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CHARACTERIZATION
OF SOME METALLIC STATE PROPERTIES
OF MENDELEVIUM
AND OTHER ACTINOIDS
BY THERMOCHROMATOGRAPHY

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I. INTRODUCTION

The experimental data accumulated in the last decade have shown remarkable differences in the chemical properties of the heavy lanthanoids and actinoids. Thus, in the actinoid series the stability of the 2+ oxidation state steadily grows from berkelium to element 102, whereas for the homologous lanthanoids this regularity has not been observed [1]. An explanation for this was given already by Brewer [2], as he predicted an increase of the localization of the 5f energy levels with increasing atomic number in the second half of the actinoid series to a greater extent than in the case of the 4f energy levels of the heavy lanthanoids.

Differences in the electronic properties manifest themselves in metallic properties, too. Thus, the lanthanoids dysprosium to thulium are trivalent metals, whereas californium is a border-line case between a divalent and a trivalent metal [3-5], and einsteinium is divalent [6]. Fermium and mendelevium should be also divalent in the metallic state, as predicted by several authors [2,7-11].

The experimental characterization of californium and einsteinium was accomplished by microtechniques [3-6]. In order to characterize elements beyond einsteinium, which now and in the foreseeable future are available only in trace amounts, one has to apply indirect methods and to deduce the metallic state properties from some correlating experimental data.

In an earlier study [12] the evaporation rates of fermium and mendelevium from molten lanthanum, which were found to be higher than those of europium, ytterbium and californium and much higher than those of americium and cerium, were taken as evidence for the divalency of metallic fermium and mendelevium.

In the present work the thermochromatographic study of the adsorption on polycrystalline metals, titanium and molybdenum, was used as an alternative experimental approach to the characterization of the metallic state properties of the heavy actinoids.

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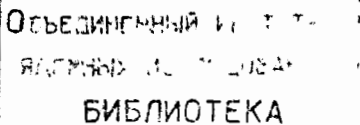
II. GENERAL CONSIDERATIONS

Generally speaking, there should be only a loose correlation between the adsorption behaviour and the bulk properties of the adsorbate. However, in the case of metallic-bonding like adsorbate-adsorbent interaction the energy of adsorption depends substantially on the metallic valency of the adsorbate[13] in analogy with the cohesive energies of metals[14]. In the case of 4f elements, lanthanoids, both the cohesive energy and the energy of adsorption vary in a peculiar way in the series. This now seems to be well understood as to be due to the fact that most of the elements are divalent in the atomic state but trivalent in the metallic or adsorbed state. The promotion energy to the trivalent state accounts for deviations from the otherwise expected smooth behaviour[15]. In this way Nikulin and Potekhina[16] explained data on the adsorption energies of lanthanoids on tungsten and rhenium. We believe that the same considerations hold in discussing the adsorption of the heavy actinoids on transition metals. Therefore, californium, einsteinium, fermium, and mendelevium having the divalent electronic configuration $5f^{n+1}7s^2$ in the ground state of the isolated atoms are expected to be adsorbed in the trivalent state only if the energy required to excite one f electron to the bonding state of the metallic adsorbent-adsorbate system is compensated by the relevant gain of binding energy. This condition may be written approximately as

$$\Delta\epsilon_{(f^{n+1}\to f^n)} < \Delta E_{ad,2} - \Delta E_{ad,3} \quad . \tag{1}$$

where $\Delta\epsilon_{(f^{n+1}\to f^n)}$ is the promotion energy of the $5f^{n+1}7s^2 \to 5f^n6d^27s$ atomic excitation, $\Delta E_{ad,2(3)}$ is the energy of adsorption of an element with the di-(tri-)valent configuration in both the free and the adsorbed state. These two values are expected to be practically constant for the elements under consideration (for the given adsorbent).

