mass was very fast but less sensitive then chemistry, which through off-line batch separations reached much lower cross-sections but only for much longer half-lives. Since then, for about dozen years, both the search in Nature and the attempts of synthesis were scarce.

Studies of the fusion–fission reactions of heavy ions [16] and ever more accurate calculations of SF half-lives of SHE [9–12] have consistently strengthened the hope for the existence of pronounced stability islands. Estimates of the production cross sections in heavy ion induced reactions, especially with ^{48}Ca projectiles, suggested that the earlier attempts of synthesis had failed just due to insufficient sensitivity; *cf.* Fig. 2. The ambitious goal to explore cross sections down to a picobarn was achieved by Oganessian *et al.*, [15, 17–20] just to the end of the last century. In weeks

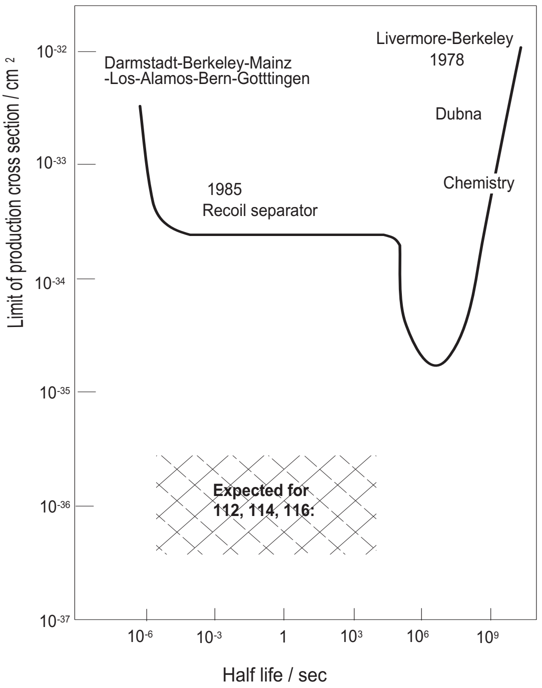

Fig. 2. Upper limits of the production cross section of SHE *versus* half-life achieved until 1985 [14]; expected range of cross section and half-lives [15] before starting the Dubna experiments of the last years.

to months of bombardment of isotopes of U, Pu and Cm by very intense beams of ^{48}Ca, they discovered several isotopes (one to three nuclei of each) of previously unknown elements 116 and 114, as well as of elements 112, 110 and 108. Fig. 3 summarizes the data in a format of the common chart of nuclides. Except for ^{293}116, the new nuclides have relatively very long half-lives — up to minutes (error bars are not shown, they are necessarily large). Presumably, these are the slopes of the "stability island" centered on ^{298}114.

Physical evidence for the assignments of Z and A is very convincing [15]. For example, the alpha decay characteristics strictly obey the well-known Geiger–Nuttall rule; also, the decay chain data are completely consistent when synthesizing daughters of ^{292}116 and ^{288}114 in the appropriate target — projectile combinations. The calculated values of half-lives for even–even nuclides reproduce the experimental data to about two orders of magnitude, which seems very satisfactory. Yet, this and other evidences for Z and A, however strong, are not direct as none of the nuclides in the above decay chains has been known before. See also Refs. [21, 22]] for the review of the field.

