ELECTRONIC STRUCTURE AND BONDING IN TRANSURANICS: COMPARISON WITH LANTHANIDES

by

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ABSTRACT

The physico-chemical properties of actinide metals, alloys, and compounds show interesting parallels and contrasts with the rare earths, beyond uranium. At first there is a transition region where the unique bonding properties of the early actinides become less prominent, due to progressive f-electron localization. Nevertheless, in contrast to the rare earths, f-electron energies remain close to the Fermi level, resulting in complex behavior as a function of temperature, pressure and structure. Particularly interesting in this region are the metallic hydrides, whose chemistry is clearly rare-earth lik, but whose electronic properties are entirely different.

At americium a major localization and f-band narrowing occurs, but the explanation of americium behavior is obscured by the occurence of the unique f⁶ non-magnetic solid-state configuration. Beyond americium, it would appear that real rareearth-like behavior finally begins; this has been born out by recent studies on the thermodynamics and cohesive energies of curium, berkelium, californium and einsteinium metals. However, a new complication arises almost immediately, in the onset of incipient stabilization of the divalent state, which already appears in californium, whose physico-chemical properties are remarkably similar to samarium. Einsteinium appears be fully divalent, thus heralding the beginning of a minf-series of truly divalent metals.

I. INTRODUCTION

A great deal of recent interest and research has been focussed on the early actinides, because of the many fascinating physico-chemical insights afforded by the broad-band bonding 5f electrons. Whereas reasonably self-consistent models have been developed describing the general properties of other elemental groups (e.g., transition metals, rare earths), such attempts have had only limited success with the early actinides. As long as the highly-extended 5f's, with energies near the Fermi level, can hybridize with other valence electrons, a complex spectrum of chemical effects can be expected.

In this respect, there are many analogies to the early transition (especially 3d) metals, where the d-electrons are also broad-band and bonding. As more d-electrons are added, localized states begin to appear, and a sharp drop in ratio of radial extension of the d-electrons compared to the metallic radius is experienced between Cr and Mn.

In the actinides, however, the drop in this ratio is more gradual, becoming finally more precipitous between plutonium and americium. The 5f electrons are at once more extended even than the 3d, but, because of the peculiar shapes of the wave functions, also more diffuse. The effect of progressive localization (or band-narrowing) of the 5f's is partially counteracted by the increase of these electrons, all remaining essentially pinned at the Fermi level. However, in compounds all sorts of behaviors can be seen, dependent on the metal-metal spacing and number of f-electrons available. Thus, magnetic compounds with at least partially localized f-electrons can be already found as early as uranium, and beyond, a plethora of effects is observed. This "atomic-size" correlation has been presented by Hill⁴ and the famous "Hill Plot" has been used, with varying degress of success, to both predict and explain magnetic effects in actinide compounds. Many actinide compounds can be shown as directly analogous to their rare-earth counterparts, ie., the metal ion often assumes a trivalent configuration. Smith and Fisk⁵ have recently discussed a number of interesting aspects concerning magnetism in transuranics, with relation to rare-earth behavior.

The situation for metals and metallic compounds is of course considerably more complicated, because atom-atom spacing is usually small and the 5f electrons continue to perturb. Plutonium exhibits no less than six phases between room temperature and the melting point. However, here the first possible glimmer of rare earth-like behavior is seen in the delta phase, which has a simple fcc structure and a metallic radius of $1.64A^{\circ}$ (and indeed the x-ray adsorption/emission resonance of <u> δ -Pu</u> shows a rare-earth-like response⁶); however a truly "trivalent" radius³ would be $1.75A^{\circ}$, which is finally satisfied at americium. We know that band-narrowing at americium (to ~ 0.6 eV) results in an abrupt shift to rareearth-like behavior, though some mystery remains because of the unique non-magnetic $5f^{6}$ ground-state configuration.

This very interesting region, and beyond then, where the metal themselves and metallic compounds begin finally to look like rare-earth homologs, is the subject of this report. Presented first is a portrayal of the properties of the actinide hydrides, a particularly revealing series of metallic compounds, each quite different but finally reaching true rare-earth behavior at americium. A recent study contrasting the solid-state properties of the plutonium-hydrogen system with the heavy rare-earth hydrides will complete this section. Finally, the electronic and thermodynamic properties of the transplutonium metals through einsteinium will be considered, in contrast to rare-earth homo-loges.