For the case of adsorption in the trivalent state, the experimental energy of adsorption $\Delta E_{ad,exp}$ can be represented as

$$\Delta E_{ad,exp} = \Delta E_{ad,3} + \Delta\epsilon_{(f^{n+1}\to f^n)} \quad . \tag{2}$$

The approximate character of this equation consists in the use of atomic spectroscopic data instead of a many-particle description of adsorption. Nevertheless, the adsorption studies provide information about the energetic position of the 5f levels in the heavy actinoids and valency in the adsorbed state, from which the metallic valency can be concluded.

To evaluate enthalpies of adsorption from the parameters of thermochromatographic experiments, the following equation was used, derived by Eichler and Zvara[17,18]:

$$\lg\left[-\frac{t_r \bar{v}_0 g}{s_1 T_0 (V/A)\exp(\Delta\bar{S}^\circ_{ad}/R)}\right] = \lg\left[Ei^*\left(-\frac{\Delta\bar{H}^\circ_{ad}}{RT_{ad}}\right) - Ei^*\left(-\frac{\Delta\bar{H}^\circ_{ad}}{RT_s}\right)\right]. \tag{3}$$

Here t_r is the retention time, $\bar{v}_0$ is the gas flow rate under standard conditions, g is the temperature gradient, s_1 is the column surface per unit of column length, V and A are the standard molar volume and area of the adsorbate, respectively, R is the gas constant, $T_0=298$ K, T_{ad} and T_s are the deposition and starting temperature, respectively, $\Delta\bar{S}^\circ_{ad}$ and $\Delta\bar{H}^\circ_{ad}$ are the differential standard entropy and enthalpy of adsorption, respectively, and $Ei^*(x)$ is the integral exponential function. The $\Delta\bar{S}^\circ_{ad}$ values, necessary for calculating $\Delta\bar{H}^\circ_{ad}$ from the parameters of single experiments, were estimated in terms of the mobile adsorption model using the equation[18]:

$$\Delta\bar{S}^\circ_{ad} = R\ln\left(\frac{c^\circ_g}{c^\circ_{ad}}r_0\left[\frac{RT}{2\pi A}\right]^{1/2}\right) + \frac{R}{2} , \tag{4}$$

where c°_{ad} and c°_g are the standard state concentrations of the adsorbate on the surface and in the gaseous phase, respectively, A is the atomic weight of adatoms, T is an average temperature, $T=(1/2)\times(T_s+T_{ad})$, and r_0 is the period of oscillation of adatoms, calculated from the maximum vibration frequency of the adsorbent, according to Debye[19] (we assume $r_0=1.1\times10^{-13}$ s for both Ti and Mo). According to[18], the standard state was defined by $c^\circ_{ad}/c^\circ_g = 1$ (cm). The experimental determination of $\Delta\bar{S}^\circ_{ad}$ by the thermochromatographic technique can be performed on the basis of equation (3) from a $\lg(t_r v_0/T_{ad})$ versus $1/T_{ad}$[18] plot.

III. EXPERIMENTAL

Production of Radioelements

The actinoids under study were produced by bombarding ^{249}Bk or ^{249}Cf with ^{22}Ne ions at the JINR 3-meter cyclotron[12,19,21]. In addition to several other nuclides, up to 10^6 atoms of ^{253}Es, 10^6 atoms of $^{252,254}Fm$, and 10^4 atoms of ^{256}Md were produced for each experiment. The recoiling nuclear reaction products were caught in a 6 μm aluminium foil together with variable amounts of target isotopes ^{249}Bk and ^{249}Cf sputtered. Trace amounts of some well-known metals which were used as reference elements, were formed in the aluminium catcher during the bom-

bardment (^{24}Na, ^{28}Mg, ^{43}K, ^{44m}Sc) or prepared by standard procedures, as described elsewhere (^{83}Rb, ^{145}Sm, ^{147}Eu, ^{169}Yb, ^{224}Ra) [21,23].

