CONF-8509147--4

Preparation, Properties, and Some Recent Studies of the Actinide Metals

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CONF-8509147--4

DE85 017710

ABSTRACT

The actinide elements form a unique series of metals. The variation in their physical properties combined with the varying availability of the different elements offers a challenge to the preparative scientist. This article provides a brief review of selected methods used for preparing µg to kg amounts of the actinide metals and the properties of these metals. In addition, some recent studies on selected actinide metals are discussed.

INTRODUCTION

The actinide metals form a unique series having properties ranging from those of the transition metals (3d, 4d, 5d elements) to the lanthanide metals (4f elements). Although in principle the actinide metals are expected to be a 5f series, interaction of the 5f electrons with the 6d and 7s electrons for the early members causes perturbations in their behavior. As this interaction changes across the series, so do the physical and chemical properties of the metals. When americium is reached in the series, under normal conditions the 5f electrons are localized and the behavior of the remaining metals becomes closer to that expected for a lanthanide metal or f-element. However, the behavior of the transplutonium metals are not mirror images of their lanthanide counterparts and greater deviations in properties are found between the metals than between comparable ionic compounds of these two series. It is the unexpected and changing behavior of the actinide metals that make them interesting scientifically and has prompted scientists to generate adequate theoretical interpretations to explain their behavior.

Scientific studies of the actinide metals have been hampered by lack of availability and also by their properties. Only three of the actinides are readily found in nature and all are radioactive and toxic. The elements are reactive, electropositive metals. In progressing across the series their availability rapidly diminishes and Es is the last element available in weighable (μg) quantities. These factors affect both the preparation and the studies that can be carried out on the metals. It is not surprising that the most extensive investigations have been done on the lighter actinide metals since they offer the least restrictions. The wealth of information that has been generated for uranium and plutonium metals has resulted from the applications that have been devised for these elements.

PREPARATION OF ACTINIDE METALS

General

Preparations of the reactive actinide metals is normally more difficult than the preparation of most of their compounds. The preparation and handling of the metals necessitates the use of a high-vacuum or an inert atmosphere and often special handling facilities. Their reactivity often creates serious problems in choosing a suitable reaction container for them. In the molten state the actinide metals can dissolve and/or alloy with many crucible materials. As the actinide elements form very stable oxides or halides, vigorous reducing agents and elevated temperatures are required for the reduction of their compounds to the metal. When the preparation of metal is carried out on a milligram scale, either due to availability or level of radioactivity, even high-vacuum systems may contain sufficient residual impurities (hydrogen, oxygen, water vapor, etc.) to react with the metal.

Several factors need to be evaluated in choosing which method is chosen for preparing a particular actinide metal. Some of these that must be addressed are: (a) the quantity of the actinide available; (2) the nature of the starting material; (3) the radioactivity and the half-life of the actinide; (4) the volatility and the melting points of the metal product; (5) the purity requirements; and (6) the preference of the experimenter and the availability of specialized equipment. This list is not inclusive and the order of importance varies with individual cases. For example, fused salt electrolysis or a pressure vessel reduction technique would not be the choice for producing sub-gram quantities of an actinide metal. Shielding or remote control operations may be more adaptable for one preparative technique than other. The volatility of the actinide metal will determine whether a distillation procedure is practical. Since the vapor pressures of the different actinide metals vary by several orders of magnitude (see Fig. 1) and their melting points range from 1133 to 2023 K, one particular preparative method will not be equally suited for all of the different actinide metals. If a high purity metal is required from a single procedure, then a selective distillation scheme may be chosen, whereas a pressure vessel reduction would be favored to prepare large quantities of a metal of moderate quality that could be further refined in a subsequent step. Finally, it may be difficult to find a laboratory equipped to perform equally well several different preparative methods.

The small quantities that are available for some of the actinides, or particular isotopes of an actinide, present special restraints. In such cases it is not possible to prepare a large quantity of metal that could be well analyzed and characterized and then be used for a number of scientific investigations. Instead, the preparation of the metal in these cases often becomes an integral part of an experiment where the major or entire preparation is needed and/or consumed. A comparable situation is encountered when the particular isotope has a short half-life. In such cases, the growth of the daughter product(s) in the metal may preclude multiple experiments over a long period of time.