II. THE ACTINIDE HYDRIDES - A UNIQUE SEQUENCE

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The series begins apparently as another transition metal row, actinium being quite similar to lanthanum, and thorium following as the homologue of zirconium and hafnium; indeed, ThH_2 has the face-centered tetragonal structure of ZrH_2 and HFH_2 . However the trend of gradually-increasing lattice constant jumps suddenly by nearly 17% in going from HfH_2 to ThH_2 . At the same time the metal-bydrogen distance increases from 2.05A° to 2.39A°, ie., from a distance characteristic of tetravalent metals to one more typical of trivalent cations. Furthermore a unique higher hydride Th_4H_{15} forms at greater hydrogen pressures. Although the f-band in thorium lies above occupied levels, the bottom of this broad band lies only about one eV above the Fermi level; thus the influence of this band could be considerable under certain circumstances.

For protactinium, where the first, broad 5f band is populated, three hydride phases form: a low temperature bcc phase, but at higher temperature a very complex C15 spinel structure first appears, followed at higher pressures by an A15 phase isostructural with β -UH₃⁷. Both the C15 and A15 phase occur with two coexisting sublattices, one with metallic bonding (with f-f overlap) and the second with widely-spaced atoms giving a net magnetic momement.

Uranium trihydride is also unusual in that it is a stoichiometric, metallic, magnetic substance. β -PaH₃-x, in contrast, exists over a rather wide stoichiometry range.

A sudden change occurs at neptunium--chemistry comparable to the late rareearth hydrides is found, but with some major differences. In contrast to the Pa + H and U + H systems, no phases exhibit magnetism; also, the lattice does not contract beyond NpH₂, with added hydrogen, but actually increases slightly. Clearly considerable work remains to be done on the neptunium-hydrogen system.

At plutonium, then, it would appear that typical late rare-earth hydride behavior is finally achieved. A cubic dihyride with extended solid solution is found, finally leading at compositions approaching H/Pu = 3, to a hexagonal phase; the lattice contracts with addition of hydrogen beyond H/Pu = 2. This chemistry parallels that found in the trivalent rare-earths, beginning at samarium and becoming predominant beyond gadolinium. Some general comparative trends and properties for the rare-earth and rare-earth-like actinide hydrides are summarized in Table I. Resistivities of the rare-earth hydrides near the composition MH_2 are in the range 25-40 $\mu\Omega$ cm (300k), ie., up to 40% more metallic than the parent metals themselves; magnetic susceptibilities, moments, etc, are similar to the parent metals. As can be seen from Table I, many experimental details remain to be completed for the actinide hydrides.

A number of studies have been reported for the plutonium-hydrogen system⁸⁻¹⁰, and results for the P-V-T relationships, phase diagram and cystal structures are in general agreement. More recently, there has been some work on solid state properties, including NMR studies¹¹ and magnetic behavior¹². Most work on this and other hydride systems has been done on powder or compacted power, often sealed in containers and "heat-treated" to a hoped-for composition, making the identity of the sample somewhat questionable. In the present study, bulk plutonium hydride samples were prepared to precise compositions using the techniques developed by Haschke and coworkers.¹³ ¹⁴ The compositions obtained were $PuH_{1 53}$, $PuH_{2 16}$, $PuH_{2 42}$, $PuH_{2 53}$, and $PuH_{2 65}$. Handling operations were carried out in argon-inerted glovebox; for compositions below $PuH_{2 75}$ there is no detectable loss of hydrogen, after quenching to room temperature. The two lower compositions had metallic luster and were crack-free, whereas the higher compositions were progressively more friable.

A. Electrical Resistivity

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Resistivity studies were carried on on these samples using a 4-terminal DC method. The metallic-appearing PuH_{1-93} produced the resistivity curve shown in Fig. 1. A sharp transition at 44k coincided with an equally sharp magnetic transition, to be discussed below; above this temperature the resistivity rose in a manner typical of metals. For comparison, α -Pu metal exhibits a resistivity of about 20 $\mu\Omega$ -cm at 4K. The higher resistivity of the hydride is then in marked contrast to the rare-earth hydrides.

