

A Search for the Isotope 263 of Element 104 – A Possible EC-branch in ^{263}Ha

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In previous attempts [1, 2] to identify the isotope 263 of element 104, Rf, the $^{248}\text{Cm}(^{18}\text{O},3n)$ reaction was used to produce this new isotope. In these experiments a total of 7 spontaneous fission (SF) events were observed after chemical separation of element 104. This observation was interpreted as preliminary evidence for the production of ^{263}Rf with a SF half-life near 500 seconds and a cross section of 140 pb.

A second attempt to identify ^{263}Rf was made in our collaborative effort to study the chemical and nuclear properties of the elements 104 and 105. The $^{249}\text{Bk}(^{18}\text{O},4n)$ reaction was used to produce ^{263}Ha [3, 4]. Chemical separations were carried out [5] isolating fractions of elements 105 and 104 to study the decay properties of ^{263}Ha and to search for evidence of ^{263}Rf which could be produced by electron-capture (EC) in ^{263}Ha . Activities from the $^{18}\text{O} + ^{249}\text{Bk}$ reaction were transported by a gas-jet to the Automated Rapid Chemistry Apparatus (ARCA) [6] where computer controlled separations were repeatedly performed, on a one minute time scale, producing Rf and Ha samples [5] for α - and SF-pulse height analysis. All these fractions had a very high degree of purity from actinides, allowing a search for SF decay at detection rates as low as one event per hour.

We observed a total of 22 fissions over the course of 155 experiments. From the well known α /SF-ratio for Fm isotopes and the information from our measured α -spectra we can attribute approximately 9 of these fission events to ^{256}Fm decay, leaving 13 SF's due to the decay of ^{263}Rf . These ^{263}Rf fission events yield a half-life of 600 seconds, close to the 500 second fission half-life observed from a previous study [3].

Taking into account the measured 6-nb ^{263}Ha production cross section [1], these 13 SF events correspond to a ^{263}Ha EC branch of $\approx 8\%$. The resulting effective ^{263}Rf production rate is about a factor of 4 larger than that expected or observed [1] rate in either the $^{248}\text{Cm}(^{22}\text{Ne},\alpha 3n)$ or $^{248}\text{Cm}(^{18}\text{O},3n)$ reaction.

For the even isotopes ^{262}Rf and ^{264}Rf theoretical calculations indicate [7] that the half-lives for SF de-

ca are shorter than the α half-lives by factors of 10^3 and 10^4 , respectively. From this one can deduce that also for ^{263}Rf spontaneous fission may be the dominant decay mode. An estimated half-life of about 1000 seconds results interpolating between the calculated SF half-lives for the even isotopes if an additional hindrance factor of 1000 is applied for the odd neutron.

From Ref. [7] an α half-life of about 10^4 seconds can be deduced for ^{263}Rf , whereas an α half-life of about 10^5 seconds is calculated using the most recent mass tables from Möller et al. [8], which give a Q_α -value of 7.6 MeV. Both half-lives are too long to be observed in our experiment with a sufficiently high sensitivity.

If, contrary to the theoretical predictions, the alpha energy of ^{263}Rf is between 7.65 and 7.74 MeV, which corresponds to a half-life interval from about 10^5 to 5000 seconds, then any alphas from ^{263}Rf would be masked by alphas from ^{214}Po impurities.

An alpha half-life between 600 and 5000 seconds can be estimated if the alpha energy of ^{263}Rf is between 7.74 and 8.0 MeV. Based on the two events we observed at 7.9 MeV an alpha branch of 30 % would result.

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Coulomb excitation of the $K=16^+$ rotational band in $^{178}\text{Hf}^G$

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The existence of long-lived high-spin isomeric nuclear states opens new and very exotic opportunities for nuclear structure studies on radioactive targets. Among all the known isomers, the $K=16^+$ isomeric state in ^{178}Hf is one of the best candidates for this kind of investigations due to its long lifetime ($T_{1/2}=31\text{y}$), relatively low excitation energy of 2.45 MeV and very high spin. This isomeric state should be mostly of 4 quasiparticle nature [1] and the deformation is expected to be roughly the same as for the ground state. The predicted properties have been recently examined by collinear laser spectroscopy experiments performed at PARIS separator in Orsay [2]. The obtained spectroscopic quadrupole moment ($Q_s=6.00(7)$ b), magnetic moment ($\mu_I=8.16(4)$ μ_N) and change in the mean square nuclear charge radius between the isomeric and ground state ($\delta \langle r^2 \rangle = -0.059(9)$ fm) confirm the theoretical predictions. While the decay properties of the isomer were also well studied almost nothing is known about excited levels built on this isomeric state. The collective properties and the interplay between single particle and collective degrees of freedom can be studied if one observes at least one transition in the $K=16^+$ rotational band.

In the Dubna – Orsay – GSI collaboration a large quantity of $^{178m2}\text{Hf}$ ($\sim 10^{14}$ atoms) has been produced in the $^{176}\text{Yb}(\alpha, 2n)$ reaction [3]. After chemical separation the target was prepared by electro-spraying the Hf solution on thin carbon foils ($40\mu\text{g}/\text{cm}^2$). The first experiment devoted to the search of excited states has been performed at the Munich tandem accelerator with a deuteron beam [4]. In the inelastic scattering on $^{178m2}\text{Hf}$ targets new excited state at energy of ~ 353 keV was observed in the particle spectra measured with the Q3D spectrograph and tentatively assigned to the first excited state of the isomeric rotational band.

In a second attempt the Coulomb excitation of $^{178m2}\text{Hf}$ has been performed at the UNILAC. The ^{208}Pb (4.77 MeV/u) projectiles were scattered on two $^{178m2}\text{Hf}$ targets containing $\sim 0.6\%$ of nuclei in the $K=16^+$ state. Separate runs have been taken with $^{178,177,176,175}\text{Hf}$ and ^{195}Pt stable targets in order to examine the γ -radiation coming from other isotopes contained in the $^{178m2}\text{Hf}$ targets. The experimental set-up, especially developed at GSI for Coulomb excitation measurements [5], consisted of eight high-efficient Ge detectors and position sensitive particle detectors covering $\sim 80\%$ of the relevant solid angle. During the off-line data analysis the projectile and target nuclei were uniquely identified by setting relevant kinematical conditions. The kinematical information allowed to make a precise Doppler shift correction of γ -rays observed in the coincidence with particles scattered in the Θ_{CM} range from 45.4° up to 69.2° . A careful analysis of the γ -spectra allowed to identify γ -lines belonging to the different isotopes. At an energy of 357 keV, an additional γ -transition has been found which was assigned to the already seen $17^+ \rightarrow 16^+$ transition. From the intensity of this line and the $4^+ \rightarrow 2^+$ ground state transition the isomer to ground state ratio has been obtained ($\sigma_{178m2}/\sigma_{178g.s.} = 0.033(9)$) which is in

agreement with a X-ray fluorescent analysis and a measurement of the target γ -activity.

Fig. 1 shows the excitation probabilities for the two excited states. The good agreement with the Coulomb excitation calculations supports the assignment of the 357 keV line to the $17^+ \rightarrow 16^+$ transition in the $K=16^+$ rotational band.

The population of higher excited states is expected to be weaker by at least one order of magnitude based on theoretical calculations. These states may be studied by making use of particle γ - γ coincidences which can be studied with the newly developed Euroball Ge detectors combined with the Crystal Ball. Mass separated isomeric targets will be available for further investigations in the nearest future.