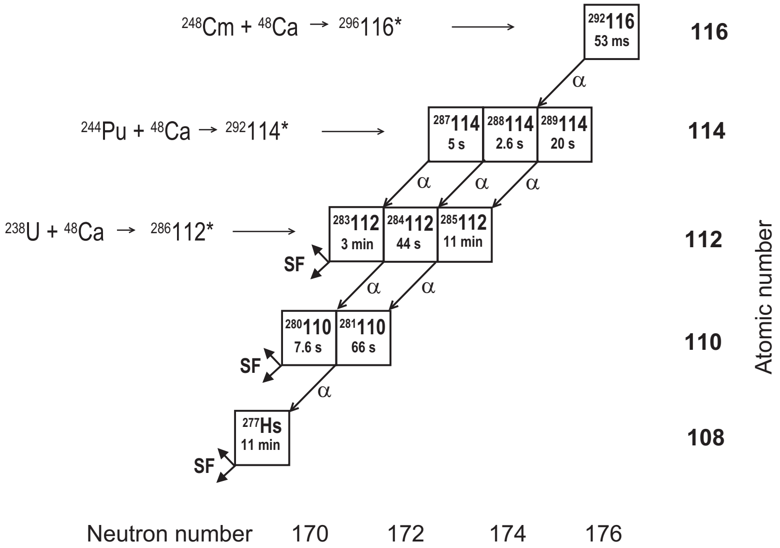

Fig. 3. The "northeast" end of chart of nuclides like at present.

Knowledge of the production cross sections and decay properties gained in physical experiments greatly contributes to the feasibility of the chemical studies of SHEs. In comparison with physical tests, a larger number of atoms per unit fluence can be observed due to the use of thicker targets and larger total detection efficiency (including chemical yield). Such studies, are of a fundamental interest *per se*. They result also in the chemical identification of the atomic number of the new nuclide and thus provide an independent (of physical means) evidence for the assignment of Z. We considered element 112 (E112) as a most attractive object of the chemical studies and identification. Its isotope mass number 283 (see Fig. 3) can be produced by bombarding a $^{\rm nat}$U target with a relatively "large" cross section — a few pb. As a homolog of Hg (see Table I), the element probably possesses unique chemical properties, "convenient" for experimentation. It is to be chemically very inert and more volatile than mercury, while all the elements from E111 down to Fr (E87) are much less volatile or even refractory metals. However, to what extent might the properties of E112 differ from mercury? This important question is to be addressed to quantum chemistry.

4. Quantum chemistry of SHE

With larger Z, the atomic electrons become increasingly relativistic. This is evident from the mere fact that in the (non-relativistic) hydrogen-like Bohr atom with a nuclear charge of 110, the binding energy of the K-electron would be $110^2 \times 13.6\,\mathrm{eV} \approx 165\,\mathrm{keV}$, a value comparable with the electron rest mass 511 keV. Because of the "relativistic effects", some chemical properties of any SHE might not strictly follow the trends observed for its lighter homologs. In particular, a "linear" extrapolation of the trend of volatility in the subgroup Zn → Cd → Hg → E112 is not automatically valid. Such peculiarities might enhance or hamper the chemical identification of superheavy nuclides. Predictions by the relativistic quantum chemistry might help to choose and design the most informative future experiments keeping in mind that only a few chemical experiments with the transactinoids and SHE are realized each year all over the world.

The required accuracies of calculations of atoms (ions) and molecules are very high. The formation energy of a SHE nucleus from free protons and neutrons is some 1 GeV. To predict the partial half-lives for α-, β- or SF-decay branch, the accuracy in decay energies of 10^{-5} relative, or 0.01 MeV, would be no doubt excellent. To predict reasonably well chemical properties, excellent would be to calculate various characteristic energies to $\pm 0.01\,\mathrm{eV}$; it means 10^{-8} (!) relative to the formation energy of a heavy atom from its bare nucleus and free electrons, which is some 1 MeV. Such accuracy is desirable, *e.g.*, when calculating the first ionization potential (IP) as the difference between the total energies of the atom and ion. Experimental values of IP for common elements are known to be $\pm 10^{-3}$–10^{-5} eV.

The atomic and molecular calculations [23] performed by variational minimizing the total energy lean upon some basic principles established several decades ago for the non-relativistic atom as a many electron system. By analogy with the Hartree–Fock theory, the Dirac–Hartree–Fock method starts with anti-symmetrized product of four-component spinors. The major calculational difficulty in treating the heaviest atoms with open electronic shells and their excited states is the "correlation energy". In the old theory, an electron experiences Coulomb interaction just with the average field created by the others. Actually, a region immediately surrounding the electron must be deficient in electrons compared to the average ("Coulomb/correlation hole"). Also the electron moves and its motion correlates with others. The most powerful up-to-date methods to cope with the correlation effects, the multi-configuration Dirac–Hartree–Fock calculations, again originated in non-relativistic quantum chemistry. Various other "effects" are either included in the formulations of the Hamiltonian or treated as perturbations. All this results in a great, ever increasing variety of approaches and appropriate computer programs.