The higher H/Pu ratios exhibited increasingly complex resistivities; beyond H/Pu = 2.14 the dp/dT became negative above 100K, signalling possible semiconductor behavior. Observed transitions were well-defined, reproducible, and increasingly complex at the higher H/Pu ratios. A second example of H/Pu = 2.65 is shown in Fig. 2. Transitions were observed in varying degrees at 44-66K, 100K, and 180K; only the first two involved concomitant magnetic effects. Resistivity features are summarized in the table of Fig. 3.

B. Magnetic Effects

Magnetic susceptibility studies were performed on all compositions from 1.4 to 230K, using the vibrating-sample magnetometer method. Sharp ferromagnetic transitions were noted with all samples; these are summarized in the tables and graphs of Fig. 3. The strong resistivity transition pinned at 100K showed only a small magnetic inflection, and no magnetic change occured at 180K. Curie-Weiss plots of the ferromagnetic transitions are shown in Fig. 4.

Clearly there is a major change in properties near the composition PuH_2 4. Resistivity transitions shift from the region near 50K to a fixed transition at 100K; at the same time, the inflection at 180K appears. This could be attributed to the freezing out of the more mobile octahederal hydrogens. An even more dramatic change is seen in the values of μ_{eff} and μ_{sat} , as shown in Fig. 3; these values actually rise with composition, instead of declining.

These observations could possibly indicate a new phase transition or transitions near H/M = 2.4 as suggested by Haschke¹⁵, which has has been observed for SmH_{and} some rare-earth fluoride systems. A coherent intergrowth involving the hexagonal and cubic phases could be involved in this region.

C. Comparison With Rare-Earths

In summary, although the chemistry of the plutonium hydrogen system seems quite like the heavy rare-earths, solid-state properties are quite different. The conduction band must be almost purely 5f in character, since what little s-d character is available in the metal will be used even before forming the dihydride. Strong electron scattering should increase the (already large) resistivity markedly, and hydrogen-f-orbital interactions will grow as more hydrogen is incorporated into the lattice. Since f-electrons bond poorly in cubic lattices, lower heats of formation might be anticipated, and this appears to be true in the actinide hydrides through plutonium (see Table I).