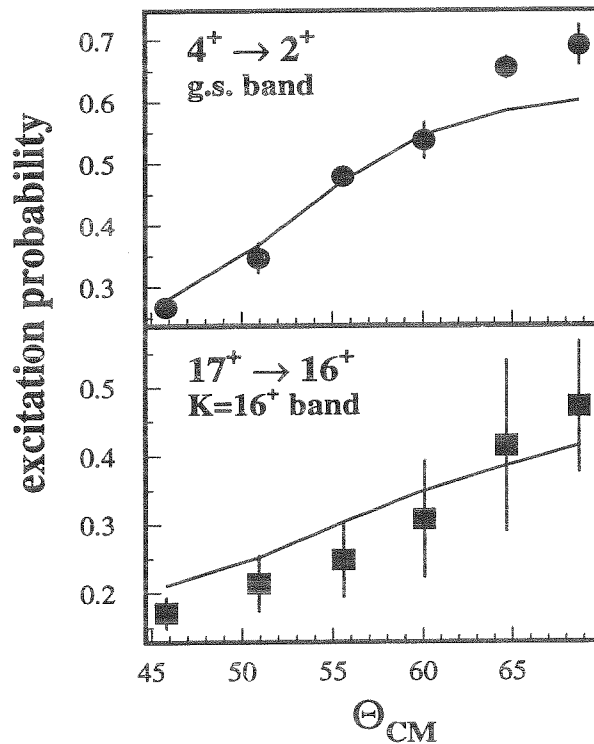


Figure 1: Comparison of the calculated and measured excitation probability for $4^+ \rightarrow 2^+$ transition in the ground state band and $17^+ \rightarrow 16^+$ in the isomeric $K=16^+$ rotational band in ^{178}Hf .

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Effect of Columnar Defects on the Elastic Behaviour of Vortices in YBCO Thin Films

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Numbers of experiments have shown that amorphous columnar defects introduced into high T_c films and crystals by swift heavy ions act as very effective pinning sites and result in enhancement of the critical current. In this paper a sensitive ac transport technique is used to determine the force displacement response in the elastic regime of vortices pinned in YBCO thin films both before and after irradiation by swift ^{238}U ions. Force-displacement measurements allow the extraction of parameters in this elastic regime which are unavailable from dc transport or magnetic measurements. In particular, the restoring force which pinning defects exert on the vortices, and the elastic limit of displacement of the vortices before they depin are extracted from these data.

The film was irradiated at room temperature with 2.7 GeV ^{238}U ions perpendicular to the film surface (parallel to the c -axis). The equivalent dose, B_{Φ} , which defines an applied field where the defect spacing equals the vortex spacing, was about 400 mT.

The transport technique for extraction on the force displacement curve involves the usual four point geometry for measurement of resistance. However we use an ac current in the kilohertz range (3.3 kHz). The resistive component of the complex resistivity measures dissipation in the sample and is analogous to a dc I-V curve, while the quadrature component is induced by reversible motion of the vortices in the elastic regime below J_c . The force displacement curve can then be generated by plotting the (Lorentz) force $F_L = BJ \sin(\omega T)$ versus the displacement which is given by $V = El = \omega B l d \cos(\omega T)$ where d is the vortex displacement. Extrapolation of the slope to the maximum pinning force (BJ_c) allows the elastic limit of displacement, d_0 , to be identified by the projection of this point onto the displacement axis.

Figure 1 shows the field dependence of d_0 for $B//ab$ and $B//c$ before and after irradiation. The inset shows the angular dependence of d_0 at 0.5 T to indicate how it decreases for $B//c$ after irradiation. The behaviour for $B//ab$ is unchanged within experimental uncertainty while for $B//c$, the columnar defects result in a decrease of the elastic limit — an important result. The decrease in d_0 is clear for all fields, but most pronounced below the matching field, $B_{\Phi} = 400$ mT. The decrease in d_0 after introduction of columnar defects implies that after irradiation, vortices parallel to the c -axis are pinned in narrower pinning wells than

before. The elastic limit after irradiation below and in the vicinity of the matching field approaches a value of 3.4 nm which is very close to the radius of the columnar tracks, $R_p = 2.5-5$ nm, and the coherence length $\xi_{ab} = 3.6$ nm. The columnar defects introduced after irradiation act to increase the number of pins, and a significant change in the residual resistance ratio (in an already highly disordered and strongly pinned system) suggests a large change in the imperfection and pinning ability of the film. More importantly, the columns ensure that the active defects are aligned. Thus bending of the vortices between pins is suppressed, resulting in an effective enhancement of the stiffness of the vortices, and the elastic limit drops accordingly.

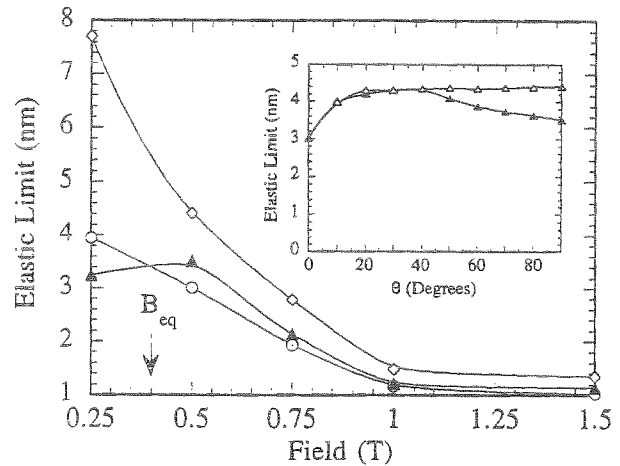


Fig. 1: The field dependence of the elastic limit at $T/T_c = 0.86$. The open dotted circles are for $B//ab$ both before and after irradiation. The open diamonds and closed triangles are $B//c$ before and after irradiation respectively. The matching field is indicated by the arrow. The inset shows the angular dependence of the elastic limit at 0.5 T (which is representative of the data for $B > 0.5$ T) before (open triangles) and after (closed triangles) irradiation.

Bose-glass behavior of the vortex system in oriented-grown $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ films with correlated disorder

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Recently, Nelson and Vinokur [1] investigated the response of a system of vortex lines to the presence of a columnar defect structure. By mapping the physics of flux lines onto the problem of localization of quantum-mechanical bosons in two dimensions, they predicted a new "Bose-glass" phase at low temperatures, with the vortex lines localized on the columnar pins. Of particular interest is the transition at T_{BG} from the Bose glass to a vortex liquid (eventually, entangled), which is identified with the experimentally observed irreversibility line. The critical behavior of this transition can be parametrized in terms of a scaling theory with two undetermined critical exponents. One, ν , describes the divergence at T_{BG} of the root-mean-squared wandering length transverse to the field direction, and another, z , the divergence of the time scale for the relaxation of a fluctuation with this size. The resistivity ρ should then vanish as $T \rightarrow T_{BG}$ from above as

$$\rho(T) \sim (T - T_{BG})^{\nu(z-2)}. \quad (1)$$

An important point is the universality of the critical exponents, i.e., their independence of the applied magnetic field. The critical-exponent relations for a Bose-glass transition are very similar to those predicted by the vortex-glass theory [2], but the Bose-glass phase and the vortex-glass phase have different underlying microscopic physics. In contrast to point disorder, which promotes vortex wandering and entanglement, the correlated disorder inhibits wandering and promotes localization.