According to the valence bond theory, each of the two interacting atoms supplies one of its unpaired valence electron to a shared pair, which attracts the nuclei. The molecular orbital (MO) theory uses linear combinations of the valence electron orbitals to obtain the required two-center MO. The "bonding" orbital has high electron density in the overlap region and so attracts the two nuclei; the characteristics of corresponding "anti-bonding" orbitals are just opposite. If the participating atomic electrons are originally paired, they must be excited to some higher atomic orbitals. For example, to make an atom with the s^2p^2ground state tetravalent, it must be "promoted" to sp^3. Actually, the latter, originally unequal orbitals are "hybridized" to reach energetically preferable tetrahedral symmetry. To avoid immense calculational expenses in evaluation of two-electron integrals for the compounds of heavy elements, the atomic wavefunctions used for constructing MOs are often finally approximated by effective sums of a few "Gaussian primitives". They have the form $\exp(-\zeta r^2)\ x^i y^k z^l$, where i, k, l are just integer exponents at the Cartesian coordinates. These and other possible approximations contribute to the large variety of approaches in molecular calculations.

In the relativistic atoms, the orbitals $s_{1/2}$ and $p_{1/2}$ with their large electron density near the nucleus have smaller (than would have non-relativistic ones) radii and larger binding energies. The orbitals $p_{3/2}$, d, f, ... with their smaller density near the nucleus and due to the efficient screening by the contracted $s_{1/2}$, $p_{1/2}$ orbitals, have lower (than non-relativistic) binding energies and larger radii. These phenomena and electron correlations mostly cause some deviations from trends in the groups of Table I.

The latest achievements in the field of relativistic atomic calculations are the values of ionization potential for some SHEs and their homologs-predecessors; see Table II. The calculations [25] also reasonably well, to 0.06 eV, reproduced the experimental excited levels in free Pb atoms: 0.97, 1.32, 2.66, 3.65, 4.33, 4.38, 5.32 eV.

TABLE II

Ionization potentials in eV. Calculations from Refs. [24–26].

	exp.	calc.		exp.	calc.		exp.	calc.
Zn	9.39		**Ge**	7.90		**Kr**	14.00	
Cd	8.99		**Sn**	7.34		**Xe**	12.13	**11.6**
Hg	10.44	**10.44**	**Pb**	7.42	**7.48**	**Rn**	10.75	**10.10**
E112	—	**11.97**	**E114**	—	**8.54**	**E118**	—	**7.21**

Thus, the values for SHE seem trustworthy. Unfortunately, today, with a few short-lived SHE atoms available, it is impossible to verify experimentally the excitation and ionization energies. The calculated ionization data are useful in discussing possible peculiarities SHE, though these characteristics do not strongly correlate with chemical properties; some chemical theories have to mediate.

Molecular calculations better meet the needs of experimenters. In general, such calculations result in the values of ionization and excitation energies of molecules, as well as bond energy, vibrational frequency and length; one can also evaluate dipole moments and polarizabilities. However, rigorous accurate molecular calculations of SHE are difficult — a compound of real interest for experimenters might take several hours of CPU time at modern supercomputers. This is why such calculations have been performed only for molecules with relatively simple structure of orbitals and energy levels. Some recent data for hydrogen halides [27] are shown in Table III.

TABLE III

Calculated and experimental values for hydrogen halides [27].

	Bond energy/eV		Bond length/nm	
	calc.	exp.	calc.	exp.
HBr	4.17	3.92	0.143	0.141
HI	2.88	3.20	0.163	0.161
HAt	2.27	2.52±0.17	0.174	—
H(E117)	2.21	—	0.194	—

Measurements of such quantities do not seem feasible in coming years. To remove the gap between the theory and experiment, the molecules of real interest to experimenters are calculated using less complicated and rigorous methods [28]. These usually yield some systematic errors when comparing the calculated and experimental values for known molecules. The trend is then used to "correct" the calculational values for the compounds of the heaviest elements to make them more credible.