TABLE I

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RARE-EARTH (-LIKE) HYDRIDES

	Const.		Minimum	AH, MH2	
MH2+MH3	(MH ₂)	Magnetic	M-H Dist.	Kcal/Mol	Valence
fcc sol. sol'n	5.663A	No	2.45A	-49.6	3
fcc sol. sol'n	5.575	Yes	2.42	-52.0	3
fcc sol. sol'n	5.518	Yes	2.39	-49.7	3
fcc sol. sol'n (?) 5.464	Yes	2.37	-5 0.5	3
fcc sol. sol'n,	hex 5.374	No	2.33	-53.5	3
fcc sol. sol'n,	hex 5.303	Yes	2.32	-46.9	3
fcc sol. sol'n,	hex 5.246	Yes	2.32	-	3
fcc sol. sol'n,	hex 5.201	Yes	2.32	-	3
fcc sol. sol'n,	hex 5.165	Yes	2.32	-	3
fcc sol. sol'n,	hex 5.123	Yes	2.32	-54.2	3
fcc sol. sol'n, 1	hex 5.090	Yes	2.32	-	3
fcc and ?	5.670	?	?	?	3
fcc sol. sol'n, b	hex 5.343	No	2.32	-28.0	?
fcc sol. sol'n,	hex 5.359	Yes	2.32	-37.0	?
fcc sol. sol'n,	hex 5.348	No	2.32	-45.5	3
fcc sol. sol'n,	hex (5.344)	?	2.32	?	3
	$\underline{MH_2 + MH_3}$ fcc sol. sol'n fcc sol. sol'n fcc sol. sol'n fcc sol. sol'n fcc sol. sol'n, f fcc sol. sol'n, f	$\frac{MH_2 \rightarrow MH_3}{(MH_2)}$ fcc sol. sol'n 5.663A fcc sol. sol'n 5.575 fcc sol. sol'n 5.518 fcc sol. sol'n 7.518 fcc sol. sol'n 7.518 fcc sol. sol'n, hex 5.374 fcc sol. sol'n, hex 5.303 fcc sol. sol'n, hex 5.303 fcc sol. sol'n, hex 5.246 fcc sol. sol'n, hex 5.246 fcc sol. sol'n, hex 5.201 fcc sol. sol'n, hex 5.165 fcc sol. sol'n, hex 5.165 fcc sol. sol'n, hex 5.123 fcc sol. sol'n, hex 5.123 fcc sol. sol'n, hex 5.343 fcc sol. sol'n, hex 5.359 fcc sol. sol'n, hex 5.348 fcc sol. sol'n, hex 5.344)	$\frac{MH_2 + MH_3}{(MH_2)}$ $\frac{(MH_2)}{(MH_2)}$ $\frac{Magnetic}{No}$ fcc sol. sol'n 5.663A No fcc sol. sol'n 5.575 Yes fcc sol. sol'n 5.518 Yes fcc sol. sol'n 7.5.18 Yes fcc sol. sol'n 7.5.364 Yes fcc sol. sol'n, hex 5.374 No fcc sol. sol'n, hex 5.303 Yes fcc sol. sol'n, hex 5.246 Yes fcc sol. sol'n, hex 5.201 Yes fcc sol. sol'n, hex 5.165 Yes fcc sol. sol'n, hex 5.123 Yes fcc sol. sol'n, hex 5.123 Yes fcc sol. sol'n, hex 5.343 No fcc sol. sol'n, hex 5.359 Yes fcc sol. sol'n, hex 5.348 No fcc sol. sol'n, hex 5.344 ?	Minimum MH_2+MH_3 (MH_2) MagneticM-H Dist.fcc sol. sol'n5.663ANo2.45Afcc sol. sol'n5.575Yes2.42fcc sol. sol'n5.518Yes2.39fcc sol. sol'n (?)5.464Yes2.37fcc sol. sol'n, hex5.374No2.33fcc sol. sol'n, hex5.303Yes2.32fcc sol. sol'n, hex5.246Yes2.32fcc sol. sol'n, hex5.201Yes2.32fcc sol. sol'n, hex5.165Yes2.32fcc sol. sol'n, hex5.165Yes2.32fcc sol. sol'n, hex5.165Yes2.32fcc sol. sol'n, hex5.165Yes2.32fcc sol. sol'n, hex5.090Yes2.32fcc sol. sol'n, hex5.343No2.32fcc sol. sol'n, hex5.359Yes2.32fcc sol. sol'n, hex5.348No2.32fcc sol. sol'n, hex5.348No2.32fcc sol. sol'n, hex5.348No2.32	MH2+MH3(MH2) (MH2)Magnetic MagneticMinimum M-H Dist. ΔH_{c} , MH_{2} Kcal/Molfcc sol. sol'n5.663ANo2.45A-49.6fcc sol. sol'n5.575Yes2.42-52.0fcc sol. sol'n5.518Yes2.39-49.7fcc sol. sol'n (?)5.464Yes2.37-50.5fcc sol. sol'n, hex5.374No2.33-53.5fcc sol. sol'n, hex5.303Yes2.32-46.9fcc sol. sol'n, hex5.246Yes2.32-fcc sol. sol'n, hex5.201Yes2.32-fcc sol. sol'n, hex5.165Yes2.32-fcc sol. sol'n, hex5.343No2.32-fcc sol. sol'n, hex5.343No2.32-28.0fcc sol. sol'n, hex5.348No2.32-45.5fcc sol. sol'n, hex5.348No2.32-45.5fcc sol. sol'n, hex5.344?2.32?

Note then that for americium the heat of formation rises suddenly to a more typical rare-earth value Resistivity studies on the americium hydrides would be interesting. Bulk studie, on curium still await a rather courageous worker; however, we can already say with some certainty that rare-earth behavior is expected, including a fully-localized magnetic moment comparable to that for the metal.