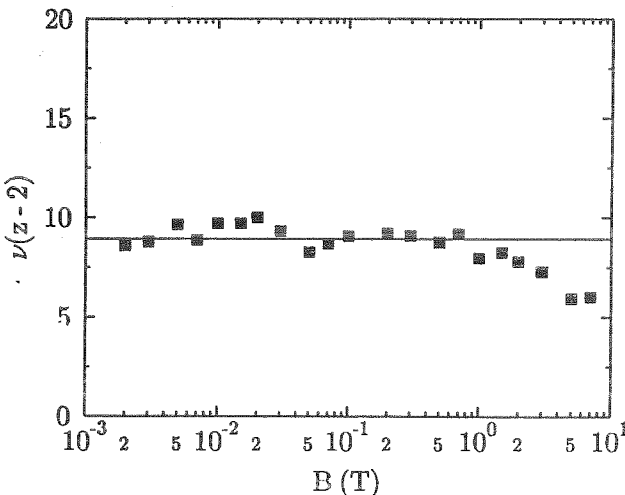


Fig. 1: Magnetic field variation of the exponent $\nu(z-2)$ (see text). The line represents the mean value for $B \leq 2$ T.

In the present work, we studied the temperature variation of the resistivity in the case of Bi-2:2:1:2 films with columnar defects along the c axis, for B parallel to the defects, induced by irradiation with 2.7 GeV ^{238}U ions. The temperature variation of the resistivity, measured with the magnetic field B applied parallel to the c axis, fits the expression (1) at low levels, with a field independent exponent up to $B \approx 2$ T (see Fig. 1).

Further, we analyzed the $T_{BG}(B)$ dependence resulting from the fit of the resistive transitions. This is illustrated in Fig. 2. At very low fields, the $T_{BG}(B)$ variation is clearly different from that proposed for the transition to a vortex glass dominated by point disorder. Instead, the magnetic field dependence of the Bose-glass temperature T_{BG} is in good agreement with the predictions of the theory of boson localization in the presence of correlated disorder. At very low fields, $1/T_{BG} - 1/T_{c0} \sim B^{1/4}$. For applied field values larger than the dose equivalent field $B_{\text{eq}} = 1$ T, the Bose-glass transition temperature approaches the melting temperature, $1/T_{BG} - 1/T_{c0} \sim B^{1/2}$. The applicability of this theory in the case of intrinsically very anisotropic superconductors, as $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$, can be understood through a reduction of the anisotropy in the presence of correlated disorder, which promotes vortex localization.

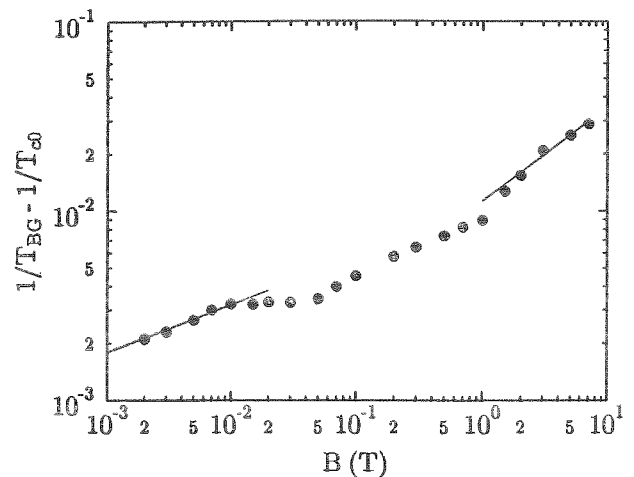


Fig. 2: Magnetic field dependence of the Bose-glass transition temperature. The dashed line represents the fit of the low field data ($B \leq 10$ mT). The continuous line represents the fit of the high field data ($B > 2$ T).

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Suppression of the Hall Sign Anomaly by Heavy Ion Irradiation and Scaling Behavior of the Mixed-State Hall Resistivity in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ Films

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HALL effect measurements in the mixed state of high- T_c and low- T_c type II superconductors frequently show an anomalous sign reversal which can not be understood within existing theories of vortex motion. For \vec{c} -axis oriented high quality Bi-2212 thin films this anomaly appears for fields $\vec{B} \parallel \vec{c}$ below 5 T near T_c where the HALL coefficient becomes negative and seems to diverge with diminishing field. Several explanations of this phenomenon were proposed, based on two band calculations, thermoelectric effects and modifications of the damping forces acting on vortex lines. The explanation due to vortex motion relies on a component of the vortex drift velocity antiparallel to the direction of the transport current. According to the Josephson relation $\vec{E} = -\vec{v}_L \times \vec{B}$ such a vortex back flow leads to a negative contribution to the HALL resistivity, whereas the vortex motion normal to the transport current results in a longitudinal resistivity. In order to check this possibility as the origin of the HALL sign reversal we investigated the behavior of the anomaly in the presence of columnar defects, which were created by irradiation with ^{238}U ions with an energy of 2713 MeV. Heavy ion induced tracks are known to act as very strong pinning centers and the vortex dynamic will be drastically changed. A hindered vortex back flow should result in a reduction of the negative HALL effect. Figure 1 shows the in situ measurements of the HALL coefficient in dependence of temperature taken immediately after each irradiation for different ion doses. All data points of figure 1 were obtained with one sample. Therefore, uncertainties are exclu-

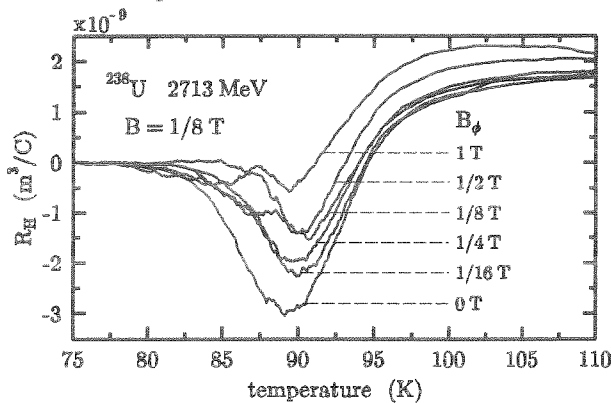


Figure 1: Behavior of the HALL anomaly in a magnetic field of 1/8 T in the presence of columnar defects for several equivalent fields B_ϕ

ded which could come from the comparison of results obtained with different samples. As can be seen clearly the anomaly decreases with increasing defect concentration and is nearly suppressed for a track density corresponding to an equivalent field of 1 T. Additional off-line measurements were performed at higher magnetic fields after warming up the irradiated sample. The smaller anomalies at fields above 3 T were nearly unaffected by the heavy ion irradiation ($B_\phi = 1$ T). This is in qualitative agreement with investigations on $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_{10}$ films¹ and gives a hint that the anomalous HALL behavior may be related to vortex motion antiparallel to the direction of the transport current.

According to Vinokur et al.² there exist a scaling between the HALL and the longitudinal resistivity $\rho_{xy} \propto \rho_{xx}^\beta$ with $\beta = 2$. In this theory columnar defects will have no influence on the exponent and only a drop of both the longitudinal and the HALL resistivity is expected in the presence of large magnetic fields. This behavior is shown in figure 2. No signi-

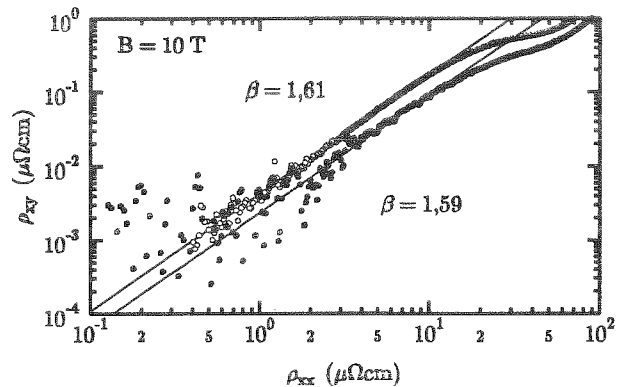


Figure 2: Scaling behavior between the HALL and longitudinal resistivity before (o) and after (•) irradiation with a dose of $4.4 \cdot 10^{10} \text{ cm}^{-2}$.

ficant difference between the values of β before and after irradiation can be seen. Obviously the scaling law does not depend on the type of defects. The deviation of β from the expected value 2 may be attributed to a temperature dependence of the proportionality given above.