Procedure

An arrangement used in the thermochromatographic experiments is shown schematically in Fig.1. The titanium and molybdenum columns were made of foils placed into quartz tubes 4.5 mm i.d. In the case of titanium as adsorbent a 50 μm tantalum foil lining was first placed into the quartz tube, in order to prevent diffusion of oxygen from the environment to titanium and reactions of titanium with silica. The behaviour of the elements listed above was studied simultaneously with the exception of ^{83}Rb, ^{145}Sm and ^{224}Ra, which were chromatographed separately in comparison with ^{47}Eu and ^{169}Yb. In order to obtain and stabilize the tracer elements in the state of free atoms, these were evaporated from molten lanthanum metal (reductant) and calcium vapour was introduced in the high-purity helium used as a carrier gas.

First, nitric acid solutions of the radioisotopes which could not be produced in ^{22}Ne bombardments were evaporated in a tantalum boat. Then the aluminium catcher and lanthanum metal were put therein, and the boat was placed into column 7 (Fig.1) in the starting position. In order to introduce calcium into the carrier gas, about 0.5 mg of calcium were added
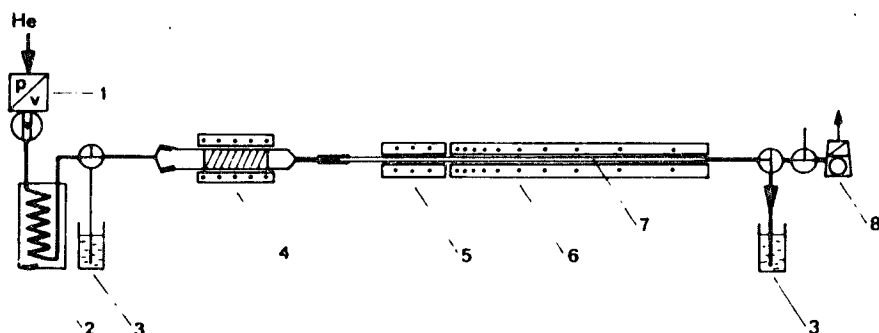

Fig.1. Schematic view of the experimental arrangement.
1 - regulators of pressure and flow rate, 2 - molecular sieves at liquid nitrogen temperature, 3 - hydraulic valves, 4 - getter (zirconium chips at 1200 K), 5 - furnace, 6 - gradient furnace, 7 - thermochromatographic column, 8 - vacuum pump.

to the lanthanum reductant. After the boats have been placed, the column was evacuated twice to 10^3 Pa and then refilled with purified helium. Furnaces 5 and 6 were heated up in some side position simultaneously and after having reached the temperature equilibrium, they were shifted to the working position to start chromatography. The experimental conditions were as follows:
- starting temperature 1425 K
- average temperature gradient 57 K/cm
- flowrate 44 cm^3/min (unless otherwise noted)
- retention time 15 min (unless otherwise noted)

Immediately after the gradient furnace has been switched off, the quartz tube was cooled by water to room temperature. Then the thermochromatographic column was removed from the quartz tube, cut into sections and its surface was contacted with fission fragment track detector foils to detect the ^{256}Fm spontaneous fission events. The registration of the growth-and-decay curve of the spontaneous fission activity over a period of 10 hours was followed by the spectrometric measurements of α- and γ-activities in 1 cm sections by Si surface barrier and Ge(Li) detectors, respectively. The statistical error (σ) in determining the relative amounts of the α- and γ- radioactive tracers did not exceed 8% and 3%, respectively. As the spontaneous fission activity ($t_{1/2} > 10$ min) of the nuclear reaction products was due to ^{256}Fm, only, arising from the decay of ^{256}Md [20], the amounts of ^{256}Md could be evaluated from the growth-and-decay curves of the spontaneous fission activity by means of a computer code. To check these results the mendelevium chromatograms were evaluated also in an independent way by comparing the distribution of the total fission activity and the distribution of fermium as determined by α-spectrometric measurements. The relative error of the ^{256}Md amounts is expected to be in the range of about 10 to 15%. The distribution of the weighable quantities of calcium was determined by X-ray fluorescence analysis.