III. THE TRANSPLUTONIUM METALS

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As stated in the introduction, all the actinide elements beyond plutonium are lathanide-like, by virture of having localized f-electrons giving more-orless expected magnetic moments. However, these f's remain rather close to the Fermi level until after berkelium, in contrast to the rare earths. In looking, then, for rare-earth homologs, one is immediately struck by similarities to the early rare-earths, rather than to those elements directly above. A useful correlation has been noted by Johansson¹⁶, in which the localizations of the two series are compared as chemical and structureal homologues, rather than in the usual periodic fashion. The correlation is shown in Table II.

A State States



This pairing is not intended to be all-inclusive; the half-filled shell effect of course introduces major perturbations. However, the parallels are clear; the actinides beginning at americum have the dhcp structure at room temperature, transforming with temperature and also pressure to fcc. Heats of varporization and chemical properties are also quite similar. It has recently been shown¹⁷ that americium will transform under pressure to several progressively-more anisotropic phases, ending finally in the α -uranium structure. This behavior can be compared to that observed with cerium and praseodymium, and is due to f electrons, 4f or 5f, being close enough to the Fermi level to bond under sufficient pressure.

Other parallels will be noted below. Interest in the transplutonium elements has grown in proportion to their more recent availability. This is partly academic, of course; the joy and challenge of entering a new frontier is obvious. However, with the advent of fast breeder technology, there will eventually be considerable quantities of these elements produced. The challenge is to adequately characterize their properties now, so that later, uses may be found and reasonable chemical predictions can be made.

The work reported here actually began in 1972 and has only recently reached fruition in the compilation of the thermodynamic properties of all the elements, americium through einsteinium. An accurate number for the cohesive energy remains the single most important parameter that can be provided for both the experimentalist and theoretician. From this value, the complete thermodynamics can be eventually derived.

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A. Nature of the Thermodynamic Analysis

An accurate vapor pressure determination produces a heat of vaporization which is then essentially the cohesive energy. In addition to the heat of vaporization (the experimental value is always of course valid in the temperature range of study), an entropy of vaporization is produced, and since good spectroscopic data are now available through einsteinium, a condensed-phase entropy (at temperature) can be obtained from the data. There remains then the extrapolation of the data to 298K.

B. The Entropy Correlation - Metallic Radius and Magnetism

Ward and Hill¹⁸ have established a correlation relating the crystal entropy S°₂₉₈ to metallic radius, atomic weight, magnetic properties and electronic structure. This correlation permits calculation of reliable entropy values for unmeasured metals, based on comparison with a closely-similar metal for which there is measured data. The crystal entropy correlates rather smoothly with metallic radius, but notable exceptions are found for the rare earths and actinides; insight into why can be found in Fig. 5. The gaseous entropies shown deviate from smooth functions dependently on radius and molecular weight, because of very large magnetic contributions from the spins of the f-electrons. If the magnetic term is subtracted, the "non-magnetic" lower line is the result.

The early actinides do not follow this correlation in the condensed phases, because there is no model from which to account for the complex 5f-bonding in these metals. However, we again expect success at americium and beyond, since the f's are localized. The importance of the estimated crystal entropy lies in the fact that the S°₂₉₈ value is the basis-point for the free-energy functions for both solid and gas. From a reasonably accurate estimate of the solid entropy, the gaseous spectrosopic data and precise vapor pressure measurements, it is possible to calculate all the thermodynamic values for the metal, up to the highest temperatures of measurement. Experimental details and examples are given elsewhere²⁰⁻²⁸ and will not be repeated here. Rather, the properties of each metal will be briefly discussed in comparison to its rare-earth (proper) homolog, and as a final example, results from a new study on einsteinium, the last element with both long enough half-life and sufficient abundance from the decay chain to permit study, will be reported.

C. Americium

The perties of americium are clearly ware-earth-like and the gas is quite simply divalent; thus it is omewhat puzzling that theoretical correlations predict a low heat of vaporization. Ward and Hill¹⁸ correctly predicted the non-magnetic crystal entropy, later confirmed by experiment¹⁹. Ward, Miller and Kramer²⁰ measured the vapor pressure with high precision on very pure 241-metal. A heat of vaporization of 67.9 \pm 0.5 kcal/mol was combined with entropy data to show the effects of the large magnetic entropy transition upon vaporization. Knowledge of these effects helps explain at least some of the discrepancies between the measured and predicted values.