In principle, many of the actinide metals can be prepared by more than one method, although one particular method may be preferred. Five preparative approaches and their applicability are presented below.

Reduction of Oxides

The first method consists of reducing an actinide oxide by an active metal at elevated temperatures (the metallothermic reduction of an oxide). The procedure can be used to prepare multi-microgram up to kilogram amounts of metal, as outlined in equations (1a), (1b), and (2) below:

$$An_2O_3 + 2\ La = La_2O_3 + 2\ An \qquad (1a)$$

$$2\ An_2O_3 + 3\ Th = 3\ ThO_2 + 4\ An \qquad (1b)$$

$$AnO_2 + 2\ Ca = 2\ CaO + An \qquad (2)$$

The first reaction represents the reduction of an actinide oxide with either lanthanum or thorium metal followed by volatilization and subsequent condensation of the actinide metal. Excess reductant, its oxide, and non-volatile impurities are left behind. Volatile impurities may be carried to the distilled product. Lanthanum metal is useful for the more volatile metals, Am, Cf, Es, and thorium metal having a lower vapor pressure, is preferred for reducing the oxides of the less volatile actinide metals, Pu, Cm, Bk, Ac. The volatility of U, Pa, and Np metals is too low for this preparative approach (see Fig. 1).

The above technique has the disadvantage that with very small quantities of actinide metal (< 5 mg) the condensed metal is likely to be in the form of thin films that are difficult or impossible to remove from the collecting substrate. The best results are obtained when an intimate mixture (pelletized) of the actinide oxide and the reductant metal is used. As the differences between the volatilities of the actinide metal, reductant metal, and/or the oxide of the reductant become smaller, the probability becomes greater that the actinide metal will contain some of the reductant or its oxide. In addition to the obvious differences in the vapor pressures of the La and Th reductants, differences in their melting points (La = 1193 K; Th = 1973 K) will also affect the reduction procedure. With lanthanum, the more favorable liquid-solid reaction will be encountered by 1200 K.

In general, this preparative approach provides an excellent preparative technique that can afford selective purifications and can yield high quality metal products. For the ultimate purity from a single distillation step, a well purified actinide oxide should be used as the starting material and an ultra-high vacuum ($<10^{-7}$ torr) system should be employed. It is advisable to discard the first deposits of the actinide metal, which may act as a getting agent and may also contain volatile impurities. The distillation of the remainder of the actinide metal is then carried out at a moderate rate while maintaining a relatively cool collection device. The latter condition minimizes contamination by and/or alloying with the collector material, and also minimizes difficulties in removing the product from the collector. Several reviews of this preparative procedure have been published [1-5].

Another approach to preparing actinide metals by the reduction of their oxides is represented by Equation (2). Typically, this procedure is used for actinide metals with moderate vapor pressures and on a larger scale (kg quantities). The reduction is carried out at ambient pressures in stirred molten salt baths (e.g., calcium chloride). The final products are usually separated mechanically rather than by distillation of the actinide metal as discussed above. Thus, the purity of the product is not as high as obtained by distillation and additional purification of the actinide metal is normally carried out. An application of this process is recycling plutonium metal, which because of its low melting point and moderate vapor pressure allows the reaction to be carried out below 900°C. In a separate procedure, a separation of americium (daughter product of ^{241}Pu) from the plutonium can be achieved by oxidizing the americium with $MgCl_2$ and then extracting americium chloride into a molten salt. This separation is achieved by equilibrium partitioning involving oxidation-reduction reactions of americium and plutonium between the molten salt and molten plutonium. Details concerning the calcothermic reduction of plutonium are available [6-9].

