Since actinide compounds and particularly the oxides have low sputtering yields, deposits in the 10–100 μg cm^{-2} thickness range require deposition times ranging from several minutes to a few hours. The glove box adaptation is made by disconnecting the control unit from the deposition chamber and the pumping unit. The glove box is divided in two compartments: one containing the deposition chamber and the other the pumping group. When metallic samples are handled, the glove box is flushed with pure argon or nitrogen.

Deposits of the following isotopes have been prepared: ^{230,232}Th, ^{231}Pa, ^{233,235,238}U, ^{237}Np, ^{239,241}Pu, ^{241,243}Am, ^{244}Cm as oxides and ^{232}Th, ^{235}U, ^{238}U, ^{239}Pu, ^{241}Am as metals.

Generally actinide thin film deposition starting from metals leads to oxide deposits. The realization of metallic layers requires special care towards the glove box atmosphere purity, particularly in the case of Pu and trans Pu isotopes.

The characterization of the oxidation state can be achieved using ESCA and the deposition rate is monitored either by integrating the ionic current or by a quartz oscillating monitor.

Electrospraying and focused ion beam appear as complementary techniques for thin film depositions of actinide compounds and particularly the scarce isotopes when classical methods such as vacuum evaporation or electrodeposition are ineffective.

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D15

Oxysulfide Glasses in the La_2S_3–La_2O_3–Ga_2S_3–Ga_2O_3 System

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Glasses were previously described in the La_2S_3–Ga_2S_3 and La_2O_2S–Ga_2S_3 systems. Actually, a very large glass former region exists in the La–Ga oxydesulfide system, in the neighbouring of Ga_2S_3 (which alone does not form glass by quenching). In order to explain the formation of glasses, a tentative phase diagram is proposed from DTA and X-rays diffraction studies. A large concentration of ternary invariants is present in the glass former region. Some new quaternary compounds have been identified, and their structures were solved. The $La_{10/3}Ga_6S_{12}O_2$ compound is only formed from glasses by convenient heat treatment. Its structure is supposed to be closely related to the structure of the glasses. Glasses are generally obtained by quenching the melt products at 1100–1200 °C. Along two eutectic valleys, glasses can be obtained after slow cooling. The thermal properties of the glasses (T_g, T_c, T_m) are described. Glasses have yellow brown colour. They are transparent in large regions of the visible and I.R. spectra.

Some informations have been obtained with Nd-doped glasses: a large nephelauxetic effect is observed in the absorption spectra, in relation with strong covalent character of the rare earth–non metal bonds. Moreover the Raman spectra of the glasses are not exactly the envelope of the Raman spectra of the crystalline products: the stronger Raman band at 230 cm^{-1} which is characteristic of a stretching mode of Ga–S_4 tetrahedra is not observed with the glasses.

D16

Magnetic Properties of Es_2O_3 and EsF_3

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The first quantitative measurements of the magnetic properties of einsteinium have been made on Es_2O_3 and EsF_3. The data were collected at temperature between 4.2 and 180 K while maintaining the samples in various applied magnetic fields. The paramagnetic moment per einsteinium atom was 10.4 ± 0.3 μ_B for the Es_2O_3 sample and 11.4 ± 0.3 μ_B for the EsF_3 sample. These values may be compared to a theoretical value of 10.6 μ_B for a $5f^{10}(Es^{3+})$ free ion calculated by using Hund's Rule and L–S coupling.

Sample Preparation. The einsteinium used in the study was purified by ion exchange chromograph techniques and 30 μg of a ^{253}Es–^{254}Es isotope mixture were obtained as a chloride solution. A micro-precipitation technique using teflon molds [1] was employed to precipitate the einsteinium as an oxalate, and this material was then calcined up to 1000 °C in air to form an off-white, Es_2O_3 product. A similar approach was used to prepare EsF_3. Electrolytic grade HF was added to the purified chloride solution of trivalent einsteinium to produce a micro-precipitate. The resulting washed precipitate was subsequently dried at 200 °C under flowing argon. X-ray diffraction analysis of the Es_2O_3 samples did not yield diffraction data, indicating the oxide was amorphous. However, from earlier work [2] it is known that einsteinium forms only a body centered cubic (bcc) sesquioxide up to 1000 °C. Monoclinic, and hexagonal forms of Es_2O_3 potentially exist but have not been reported. A radiation-induced transformation from bcc to the hexagonal form has been observed at room temperature. Efforts to prepare EsO_2 have been negative. It was also not possible to obtain X-ray diffraction data from the EsF_3 products. Due to a more transparent nature of the EsF_3 sample, it was possible to examine it by absorption spectrophotometry. These measurements showed that the einsteinium existed in the 3+ state.