Ward, Kleinschmidt and Haire²¹ extended measurements into the liquid range, using the 243-isotope. The result was a perfect match and smooth extension of the 241-data.²⁰ An additional series of experiments were performed with various concentrations of americum dissolved in lanthanium. These Raoult's-Law studies gave

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the correct vapor pressure and heat of vaporization, demonstrating the ideality of this solution. It should be noted that lanthanum was used as the model for the crystal entropy of americium. In terms of the rare-earth/actinide pairing of Johansson (Table II), the entropy of praseodymium with the magnetic contribu ion removed would have given a similar result.

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D. Curium

The vapor pressure of high-purity 244-curium metal was measured by Ward, Ohse and Reul²² in both the solid and liquid phases. This work was reported as definitive in the IAEA compilation of the thermodynamics of the actinide metals.²³ However, the Tables A1.14 are improperly calculated and the ΔH°_{298} value given is incorrect; it should be 92.6 kcal/mol.

The crystal entropy for curium was calculated using gadolinium as a model, citing many similar physico-chemical properties as the basis for comparison. To have used neodynium (see Table II), with appropriate corrections for differing magnetism would have produced a similar value. However, there are also low-lying and contributing electronic states in both curium and gadolinium, and it is clear that the strong stabilization from the half-filled shell is an important factor.

E. Berkelium

Ward, Kleinschmidt and Haire²⁴ have measured the vapor pressure and thermodynamics of both solid and liquid 249-berkelium metal, using a 6 mg sample. This isotope is an intense soft-beta emitter, so data were taken primarily with the mass spectrometer; a set of calibrating targets was also prepared, and later counted accurately by means of the ingrowth of the californium daughter.

Neodymium was used as a crystal entropy model, because this element exhibits a similar heat of sublimation and melting point, is a trivalent metal with divalent gas, and has the same crystal structures. From the correlation in Table II, promethium would have perhaps been more appropriate, but no data exist as yet for that element. Berkelium metal develops essentially its expected magnetic moment of 9.72 Bohr magnetons; this value was employed to calculate the magnetic entropy. Published $\Delta Cp^{\circ}(T)$ values for neodyium were also used.²⁵ The heat of sublimation $\Delta H_{298}^{298} = 74.1 \pm 11.5$ kcal/mol agrees well with the theoretical predictions; these relationships will be discussed below.

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F. Californium

Ward, Kleinschmidt and Haire²⁶ have measured the vapor pressure of 249-californium metal, using a 2 mg sample. The thermodynamic data clearly establish californium as a trivalent metal, but with a heat of vaporization of only 46.9 \pm 0.3 kcal/mol, and with a vapor pressure midway between that for samarium and europium.

Californium is the first element in the sequence of actinides to show strong divalent tendencies. Its chemistry is remarkably similar to that for samarium, in agreement with the correlation in Table II. The progressive stabilization of the divalent ground state will be considered below. Several experiments at Oak Ridge and Los Alamos^{27,28} have indicated the possibility of a divalent form of the metal, at least in thin films; divalent surface states have been demonstrated for samarium.²⁹ We have performed Raoult's-Law vaporization studies with a 1.5 atom percent solution of californium dissolved in liquid europium, over the temperature range 958-1140K. The californium data points fell squarely on the trivalent line of Ref. 26, indicating that vaporization from a very dilute divalent solvent still does not induce divalency in californium. Thus the phase may only be scable (as in samarium) as a thin film.

G. Einsteinium

Raoult's-Law vapor pressure studies have recently been performed on a sample of le s than 100 micrograms of 253-Einsteinium dissolved in ytterbium, to form a 0.23 atom percent solution. Preliminary studies with a much smaller sample had indicated extreme volatility for einsteinium, ie., probable divalency. Previous experien. with Raoult's-Law evaporations from dilute solutions had been very good; however, in this case the vapor-pressure studies had to be done from the solid, because of the very high vapor pressures of both einsteinium and ytterbium.

Eighteen target exposures were taken over the temperature range 180°C to 529°C, plus one short high-temperature excursion to 580°C to view the einsteinium peak with the mass spectrometer and check for absence of oxide vapor species. These data points were corrected for radioactive decay due to the short half-life (20.5 days); correction was also made for sample depletion of the more volatile einsteinium (the element is so radioactive that deposits of a few picograms gave target counts over 50,000 alpha-counts per minute).