When speaking about chemical properties, one usually means bulk properties of metals, crystals and solutions of compounds as well as their behavior in reactions. Any calculations from first principles are hardly possible. Of our primary interest were bulk properties of condensed phases like volatility or thermodynamics of crystals and metals. In this case, one has to find a way how to translate forth and back between, say, the adsorption energy of single atoms (molecules) on a surface and the macro-chemical terms: sublimation, vaporization energy, boiling point. The necessary mediation is again accomplished by various chemical theories or just empirical correlations between the bulk characteristics and the calculated parameters of the molecules.

4.1. Element 112

Element 112 chemistry seems to be unique but relatively simple case to discuss. Below are shown the boiling points of the metals adjacent to Hg in Table I and the electronic structure of their outer orbitals as well as the bonding energies of some homonuclear diatomic molecules. To form chemical or metallic bonds, the two s electrons in Zn, Cd and Hg must be unpaired and excited to the sp configurations. This is energy consuming and makes dimeric metal molecules, especially Hg_2 extremely weakly bound. Au and Tl, the mercury neighbors in the row, have unpaired valence shell electrons and bonding in their dimers is much stronger.

In bulk metal there is more chance for Hg electrons to join the conductivity zone. But again, due to the progressive relativistic stabilization of the s^2 closed shell, Hg metal has a considerably lower boiling point (as well as the melting point) than Zn and Cd, and much lower than Au and Tl.

Boiling points/^{0}C

$d^{10}s$	$d^{10}s^2$	s^2p	Bonding energies/eV
	Zn 906		
	Cd 767		
Au 2950	Hg 357	Tl 1457	Au_2 2.3 Hg_2 **0**.043 $Tl_2$0.61
	112 ?		

Then, what one can expect for E112? On the base of relativistic calculations we now understand the trends in columns and rows shown above. E112 metal must be even more volatile than Hg, though hardly more volatile than Rn, whose boiling point is -62°C. The metallic and chemical bonds of E112 must be weaker than of Hg. All this makes some room for an extreme assumption that the element might behave almost like an inert gas. Still, it will react with very strong oxidation agents (fluorine) to yield not only difluoride, like Hg, but possibly also tetrafluoride, which is not known for Hg but well known for Xe (and very probably exists for Rn). Bonding of E112 with fluorine is to be weaker than for E118 because the latter must be the true EkaRn and contain not too strongly bound outer $p_{3/2}$ electrons [23].

5. Chemical identification of element 112

Yakushev *et al.*, [29] in 2000 at Dubna performed the ever first experiment with E112, aiming at eka-Hg. The second test was done late in 2001 [30]. Now the researchers allowed also for the possibility that E112 is much more volatile and chemically inert than Hg [31]. To that end, two detection devices in series were used capable of detecting E112 also if it behaves like Hg rather than like Rn.

The essential components of the experimental installation are schematically shown in Fig. 4. The atoms recoiling from the target were thermalized in flowing helium, in which Hg is stable in atomic state. Single Hg atoms stick to inert surfaces only at below −150°C; at ambient temperature, they could be almost without loss transported by the gas to the SF detectors. This provided fast, continuous and selective isolation of Hg and E112 — other heavy metals, which could interfere in measurements, were adsorbed on the walls of the gas duct.

The first detection device consisted of passivated ion-implanted silicon detectors (PIPS) coated with $40\mu\mathrm{g/cm}^2$ of Au, which strongly adsorbs Hg at room temperature. If not retained on the PIPS, the atoms of E112 were carried into the second device — a flow-through ionization chamber optimized for registration of the fission fragments. For conclusive identification of the rare spontaneous fission events, the PIPS detectors and ionization chamber were placed inside an assembly of neutron counters mentioned in Sec. 2, which detected the expected burst of prompt fission neutrons in coincidence with fission events [7].