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Dependence of the transport efficiency of a He(KCl) gasjet on the electrostatical conditions ^B

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Previous experiments at the tandem accelerator of the MPI in Heidelberg indicated a dependence of the transport behaviour of the He(KCl)-gasjet on the acquired charge distribution in the the recoil chamber [1]. A new set of experiments was performed to verify the obtained results and to increase the transport efficiency. The reaction used for this investigation at the MPI was ¹⁸¹Ta(¹²C,xn)¹⁸⁹⁻¹⁹²Au with a beam energy of 77 MeV. The beam intensity was kept at 1 μ A (AC) for these studies. Also, the experimental setup was the same as in the preceding experiments. The beam dump in the sample cup inside the recoil chamber had been changed from copper to carbon. This was done to reduce the amount of particles produced by sputtering out of the beam dump. The sputtered particles of the copper beam dump could be seen in earlier experiments at GSI [2].

First, the distance of the sample cup from the target was adjusted. The maximum of the transported yield was found at a distance of 5 mm to 10 mm.

The repetition of the investigations concerning the flow and pressure dependence of the transport yield showed the same behaviour as in the previous experiments, however, the transport yield was higher than before. This was attributed to an increase of the initial aerosol particle concentration without the beam. The particle concentration in the previous experiment was $1.9 \cdot 10^6$ cm⁻³ with a mean geometric diameter D_g of 96 nm and a spread factor of 1.6. During these experiments, the aerosol particle concentration was $3.7 \cdot 10^6$ cm⁻³ with a D_g of 61 nm and a spread factor of 1.53. This could be achieved with a dry KCl salt and an shorter residence time in the tube filter. Now, the transport yield with a 25 m long polyethylene(PE) capillary (inner diameter of 2 mm) was about 60% at a helium flow of 2.1 l min⁻¹ and absolute pressure in the target chamber of 1.35 bar. Another point of investigation was the temperature in the recoil chamber, which was measured with a thermocouple. The temperature has an influence on the mobility of the reaction products and the aerosol particles in a way that a reduced temperature reduces their mobility. This could help to avoid losses to the walls of the recoil chamber. However, a decrease of the temperature from normally 31°C with the ion beam to 11°C did not show an influence on the yield and the size distribution of the aerosol particles.

The electrostatical conditions were changed by applying a positive or negative voltage to the sample cup. Lower voltages (± 38 V, ± 80 V, ± 200 V) did not affect the yield and the size distribution. The yield dropped to 50% at +800V and to 41% at -800V. The size distribution at -800V changed also.

The particle concentration fell from $2.3 \cdot 10^6$ cm⁻³ to $1.1 \cdot 10^6$ and D_g decreased from 109 nm to 87 nm.

The spread factor changed from 1.77 to 1.73. This can be explained by the charging of the aerosol particles due to the ionisation of the helium in the ion beam. In case of a high negative voltage, the positively charged particles are attracted to the walls of the sample cup and are lost. The determination of the fraction of positively and negatively charged particles was done with the DMPS/C-system. To this end, the "neutraliser" of the system, which brings the particles to a known charge distribution, was removed. The fraction of positively charged particles for the investigated size distribution (25 m PE-capillary, inner diameter 2mm, He-flow 2.1 l min⁻¹ in Table 1) is 11.1% and approximately the same amount is negatively charged by using the neutralizer. Without the neutralizer, there are 11.9% negatively charged and 15.5% positively charged. There is a surplus of positively charged particles even after passing through the capillary. The presumably large charge state disequilibrium in the sample cup may be caused by the Helium as a carrier gas, which has a high ionisation potential and tends to recombine with electrons, which are separated in the ion beam plasma. A large excess of positively charged aerosol particles leads to their loss to the walls in the beginning of the capillary, where gradually an increasing electrical potential builds up that might act as an electrostatical filter.

The results obtained by changing the capillary are shown in Table 1. It is obvious that the transport yield and the size distribution depend on the capillary material and the inner diameter. The stainless steel capillary shows the best yield and the smallest influence on the size distribution. This indicates that the non-equilibrium charge distribution acquired in the recoil chamber together with the use of a non conducting capillary are the major cause for the losses of the activity. Therefore, the actions to be taken for a high and stable transport yield are to bring the charge distribution acquired in the recoil chamber to an equilibrium with a neutralizer or the use of a conducting capillary. There, the deposited charged particles do not interact with the charged aerosol particles and the losses in the capillary are only caused by diffusion onto the capillary walls.

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Table 1. Influence of different capillaries on the transport yield of the KCl jet and size distribution of the KCl particles

Capillary Material	Diameter mm	He-Flow l min ⁻¹	D_g nm	Concentration cm ⁻³	Spread Factor σ	Yield %
PE	1.5	1.1	66	$0.63 \cdot 10^6$	1.72	28
PE	2.0	1.1	75	$0.78 \cdot 10^6$	1.64	43
PTFE	2.0	2.1	120	$0.98 \cdot 10^6$	1.78	41
PE	2.0	2.1	109	$2.30 \cdot 10^6$	1.77	57
Steel	2.0	2.1	76	$3.30 \cdot 10^6$	1.73	93

Extraction of Zr,Hf,Nb,Ta,Pa, and Np into Aliquat 336 from pure HCl solutions

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To characterize the chloride complexing of element 105 relative to that of its homologs we have previously studied the extraction of M^{4+} and M^{5+} ions into tri-iso-octyl amine (TiOA) from fluoride-free HCl solutions [1]. We found that the TiOA/HCl system should be suitable for the purpose envisaged. However, a very slow extraction and back extraction kinetics prevented its application in chromatographic separations using columns of ARCA dimension (1.6x8mm). Therefore, we have performed a systematic study of partition and column experiments with other aliphatic amines such as tri-n-octyl amine (TOA), tri-caprylyl amine (Alamine 336), and methyl-tri-caprylyl ammonium chloride (Aliquat 336) and also with anion exchangers based on a styrene divinylbenzene polymer support like Dowex 1x8, Dowex 1x4, Dowex 4x4, and Aminex A-27 in fluoride-free HCl solutions in order to find a system in which the kinetics is acceptable.

The extraction behaviour of the group-5 and pseudo group-5 elements in the investigated systems was nearly identical to that of the TiOA/HCl system [1]. For example, Fig. 1 shows the extracted activity of Pa, Np⁵⁺, Nb, Ta, Zr and Hf into Aliquat 336 from HCl solutions. In all cases, no extraction is observed at HCl molarities lower than 1 M HCl. With increasing HCl molarities, the elements start forming neutral and anionic chloro and oxo-chloro complexes such as $[MOCl_4]^-$ and $[MCl_6]^-$. The sequence of extraction from 1 M HCl up to 12 M HCl is Pa>Np⁵⁺, Nb>Ta>Zr,Hf which is the complete inversion of the known sequence Ta>Nb>Pa in the TiOA/HCl system containing 0.03 M HF [2]. In agreement with previous studies [1], there is observed a largely identical behaviour of Np⁵⁺ to that of Nb. All tracers were carrier-free including the Ta-activity. This carrier-free Ta-activity was extracted from HCl concentrations >6 M into the organic phase contrary to the non carrier-free ¹⁸²Ta activity [1], which forms non extractable polymeric ions in pure HCl solutions [3]. This was also in agreement with the previously observed extraction from 10 M HCl of Ta freshly produced at an accelerator [2].