Temperatures were changed in random fashion, and in no instance was an apparent effect due to surface depletion or inhibited diffusion seen. The target data fell on a straight line, which, when plotted using Raoult's-Law for the solubility and assuming an ideal solution, gave vapor pressures compatible with the expected thermodynamics. Ytterbium was used as a model for calculating the crystal entropy, and the ΔC^{o}_{p} values for ytterbium were also employed. The full magnetic entropy of the $5f^{11}$ configuration for einsteinium was assumed. Spectroscopic data³⁰⁻³² from 29 levels to 39000 cm⁻¹, were used to calculate thermodynamic functions for einsteinium gas.

A heat of vaporization $\Delta H^{\circ}_{298} = 30.6$ kcal/mol was derived from the data, showing einsteinium to be truly divalent, with a volatility comparable to that for strontium.

H. Thermodynamics of the Transplutonium Metals

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Various theoretical correlations^{3,15,33} have had considerable success in predicting the physico-chemical properties and thermodynamics of the rare-earths but failed badly for the early (f-bonded) actinides. One might then expect the correlations to work well again for the more rare-earth-like late actinides, and (except for americium) this appears to be the case. Indeed, the correlations given by Samhoun³⁴ agree with the results given here for berkelium, californium, and einsteinium. However, there is no corresponding half-filled shell in the actinide series at this point, and the divalent state continues to be the preferred electronic configuration. LITERATURE CITED

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Figure Captions

- 1. Electrical resistivity for solid PuH1.93.
- 2. Electrical Resistivity for solid PuH2.65.
- 3. Summary of electrical and magnetic properties of PuHy.
- 4. Curiz-Weiss plots for three PuH_{x} compositions.

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- 5. Comparison of gaseous entropies for the lanthanides and actinides, at 298K and 1400K. ♥ Magnetic actinides; ♥ Non-magnetic actinides; ♥ Non-magnetic lan-thanides, ♥ Non-magnetic lanthanides; ♥ Low-lying levels removed.
- 6. Summary of heats of sublimation and crystal entropies for the 7th-row metals; left scale on graph-actinide dioxides, right scale - actinide metals. Solid dots: author's work.

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X =	1.93	2.16	2.42	2.53	2.65
s _o (Å)	5.359	5. 350	5.339	5.340	5.337
θ _{CW} (K)	44	55	59	61	66
C x 10 ⁻² (emu·K/mole)	9.3	9.0	7.0	8.0	9.2
μ _{ecī} (μ _B /mole)	0.86	0.85	C.75	0.80	0.85
$(\mu_{B}/mole)$	0.57	0.43	0.31	0.39	0.44

ELECTRICAL AND MAGNETIC PROPERTIES OF PuH_x

RESISTIVITY FEATURES:

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@ 4565	s	S	S		
e 100			?	S	S
@ 180	?	?	VW	W	S

S = strong W = weak VW = very weak ? = suggestion



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HEATS OF SUBLIMATION AND CRYSTAL ENTROPIES FOR THE 7th ROW METALS			
Element	S°,298 (cal/mole-deg.)	ΔH °298 (Kcal/mole)	
Ra ^N	16.4±0.2 ⁽¹⁾	(3)	
Ac ^{III}	14.8±0.2 ⁽¹⁾	(3)	
Th ^{IV}	12.76	142.7	
• Pa?	12.4 ⁽⁴⁾	136.4 ⁽⁵⁾	
U ?	12.0	127.0	
Np?	12.06	111.1	
● Pu?	13.42	82.0	
• Am ^{III}	13.2±0.2 ⁽¹⁾	67.9	
• Cm ^{III}	17.2±0.2 ⁽¹⁾	92.6	
• Bk ^{NI}	18.7±0.3 ⁽¹⁾	74.1	
● Cf ^{ill}	19.2±0.2 ⁽¹⁾	46.9	
● Es ^{II}	21.4±0.3 ⁽¹⁾	30.6	

- (1) From entropy correlation
- Los Alamos supported work

⁽³⁾No measured values

(4) Estimated

⁽⁵⁾Tentative data