IV. RESULTS AND DISCUSSION

At first a series of experiments in titanium columns with ^{249}Cf only and by varying $\bar{v}_0$ and t_r was carried out in order to determine ΔS^o_{ad} and ΔH^o_{ad} experimentally by the second law method [18]. The parameters and results of these experiments are summarized in the Table and Arrhenius plot of $\lg(\bar{v}_0 t_r/T_{ad})$ versus $1/T_{ad}$ is shown in Fig.2. From the least square fit we found

$$\Delta \bar{H}^{\circ}_{ad} = -(162\pm8) \text{ kJ/mole and}$$

$$\Delta \bar{S}^{\circ}_{ad} = -(144\pm11) \text{ J/mole K.}$$

The $\Delta \bar{H}^{\circ}_{ad}$ values in column 4 of the Table were calculated with $\Delta \bar{S}^{\circ}_{ad} = -159$ J/mole K (estimated according to equation (4)). The experimental entropy value determined by the second law method was used to calculate the $\Delta \bar{H}^{\circ}_{ad}$ values in column 5. The $\Delta \bar{H}^{\circ}_{ad}$ values calculated according to equation (3) as well as Fig.2, show good reproducibility of the technique over a large range of retention time and flow rate.

Table

Thermochromatography of Cf in titanium columns.
Experimental parameters and thermodynamic data

Gas flow rate, $\bar{v}_o$ cm^3/min	Retention time, t_r min	Deposition temperature, T_{ad} a), K	$-\Delta \bar{H}^{\circ}_{ad}$ b) kJ/mole	$-\Delta \bar{H}^{\circ}_{ad}$ c) b) kJ/mole
16.6	5	840	175	163
16.6	10	820	176	164
16.6	30	775	173	162
16.6	60	765	176	163
44	15	775	176	164
44	60	720	172	161
45	65	720	172	161
52	300	690	176	163

a) Estimated uncertainties < $\pm$40 K; b) $\Delta \bar{H}^{\circ}_{ad}$ was calculated with $\Delta S^{\circ}_{ad} = -159$ J/mole K; the estimated uncertainties in $\Delta \bar{H}^{\circ}_{ad}$ are < $\pm$20 kJ/mole; c) $\Delta \bar{H}^{\circ}$ was calculated with $\Delta \bar{S}^{\circ}_{ad,exp} = -144$ J/mole K.

The distribution of trace amounts of the elements Na, K, Rb, , Ra, Sm, Eu, Yb, Cf, Es, Fm and Md along the titanium column after the thermochromatographic process and the temperature profile along the column are shown in Fig.3. The trivalent metals, Sc and Bk reminded in the lanthanum aluminium melt. We have not presented in Fig.3 the distribution of the weighable amounts of calcium ($500~\mu g$) along the column since the sensitivity of the X-ray fluorescence measurements was too low, to measure the concentration profile of the calcium
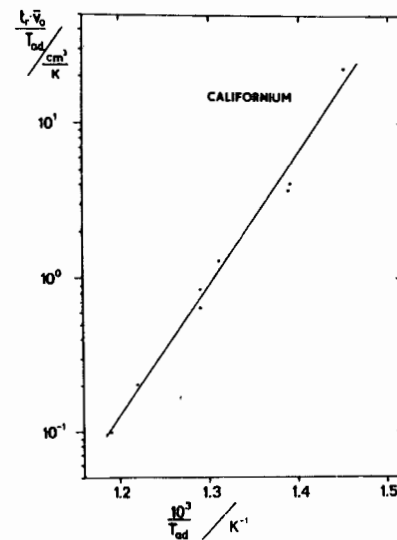