Carrier-free activity of ¹⁷⁵⁻¹⁷⁷Ta and ¹⁷⁵Hf has been obtained by an irradiation of a Lu₂O₃-target with 40 MeV alphas at the compact cyclotron at Karlsruhe. After irradiation, the target was dissolved in hot 12 M HCl to prevent hydrolysis. The Ta tracer showed a greater tendency to hydrolyze than the other group-5 and pseudo group-5 elements. Only when stored in 12 M HCl, a reproducible behaviour of the Ta tracer was observed. When stored in lower acidities such as 9 M and 6 M HCl, the Ta tracer formed hydrolysed species within 60 and 20 hours, respectively. These hydrolysed species could not be extracted into the organic phase irrespective of the HCl concentration.

All investigated systems showed a nearly similar behaviour in the partition experiments but a different behaviour in the column experiments. With other tertiary amines such as TOA and Alamine 336, a similarly slow extraction and back extraction kinetics as observed with TiOA/HCl [1] was found. Also with anion exchange resins, unsatisfactory results were obtained. Only with the quaternary amine Aliquat 336 on an inert support (Voltaief, 32-63 μm), we found acceptable chromatographic separations using columns of ARCA dimen-

sion. In Fig. 2, Eu, Nb, Ta, Pa, Zr, and Hf were fed onto the column from 10 M HCl. Zr, Hf, and Ta were eluted in 6 M HCl, Nb in 4 M HCl, and Pa in 0.5 M HCl. Thus, the system is highly suited for a common extraction of the elements and it also allows one to differentiate between Ta, Nb, and Pa at lower HCl concentrations.

We conclude that the Aliquat 336/HCl system should make possible an investigation of the chloride complexing of element 105 relative to that of its homologs.

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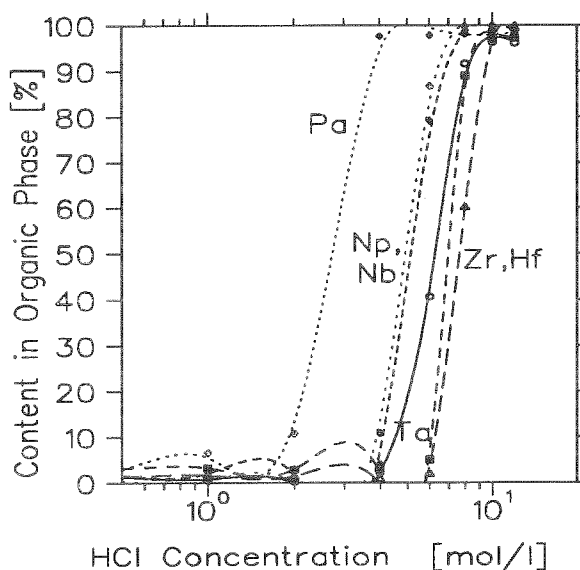


Fig.1: Extracted activity of Pa, Nb, Np, Ta, Zr and Hf into Aliquat 336 vs. HCl molarity. All tracers were carrier-free.

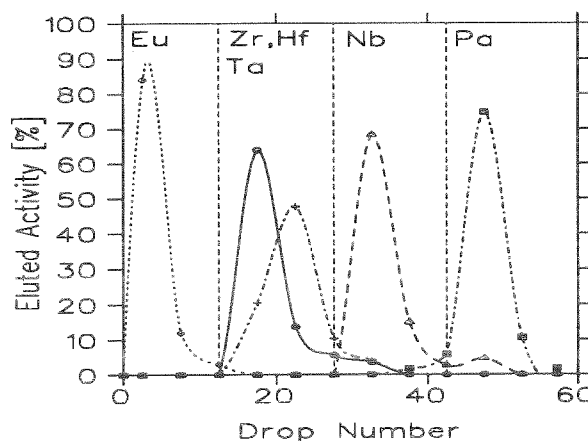


Fig.2: Separation of Eu, Pa, Nb, Ta, Zr, and Hf on a 1.6x8 mm Aliquat 336/Voltaief column using fluoride-free HCl solutions. Eluents: Eu in 10 M HCl, Zr, Hf, and Ta in 6 M HCl, Nb in 4 M HCl, and Pa in 0.5 M HCl.

Preparing Reduction Experiments for 105⁵⁺ and 106⁶⁺

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Based on their placements in the periodic table in group-5 and 6, the most stable oxidation states of element 105 and 106 are expected to be the pentavalent and hexavalent state, respectively. For element 105 this is experimentally verified [1]. Relativistic atomic calculations have shown that the relativistic stabilization of the s and p_{1/2} orbitals in the transactinides may influence the stability of oxidation states. This makes a search for lower oxidation states under reducing conditions an interesting goal of experimental investigations.

Previously, we have searched for a lower oxidation state in element 103, Lr [2]. There was no experimental evidence for the reduction of Lr³⁺, although in the same experiments Md³⁺ was reduced to Md²⁺. The resulting limit for the reduction potential of the Lr³⁺/Lr²⁺ couple was E⁰ < -0.44 V. Reduction was attempted in 0.03 M HCl/0.01 M Cr²⁺ solution.

In order to prepare reduction experiments with 105⁵⁺ and 106⁶⁺ we have studied the anion exchange of Nb, Np, and Mo into the anion exchanger Dowex 1x8, and elutions of neutral or anionic Mo fluoride complexes from a cation exchanger, Dowex 50Wx8. After absorption onto the anion exchange column from 10 M HCl as anionic chloride complexes, pentavalent Nb and Np can be stripped from the anion exchange column in dilute HCl. Trivalent ions would not be sufficiently complexed in 10 M HCl and would run through the column. Thus, the following procedure is suggested and demonstrated in Fig. 1: After washed with 10 M HCl/0.01 M Cr²⁺ whereby Nb⁵⁺ is quantitatively reduced to Nb³⁺ and is eluted from the column. The reduction potential of Cr²⁺ is insufficient to reduce Zr⁴⁺. Thus, the latter ions remain on the column and are subsequently stripped from the column in 1 M HCl. Identical results are obtained with Np⁵⁺/Np³⁺ and Zr⁴⁺.

For the group-6 elements Mo and W and element 106, their common elution from a cation exchange column as fluoride complexes, MO₂F₂, is suggested in 0.03 M HCl/10⁻³ M HF [3]. Under these conditions, Zr sticks to the column. If 0.01 M Cr²⁺ is added to the 0.03 M HCl/10⁻³ M HF solution, see Fig. 2, hexavalent Mo and W are reduced to the trivalent cations and stick to the column. They can subsequently be eluted, together with Zr⁴⁺, in 4M HCl/10⁻² M HF.

An alternative reduction experiment with the group-6 element works as follows: The activities stick to the anion exchange column in 7 M HCl/10⁻¹ M HF [4]. Reduction to trivalent ions and their elution from the column is achieved upon adding 0.01 M Cr²⁺ to the latter solution. Non-reduced hexavalent metal ions would remain on the column; these could be subsequently eluted in 0.1 M HCl/0.03 M HF.