Experimental Approach. For the measurement of the molar magnetic susceptibility, χ_M, the total sample moment, $\chi_M nH$ (n = number of mol and H = applied field), produces the effect upon the experimental apparatus. Since n is such a limited quantity for einsteinium samples a very sensitive apparatus is required to make the measurements. We have constructed a SQUID instrument especially for such measurements [3] and a minimum measurable molar susceptibility of 1.9×10^{-6} (emu/mol) has been achieved for a 1 microgram sample.

Special care was used to avoid contaminating the sample with magnetic materials. The sample holder consisted of an 0.6 mm ID sapphire tube with 0.5 mm diameter gold inserts on each end which crush the sample in the middle of the sapphire tube for good thermal contact. A secondary tube of quartz was then placed around the sapphire holder.

In the solid state compounds, Es_2O_3 and EsF_3, the 3+ ionic state of einsteinium would be assigned a $5f^{10}$ configuration. If it is assumed that the 5f electrons interact only slightly, the molar magnetic susceptibility, χ_M, should behave as:

$$\chi_M = N_A\mu^2/3k(T + \theta_p)$$

In this equation, it can be seen that χ_M^{-1} should be linear with temperature, T. In Fig. 1 we show a plot of χ_M^{-1} *vs.* sample holder temperature for our 4.08 μg sample of Es_2O_3. Since little departure from linearity was observed (indicating negligible permanent moment alignment) with decreasing temperature, a linear least squares fit was made to the data to obtain $\mu = 10.4 \pm 0.3$ μ_B per 'heavy' atom and $\theta_p = 53 \pm 5$ K.

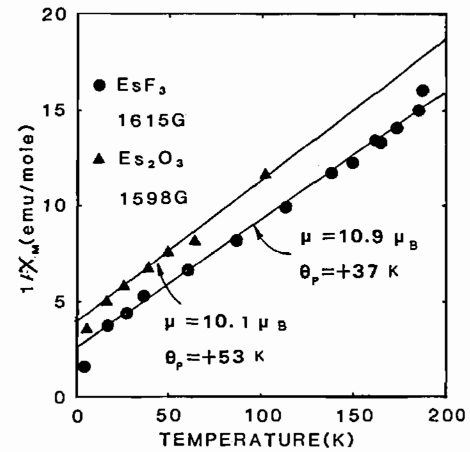

Fig. 1. Susceptibility plot.

At the time of the magnetic measurements on the Es_2O_3, the sample was 4 days old (*i.e.* 4 days after purification). Based on its half-life, 13% of the einsteinium should have decayed to berkelium. Although the ^{249}Bk daughter present in the sample at the time of measurement was produced from a 6 Mev α-decay, we have assumed that it existed as Bk_2O_3 in our sample. This assumption is consistent with other studies which have followed the growth of daughter and grand-daughter products of einsteinium compounds [4]. The +3 free ion of berkelium should have a $5f^8$ electronic configuration and a corresponding free-ion moment of 9.7 Bohr magneton per atom. Since our Es_2O_3 sample was actually a mixture of einsteinium and berkelium oxides, the experimental moment should be corrected for the berkelium content. A simple correction can be made by assuming that each material behaves independently and that their moments are additive. Thus, if a mixture of atoms (87% einsteinium and 13% berkelium) gave a moment of 10.1 ± 0.3 Bohr magnetons per atom, then the einsteinium atoms should have a moment of 10.5 ± 0.3 per atoms. This latter value is consistent with calculated value of 10.61 μ_B for a $5f^{10}$ (Es 3+ ion).

A similar magnetic study was made for a 3.25 μg sample of nominally EsF_3 ten days after its preparation, so that 31% of the einsteinium had decayed to berkelium. The data is also shown in Fig. 1 for an external field of 1615 gauss. A linear least squares fit to this data yields a moment per 'heavy' atom of $\mu = 10.9 \pm 0.3$ μ_B and $\theta_p = 37 \pm 5$ K. A similar correction for the berkelium daughter gives a moment of 11.4 ± 0.3 μ_B per einsteinium atom.