Experimental: A target of ^{238}U oxide was 2 $\mathrm{mg/cm}^2$ thick and contained Nd to produce also Hg activities; the beam current was $\approx 0.5\,p\mu$A of 264 MeV ^{48}Ca ions. The target chamber was continuously flushed with 500 cm^3/min of helium; the transportation distance was 25 m with 80 % efficiency measured for Hg. Eight consecutive pairs of PIPS detectors coated with Au were used while the 49-s ^{185}Hg deposited on the surface of the first pair of PIPSs to 95%. The cylindrical Frish grid ionization chamber, was 5000 cm^3 in volume; to improve its counting performance, some argon and methane were added to the helium carrier gas at the chamber inlet.

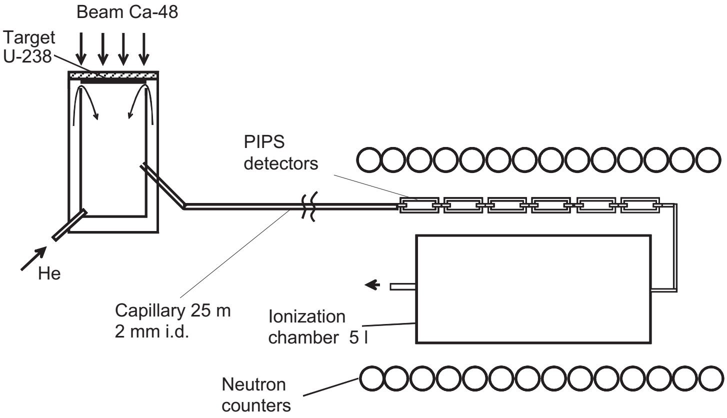

Fig. 4. Schematic of FLNR experiments on chemical identification of element 112; not to scale [30].

Results: The total beam dose in 24 days amounted to 3.5×10^{18} ions. The degree of purification of the volatile fraction from non-volatile products was regularly controlled and proved to be better then necessary. The PIPS detectors did not detect any event of two coinciding large pulses from opposite detectors followed by neutron counts. Meanwhile, the ionization chamber detected eight fission events followed by prompt neutrons. The background of the ionization chamber was measured before and after the experiment for a total of 14 weeks to detect four fission events followed with neutrons *i.e.*, about one per the time of experiment. The 68% and 95% (Bayesian) shortest confidence interval for the average *"net" number of decay events of E112 per the given fluence are* $4.5 \le N \le 10.2$ *and* $2.6 \le N \le 14$*, respectively.* The data are consistent with the production cross section from the physical experiments. All this means that *E112 behaves in the particular experimental conditions more like ekaRn rather than ekaHg.*

6. Some prospects

The extremely important result on chemistry of E112 suggests the next step of the studies. It is planned to identify α-active $^{284}112$ as the member of the decay chain of $^{288}114 \rightarrow ^{284}112 \rightarrow ^{280}110$ (SF) obtained in the reaction $^{244}\text{Pu} + {}^{48}\text{Ca}$ (see above). A row of semiconductor particle detectors will form a sort of chromatographic column with a negative longitudinal temperature gradient over the temperature range from ambient down to LN_2. It will be possible to measure the lifetime and α-particle energy of $^{284}112$ nuclei, as well as lifetime and total kinetic energy of fission fragments of $^{280}110$. The ekaRn-like congener of Hg must adsorb from flowing gas on the detectors somewhere within this range thus providing quantitative measure of relative volatilities of element 112 and Rn. This seems to be the first occasion to confront detailed quantum chemistry calculations with experimental data. However experimentally difficult, the chemical identification of element 114 itself seems feasible and will be attempted in near future. The element is to be more inert than Pb and hardly capable of forming compounds in the gaseous phase [32].

The analysis of the most advanced calculations of alpha decay and SF half-lives of even–even isotopes [9–12] plus some (still more uncertain) estimates of beta stability infer that some isotopes of element 108 might be the candidates to survive in Nature. This might lead to revitalization of these efforts [13]. During the first period mentioned in Sec. 2, ekaOs was not searched for thoroughly.

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