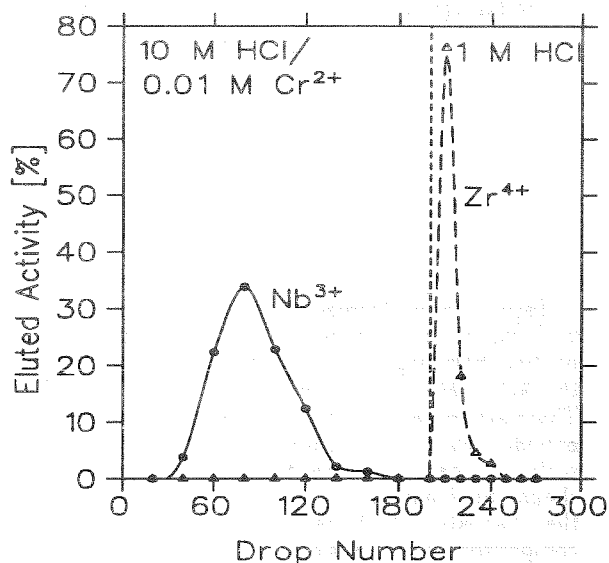


Fig.1: Elution of the reduced species Nb³⁺ in 10 M HCl/0.01 M Cr²⁺ from an anion exchange column (1.7x25 mm) followed by the stripping of Zr⁴⁺ in 1 M HCl.

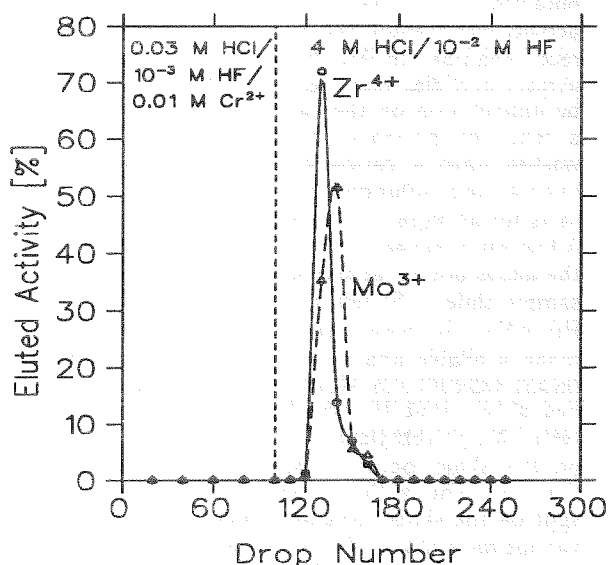


Fig.2: Mo⁶⁺ in the form MoO₂F₂ would run through the cation exchange column (1.7x25 mm) in 0.03 M HCl/10⁻³ M HF. Addition of 0.01 M Cr²⁺ to that solution reduces Mo to the trivalent oxidation state which sticks to the column. Mo³⁺ and Zr⁴⁺ are stripped in 4 M HCl/10⁻² M HF.

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Tests of the chemical separation of the group 4 and 6 elements based on fluoride complexation^B

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Tests were performed at the Paul-Scherrer-Institut in Villigen to investigate the chemical behaviour of the homologs of elements 104 and 106 with the Automated Rapid Chemistry Apparatus (ARCA). These experiments with the elements Hf and W should provide data on their aqueous chemistry in the tracer scale. At the same time, the experimental conditions should be identical to the planned investigation of the chemistry of elements 104 and 106, so that a comparison of the results is possible. The recently found new isotopes of the element 106, ²⁶⁵106 and ²⁶⁶106 with their relatively long half-lives open up the possibility to carry out such experiments with the chemical device ARCA.

Hf was produced by the bombardment of a natural Samarium target with a ²⁰Ne beam and tungsten was obtained in the ²⁰Ne + ¹⁵²Gd reaction. The produced activity was transported by a He(KCl) gasjet from the recoil chamber to ARCA. There, the activity bearing aerosol particles were separated from the carrier gas by impactation on the sample slider of ARCA. After a collection period of one minute, the activity was washed onto a cation exchanger Aminex A-6 with mineral acid solutions containing HF [1]. The flow rates for all experiments were kept a 1 ml/min.

A first set of experiments was carried out to investigate the losses due to adsorption of Hf, Lu and W on the sample slider. Sliders of different materials (Kel-F, PEEKEK, Stainless Steel, Titanium, PMMA) were made available and tested. This was done because recent experiments at Lawrence Berkeley Laboratory had shown that Hf adsorbs on teflon and they also tested Ni, polyethylene, and mylar [2]. The adsorption on the slider occurred also in our experiments at the PSI. The activity bearing KCl aerosol particle spot on the sliders was attempted to be dissolved by various mineral acid/HF mixtures, see Table 1, and the dissolved activity was eluted through empty columns in ARCA. It turned out that the best dissolution of Hf and W was achieved from a titanium slider. Other materials showed larger losses of activity due to adsorption on the slider in the sequence Kel-F < PEEKEK < PMMA < stainless steel. Overall yields for the collection of the activity on a titanium slider and its dissolution and elution through ARCA are given in Table 1. Best results under conditions suitable for experiments with elements 104 and 106 are achieved with 0.1 M HNO₃/ 1·10⁻³ M HF.

In a second part, the chemistry of Hf was investigated on a cation exchange column (Aminex A6) with fluoride ion as the complexing agent. Various concentrations of HF in 0.05 M HCl, 0.1 M HCl, 0.5 M HCl and 0.1 M HNO₃ were tested. The HF concentration varied between 1·10⁻⁴ M and 1·10⁻²

M. The elution time for the first fraction which normally contains tungsten [1] was 6 seconds. In the second fraction with an elution time of 10 seconds, Hf was stripped from the column with a solution of 5·10⁻³ M HF in 0.1 M HCl. Apparently, as shown in Table 2, these conditions were insufficient for a complete stripping of Hf from the column (Fraction 2.). For HF concentrations below 2.8·10⁻³ M, the W fractions (Fraction 1.) were free of Hf. The same limiting HF concentration holds for 0.05 M, 0.5 M HCl and the 0.1 M HNO₃. Both the W and the Hf-fraction were always free of Lu. This shows that a separation of W from the group 4 and group 3 elements is possible with the ARCA technique and that fluoride complexation allows to separate and identify element 106 in our planned experiments.

Table 1. Influence of different mineral acid solutions on the dissolution of Hf and Lu from titanium

Acid solution	Hf [%]	Lu [%]
0.1M HNO ₃ / 1·10 ⁻² M HF	74	68
0.1M HNO ₃ / 1·10 ⁻³ M HF	74	71
0.1M HNO ₃ / 1·10 ⁻⁴ M HF	53	53
0.05M HCl / 1·10 ⁻³ M HF	61	60
0.1M HCl / 1·10 ⁻³ M HF	54	51

Table 2. Separation of Hf with HF in 0.1 M HCl on a cation exchange column

Fraction	Acid solution	Hf [%]
1.	0.1M HCl / 1·10 ⁻⁴ M HF	-
2.	0.1M HCl / 5·10 ⁻³ M HF	32.1
1.	0.1M HCl / 5·10 ⁻⁴ M HF	-
2.	0.1M HCl / 5·10 ⁻³ M HF	29.7
1.	0.1M HCl / 1·10 ⁻³ M HF	-
2.	0.1M HCl / 5·10 ⁻³ M HF	35.7
1.	0.1M HCl / 2.8·10 ⁻³ M HF	28.6
2.	0.1M HCl / 5·10 ⁻³ M HF	27.1
1.	0.1M HCl / 5·10 ⁻³ M HF	29.7
2.	0.1M HCl / 5·10 ⁻³ M HF	9.6

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Spontaneous Deposition of Polonium on Palladium

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In the past, the identification of heavy actinides and trans-actinides produced in hot fusion reactions with actinide targets has often been hampered by the simultaneous production of bismuth and polonium isotopes (notable $^{212}\text{Bi}/^{212}\text{Po}$ and $^{211\text{m}}\text{Po}$, $E_{\alpha}=8.883$ MeV) presumably produced from a lead impurity in the actinide target. In our planned experiments on the chemical behaviour of element 106, the presence of $^{211\text{m}}\text{Po}$ would be particularly disturbing as it would mask the α -activities of the isotopes $^{265}\text{106}$ ($E_{\alpha}=8.81, 8.85$ MeV) and $^{266}\text{106}$ ($E_{\alpha}=8.65$ MeV) produced in the ^{22}Ne on ^{248}Cm reaction [1].