Since the initial measurements, successive studies have been made on samples to follow the magnetic character as a function of the ingrowth of the berkelium daughter. No surprises have been encountered. The average moment per heavy atom follows the predicted value for a simple mixture of $5f^{10}$ and a $5f^8$ atomic configurations.

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D17

The Reaction of Plutonium with Water: Phases in the Pu + O + H System

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In early reports, the reaction of plutonium with water is described as "very slow at room temperature" [1]. The product is a finely divided black solid which prior workers have identified as hydrated oxide or hydroxide [2]. Results of recent experiments with synthetic sea water show that the Pu + H_2O reaction is quite rapid and that the quantities of H_2 produced are less than half those expected for the formation of $Pu(OH)_3$ or $Pu(OH)_4$ [3]. The primary measurement described in this report was designed to determine the reaction rate of Pu with 1.0 *M* $CaCl_2$ solution, but kinetic measurements which continued for more than 450 days have provided valuable insight into the chemistry of the complex Pu + U + H system.

Kinetic measurements and the preparation of solid hydrolysis products for analysis were made with a stainless steel system fitted with a glass liner for containment of the reactants. Rates and extents of reaction at 23 ± 2 °C were monitored by PVT methods. Both α-phase and δ-stabilized Pu were reacted with aqueous salt solutions having a wide range of concentrations. Samples of the initial hydrolysis product were isolated by removing residual water under dynamic vacuum or with molecular sieve.

The reaction of Pu with H_2O to form the black product is rapid when catalyzed by salt. The reaction rate R (mgPu cm^{-2} hr^{-1}) is dependent on the anion concentration X (mol l^{-1}) as follows: $R = 1.2X^{0.7}$ for $10^{-7} \leqslant X \leqslant 1$ *M*. Small variations are observed for different anions and cations and for α- and δ-phase Pu.

When the quantity of H_2 formed during the extended experiment (α-Pu + 1.0 *M* $CaCl_2$ solution) is graphed against time, a series of linear curves with successively lower slopes is observed. Each linear (constant rate) section is attributed to the occurence of a specific equilibrium hydrolysis reaction. During the first linear segment, Pu is completely converted to black product. During the second segment, that product reacts with water at a slower rate to produce additional H_2 and a third product, *etc.* It is convenient to formulate the quantity of H_2 as mol H_2 produced per mol Pu because this ratio is directly correlated with the net chemical reaction; *e.g.*, this ratio is 1.5 and 2.0 for formation of $Pu(OH)_3$ and $Pu(OH)_4$, respectively. Least squares analysis of the data for the extended test show that sharp slope changes occur at the following H_2/Pu ratios: 0.507, 1.078, 1.455, 1.716, 1.763, 1.803, 1.831 and 1.993. Eight different hydrolysis products apparently form in succession. The breaks near 1.5 and 2.0 correspond to the formation of products containing trivalent and tetravalent Pu. The products existing at 0.50 and 1.07 must either have Pu in a valence state less than three or contain hydride, while those formed between the 1.50 and 2.00 ratios are mixed-valent.

The black product formed at $H_2/Pu = 0.50$ has been identified as plutonium monoxide monohydride, Pu(O)H. This assignment is based on the results of chemical, TG, XRD, and XPS analyses. The data show that the product is not an hydroxide or hydrated oxide and that it is chloride-free. XRD results for wet and dry products give identical fcc patterns with a = 540.1(2) pm. Although the parameter is similar to those of PuH_2 (a = 535.9 pm) and PuO_2 (a = 539.7 pm), thermal decomposition results show that the product is not a mixture of hydride and oxide. The observed parameter is consistent with that expected for a fluorite-related oxide hydride. Hydrolysis of Pu is described by the reaction: $Pu + H_2O \rightarrow Pu(O)H + 1/2H_2$. XRD results are given in Table I.

TABLE I. X-ray Diffraction Intensities for the Plutonium Monoxide Monohydride.

hkl	I/I_0 (%)
111	100
200	34
220	45
311	42
222	8
400	5
331	11
420	10
422	8
333	9

Our identification of the other hydrolysis products is based on results for the initial product and on the well-known phase relationships of Pr + O [4]. Particularly important observations are: (a) The product does not contain hydroxide, and this anion is not