Fig.2. Thermochromatography of Cf in titanium columns. Arrhenius – plot of the data (cf. also values in the Table).
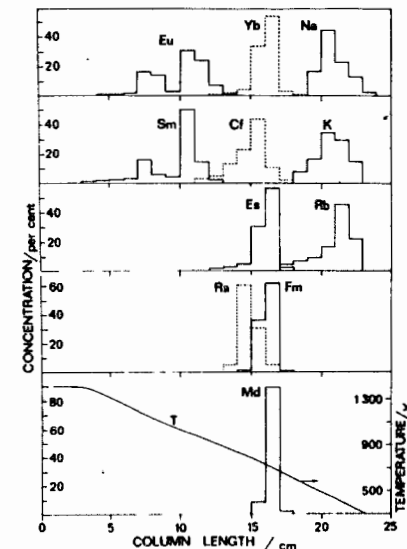

Fig.3. Thermochromatography in titanium columns. Distribution of trace amounts of Na, K, Rb, Sm, Eu, Yb, Ra, Cf, Es, Fm and Md along the column.

band down to the trace level. At the concentration maximum of the calcium band – in the region of the Eu low-temperature peak – little crystallites of metallic calcium were visible. Calcium has a stabilizing function for the elementary state of the elements studied, since it is expected that the potential oxygen impurities in the gaseous phase react preferably with calcium present in a several orders of magnitude higher concentration than the tracers. Furthermore, calcium influences the chromatographic distribution of the trace components, as their thermochromatograms result from interactions of single atoms with the titanium surface as well as with the calcium layer. In the presence of calcium the minute aluminium quantities evaporated from the melt should not alter the thermochromatographic behaviour of the studied elements, since the thermochromatograms of Sm, Eu, Yb, and Cf from experiments without aluminium were the same as those presented here[24].

In the presence of weighable quantities of calcium, Sm and Eu were deposited in two peaks (Fig.3) whereas without calcium[13] Eu was deposited only as a single peak
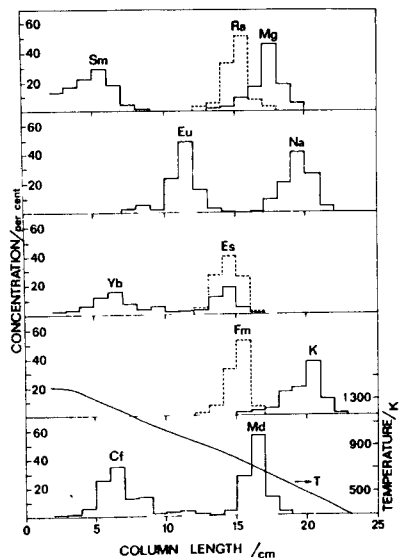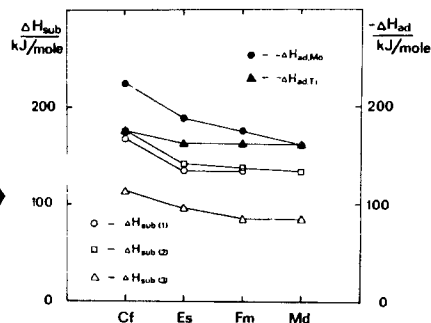
Fig.4. Thermochromatography in molybdenum columns. Distribution of trace amounts of Na, Mg, K, Sm,, Eu, Yb, Ra, Cf, Es, Fm, and Md along the column.

Fig.5. Comparison of the experimental enthalpies of adsorption with predicted enthalpies of sublimation. $\Delta H_{ad,Mo(Ti)}$ enthalpy of adsorption on molybdenum (titanium), ΔH_{sub} – enthalpy of sublimation; (1) – ref.[8] , (2) – ref.[10] , (3) – ref.[9] .

at (1125 ± 50) K. We believe that, as these elements interact with the adsorbent more strongly than calcium, the high temperature band corresponds to the "true" adsorption on titanium whereas the low temperature peak results from masking of the adsorbent by calcium. All the atoms of Sm and Eu interacting during the chromatographic process only with calcium, are carried down to the deposition band of calcium.