Therefore, we have performed a systematic study of Po deposition on Pd-foils as a function of temperature and time of deposition from various mixtures of mineral acid solutions. As it was intended to include the Po deposition on Pd in all separations with ARCA [2], a fixed volume of the solutions and a fixed surface of the Pd-foils were chosen, and the volume to surface ratio was similar to that of typical ARCA-fractions and the inner surface of the tubing from the chromatographic column to the sample collector (supposing this tubing were made of Pd). Activity of ^{210}Po was obtained by chemical separation from its long-lived mother, ^{210}Pb , using a 3x100 mm cation exchange column (Dowex 50x8). Feeding of the $^{210}\text{Po}/^{210}\text{Pb}$ activity onto the column occurred in 0.2 M HCl, and Po was eluted in this solution. Pb was eluted subsequently in 1 M HCl.

When using 1 ml of 0.05 M HCl/ 10^{-3} M HF and a 10x10 mm² Pd-foil of 6 μm thickness, only unsatisfactory results were obtained. Even after 10 min time of deposition at a temperature of 80° C incomplete separation of Po was observed. Therefore, the Pd-foil was saturated with hydrogen [3] by electrolysis: A vessel containing two Pd-foil electrodes immersed in dilute sulfuric acid was operated at a potential of 5 V for a time of 30 min. Fig.1 shows the dependence of deposition of Po on such a 10x10 mm² Pd/H₂ foil as a function of time of deposition at different temperatures. Evidently, quantitative deposition of Po is achieved only for high temperatures and times > 30 s. This is not acceptable for the planned experiments on element 106.

In order to increase significantly the surface of the Pd, we used finely powdered so-called "Pd-black" which was also saturated with hydrogen by electrolysis. The Pd-black/H₂ was filled in Teflon tubings of different diameters and heights. The Po activity was pumped through these tubings with a flow rate kept at 1 ml/min. The best results with a minimized quantity of Pd-black/H₂ were obtained with a 0.5x5 mm Pd-black/H₂ column which retains the Po activity quantitatively.

In further experiments, different aqueous solutions of mineral acids were used. No significant differences for mixtures of 0.01 M to 0.5 M HCl and HNO₃ containing 10^{-4} to 10^{-2} M HF were observed. These mixtures of mineral acids are candidates to test the fluoride complexing of element 106 relative to that of its homologs Mo and W. It was also checked that the retention of Po in the Pd-black/H₂ column was effective over long times. The retention did not decrease significantly in a test pumping mineralic acid solution through the column for

5 hours at 1 ml/min where the Po yield was checked every hour.

Finally, the influence of the Pd-black/H₂ column on the lighter homologs of element 106 was studied. Tracers of Zr⁴⁺, Nb⁵⁺, Np⁵⁺, Mo⁶⁺, and other fission products of uranium were pumped through the Pd-black/H₂ column to check the deposition on Pd with various flow rates. Only iodine and tellurium were found to be deposited on Pd-black/H₂. In order to check whether the Pd-black/H₂ reduced Nb⁵⁺, Np⁵⁺, and Mo⁶⁺ to lower oxidation states we tested the chromatographic behaviour [4] of these tracers after passing them through the Pd-black/H₂ column. The chromatographic behaviour was identical to that in the pentavalent and hexavalent oxidation state respectively, so that no reduction to lower oxidation states was observed.

Thus, we conclude, that the use of Pd-black/H₂ is highly suitable for the retention of interfering Po activities in the forthcoming experiments on element 106. We are now integrating a Pd-black/H₂ column into the tubing that the effluent from the cation exchange column in ARCA is passing. We anticipate that this Pd-black/H₂ column is effective for many hours of successive element 106 separations.

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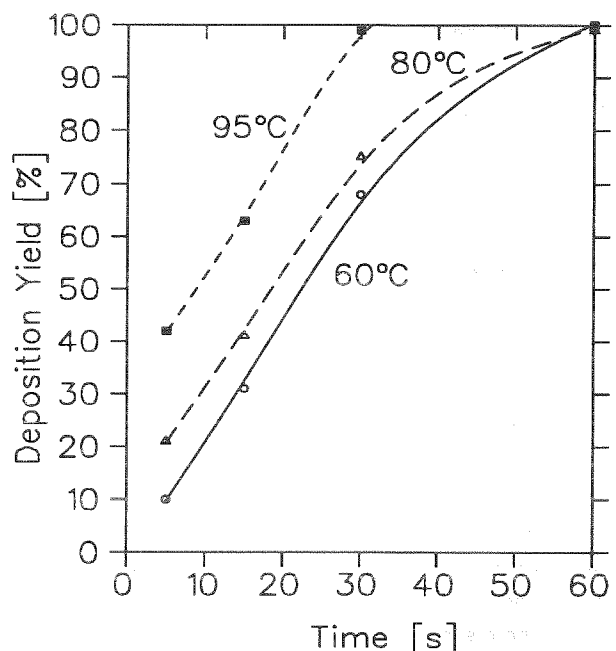


Fig.1: Deposition yield of ^{210}Po onto a 10x10 mm Pd-foil saturated with hydrogen from 1 ml 0.05 M HCl/ 10^{-3} M HF at different temperatures as a function of time of deposition

Thermochemical Stability of Group 6 Oxychlorides $MOCl_4$, where $M = Mo, W$, and Element 106, Sg .

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Due to special conditions of the gas-phase chromatography experiments (high temperatures, etc.) the right choice of the species under investigation is of great importance. Since many halides and oxyhalides of Mo and W are thermally unstable, investigations of the stability of the analogous compounds of Sg is therefore one of the main tasks of the present theoretical investigations accompanying the experimental work.

Gaseous oxide tetrachlorides of group 6 elements are more stable than the corresponding hexachlorides, which were studied in our previous work¹. Nevertheless their stability towards thermal decomposition is different: $MoOCl_4$ is thermally unstable and decomposes to $MoOCl_3$ at 25°C, while $WOCl_4$ proves to be rather stable. A question, whether $SgOCl_4$ is stable or not, is therefore very important.

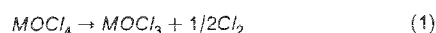
With this aim in view, calculations of the electronic structure of $MOCl_4$ ($M = Mo, W$, and Sg) have been performed using the Dirac-Slater Discrete-Variational method².

Some electronic structure data for the $MOCl_4$ molecules, where $M = Mo, W$, and Sg , as a result of the calculations, are presented in Table 1. The data show trends similar to those for the MC_l_6 species¹. The OP(M=O) and OP(M-Cl) data are nevertheless indicative of the fact that the increase in covalency in $SgOCl_4$ compared to $WOCl_4$ comes mainly from the metal-oxygen interaction.