For the elements deposited at lower temperatures than calcium, we may conclude that they interact with titanium not less strongly than the divalent calcium, do not form stable intermetallic compounds with calcium and are more volatile than calcium. The deposition of Cf, Es, Fm, and Md at lower temperatures than calcium, in the region of the divalent Ra and at higher temperatures than the monovalent alkali metals Na, K, and Rb, provides evidence that these heavy actinoids are di-

valent metals. Thermochromatograms of trace amounts of Na, K, , Mg, Sm, Eu, Yb, Ra, Cf, Es, Fm, and Md resultant from experiments in molybdenum columns are shown in Fig.4. As in the titanium columns, the distribution of Eu in its low temperature peak follows the distribution of the weighable amounts of calcium. Molybdenum was chosen as a metal characterized by stronger adsorbent – adsorbate interactions than titanium.

As is seen from Fig.3, in titanium columns only Sm and Eu are deposited partly at higher temperatures than calcium, whereas in molybdenum columns this is also the case for Yb and Cf. We believe that the deposition of Sm , Yb and Cf in molybdenum columns at higher temperatures than calcium is to be considered as adsorption in the trivalent state due to the transition of one f -electron to the conduction band. On the other hand, as in titanium columns, the deposition of Es, Fm and Md in the region of the divalent metals Mg and Ra is to be considered as adsorption in the divalent state.

As was discussed earlier[24] the behaviour of Cf in thermochromatographic titanium columns was taken as evidence for the divalency of Cf in the metallic state. We believe that adsorption of Cf on molybdenum in the trivalent state does not contradict this conclusion, because the behaviour of Cf on molybdenum is similar to that of the divalent lanthanoid metal Yb. Furthermore, the evaporation rate of Cf from molten lanthanum was found to be intermediate between those of Eu and Yb[12] and this also confirms the divalency of Cf.

From the results of the thermochromatographic experiments presented here we conclude that the energetic positions of the 5f-levels relative to the Fermi-levels of the heavy actinoids Es, , Fm, and Md are not only lower than that of Cf but even lower than those of the 4f-levels of the lanthanoid Yb. The actinoids Es, Fm, and Md , without doubt, occur to be divalent alkaline earth-like metals.

Enthalpies of adsorption calculated for heavy actinoids according to equations (3) and (4) are shown in Fig.5 in comparison to the enthalpies of sublimation predicted by several authors [8-10]. Generally there is a good correlation.

For more quantitative interpretations of the results of the thermochromatographic experiments reported here, the amount of the available experimental data and the extent of theoretical understansing of adsorption are so far not sufficient. However, there is further experimental evidence for considerable differences in the properties of the heavy lanthanoids and actinoids.

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SUBJECT CATEGORIES
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Хюбенер З., Звара И.   E12-82-103

Характеристика свойств металлического состояния менделевия
и других актиноидов с помощью термохроматографии

Термохроматографическим методом изучалась адсорбция
следовых количеств Cf, Es, Fm и Md на поликристаллических
титане и молибдене в сравнении с несколькими хорошо изученны-
ми металлическими элементами. Данные приводят нас к выводу,
что Es, Fm и Md двухвалентны в металлическом состоянии,
и, более того, что их f уровни расположены по отношению
к энергии Ферми ниже, чем в случае Cf и Yb. Была найдена
корреляция между экспериментальными энтальпиями адсорбции
тяжелых актиноидов и их предсказанными энтальпиями возгонки.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Hübener S., Zvara I.   E12-82-103

Characterization of Some Metallic State Properties
of Mendelevium and Other Actinoids by Thermochromatography

The adsorption of the heavy actinoids Cf, Es, Fm,
and Md on polycrystalline titanium and molybdenum has been
studied by thermochromatography in comparison with several
well-known metallic elements, in trace amounts. The data lead
us to suggest that Es, Fm, and Md are divalent in the metal-
lic state and, moreover, that the position of their f energy
levels relative to the Fermi-energy is lower than in the cases
of Cf and Yb. A correlation was found between the experimental
enthalpies of adsorption of the heavy actinoids and their
predicted enthalpies of sublimation.

The investigation has been performed at the Laboratory
of Nuclear Reactions, JINR.