Table 1. Effective charges (Q), energy gaps (ΔE), overlap populations (OP), and dipole moments (μ) for $MOCl_4$ ($M = Mo, W$, and Sg)

Parameter	$MoOCl_4$	$WOCl_4$	$SgOCl_4$
Q_M	1.00	1.04	0.90
ΔE , eV	1.01	1.90	2.39
OP(M=O)	0.52	0.70	0.77
OP(M-4Cl)	1.30	1.69	1.71
OP(tot)	1.86	2.35	2.40
μ , D	0.14	0.49	1.03

For the reaction of the thermal decomposition



the partial OP data from Table 1 were used to estimate the energies of the ionic (E_i) and covalent (E_c) contributions to each M=O and M-Cl bond. The obtained E_i and E_c values along with E_{dis} being a sum of them are shown in Table 2. From Table 2 one can see that the strength of the Sg=O bond in $SgOCl_4$ is of the order of the W=O bond strength, while the Sg-Cl bonding is weaker and of the order of the Mo-Cl one. Thus, one can expect seaborgium oxide tetrachloride to decompose via reaction (1) similar to that of molybdenum oxide tetrachloride.

Table 2. Energies of the ionic (E_i) and covalent (E_c) contributions (in eV) to a single metal-ligand bond energy in $MOCl_4$ ($M = Mo, W$, and Sg)

Compound	M = O			M - Cl		
	E_i	E_c	E_{dis}^a	E_i	E_c	E_{dis}^a
$MoOCl_4$	2.59	3.90	6.49	1.07	2.44	3.51
$WOCl_4$	2.83	4.52	7.35	1.17	2.73	3.90
$SgOCl_4$	2.29	4.86	7.15	0.83	2.69	3.52

^a $E_{dis} = \Delta H_{dis}$ (thermochemical)

The dissociation energy (into atoms) of $SgOCl_4$ was calculated as 21.24 eV (or 489.79 kcal/mol), which can be compared with ΔH_{dis} for molybdenum and tungsten oxide tetrachlorides of 473.62 kcal/mol (20.54 eV) and 529.42 kcal/mol (22.96 eV), respectively.

The enthalpy of formation of the gaseous $SgOCl_4$ was calculated using ΔH_{dis} and $\Delta H_{sub}(Sg)$ of 200 ± 6 kcal/mol.³ The obtained value of the ΔH_{form} of $SgOCl_4$ of -114 ± 6 kcal/mol is less negative than those values for $MoOCl_4$ and $WOCl_4$ (Fig. 1).

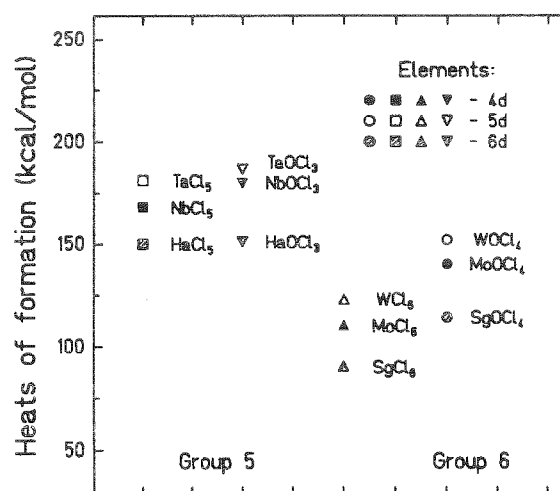


Fig 1. Formation enthalpies of group 5 and 6 gaseous halides and oxyhalides.

The probable decomposition of $SgOCl_4$ into $SgOCl_3$ will result in the shift in the temperature of adsorption in the gas-chromatography column to the area of much higher values, since the volatility decreases with decreasing valency of the metal atom.

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A New Semiempirical Method to Estimate Sublimation Enthalpies of Metals

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The main purpose of the work was to develop a model for calculating sublimation enthalpies (ΔH_s) of metals of s, p, d and f-elements with the final aim to calculate ΔH_s of the transactinides ($Z = 104-112$). The knowledge of these values is very important not only for estimating the volatility of elements, but also for calculating such properties of their compounds as enthalpies of formation, sublimation, etc. Existing estimates of ΔH_s of elements 104 and 105 are very rare and have a large discrepancy in values.

On the basis of previous theories¹⁻⁴ of the electronic structure of metals, a new semiempirical model has been proposed, taking into account electronic configurations of elements in the free atomic state and in the metal, and the promotion energy between these two states. Finally, the calculations of ΔH_s have been done using the following proposed formula

$$\Delta H_s = E_c = C_{nd} \frac{Z}{\gamma} \quad (1)$$

where C_{nd} is an empirically defined coefficient, Z - atomic number, and γ has the following expression

$$\gamma = \frac{\sum_L (2L+1)_M}{\sum_L (2L+1)_M + (2L+1)_A} \quad (2)$$

Here $(2L+1)$ is the degree of degeneracy of each state with quantum number L for the electronic configuration in the metal (M) and free atom (A). Each change in the electronic configuration of the free atom or participation of p-orbitals in the metal-state formation changes the character of the dependence of ΔH_s (or cohesive energy, E_c) on Z .

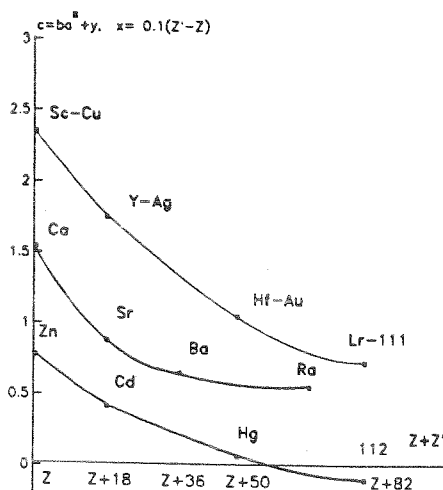


Fig. 1. Dependence C_{nd} on Z .

It was found that C_{nd} decreases within the groups of elements according to the following rule

$$C_{nd} = ba^x + y \quad (3)$$

where $x = k\Delta Z$ and ΔZ is the difference in the number of electrons between an element of a nd-series and an element of the 3d-series (Fig. 1); $k=0.1$ is an empirical parameter, and a , b and y - parameters determined from the known experimental ΔH_s for each group of the Periodic Table. Thus, the obtained values are $C_{3d} = 2.35$, $C_{4d} = 1.75$, $C_{5d} = 1.05$, and $C_{6d} = 0.728$.

The calculated values of ΔH_s for metals of the 2-8 groups are shown in Fig. 2. A good agreement between the calculated and all known experimental values gives a proof for the reliability of the proposed formula. The obtained ΔH_s for the transactinides are listed in Table 1.

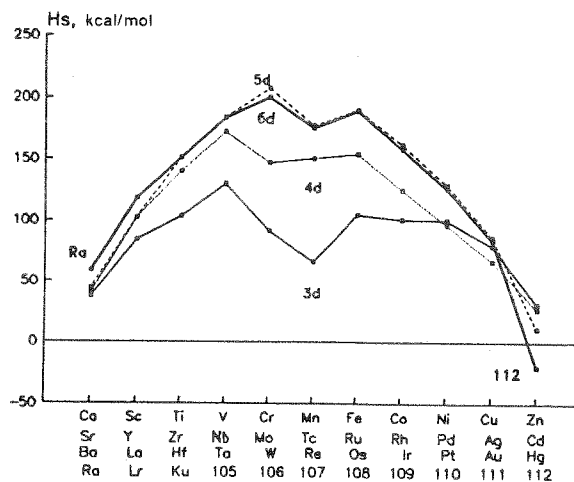


Fig. 2. Calculated sublimation enthalpies of the metals.

Table 1. Sublimation enthalpies of the transactinide metals (in kcal/mol).

104	105	106	107	108	109	110	111
151.4±9	183.5±7	193-206	175	189	158	125.9	84

The two values for element 106 are connected with two different supposed electronic configurations in the metal - d^5s and $d^5p + d^4sp$, respectively).

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