Reduction of Halides

The second method for preparing actinide metals involves the reduction of an actinide halide with an active metal at an elevated temperature (metallothermic reduction of a halide). This procedure has been used to prepare from microgram to kilogram quantities of actinide metals. The general reactions for reduction of fluorides are shown in equations (3) and (4) below:

$$AnF_3 \text{ (or tetrafluoride)} + 3\ Li = 3\ LiF + An \qquad (3)$$

$$AnF_4 + 2\ Ca = 2\ CaF_2 + An \qquad (4)$$

The third equation represents reductions done for smaller quantities of actinide, where the excess reductant and its halide are volatilized away from the actinide metal. In this procedure the volatility of the actinide metal must be low enough to permit the excess reductant and its by-products to be vaporized away from the actinide product. The reduction of a fluoride with lithium vapor provides the best combination for the approach. Oxygen free fluorides are required for preparing high quality metals and fluorination with fluorine or chlorine trifluoride is preferred over hydrogen fluoride. One of the most common problems with this technique involves oxide impurities in the product, usually due to incomplete fluorination of the starting material. To obtain high quality metals all reactants must be of the highest purity. Any non-volatile impurities will remain in the actinide metal. Many of the actinide metals can be prepared in this manner. However, the vapor pressures of Cf and Es metals (and presumably Fm, Md, and No metals) are higher than that of LiF which prevents its complete separation from the metal product. The vapor pressure of Am metal is only marginally lower than that of LiF. This technique is well suited for preparing up to 20 mg quantities of Cm or Bk metals. The procedure has the distinct advantage that even microgram amounts of actinide metal can be obtained in a bulk form rather than as a thin film as obtained from distillation. With larger quantities of actinides, it is more difficult to prepare completely oxygen-free fluorides and with higher alpha radiation levels, the neutron background from the (α,n) reaction with fluoride becomes appreciable. Reviews of this procedure have been published [1-4].

A closely related preparative technique is given in Equation (4) where the fluoride is reduced with an alkaline earth metal. The procedure is commonly used for preparing larger quantities of actinide metals. The volatility of calcium fluoride, which is similar to that of lanthanum metal, is lower than several of the actinide metals so that in this preparative approach the salt by-product is not distilled away. Normally, the highly exothermic reaction is carried out in a pressure reactor and the final products separated mechanically. Several industrial-scaled processes (kg amounts) use this preparative approach for Th, U, Pu, Np, and Am metals, and a subsequent refining of the actinide metal is often carried out to yield metals of sufficient purity for research. The process can be described using Pu as an example. In this case PuF_4 would be prepared and reacted with an excess of calcium metal in presence of calcium fluoride and iodine (added as a initiator). Sufficient heat is generated to melt the salt phase and allow the plutonium metal that is generated to coalesce in the bottom of a crucible. A comparison can be made between this process to the oxide reduction. The oxide process can give better yields, use a wider range of starting materials but does not normally provide purification. The fluoride reduction procedure requires starting materials of better quality, gives slightly lower yields, has a radiation problem from (α,n) reactions with fluoride, but can provide higher quality products. Procedures similar to that described for Pu have been used to prepare other actinide metals [6-9].

It is also possible to prepare actinide metals by reducing halides other than the fluorides with a reactive metal. One example of this is the reduction of multi-gram amounts of molten $PuCl_3$ with Ca metal [10]. An advantage of this approach is that the reaction is less exothermic and does not require a pressurized vessel. A disadvantage is that the $PuCl_3$ has a higher affinity for water, which is detrimental to the reduction reaction.

Reduction of an Actinide Carbide

An actinide metal can also be prepared by reducing its carbide with certain transition metals that form very stable carbides, which have low vapor pressures. The procedure has not seen widespread use but can offer advantages in certain situations. The reduction using tantalum as the reductant is shown in Equation (5) below:

$$AmC + Ta = TaC + An \tag{5}$$

The actinide metal it obtained by distilling it away from the mixture. This technique can be considered to be a general preparative technique but actinide metals with very low vapor pressures offer distillation problems (Th, Pa, U, and Np). The method would be applicable for preparing the transneptunium metals. The procedure does require the extra step of preparing the actinide carbide, which may be prepared by reacting the actinide oxide with carbon at high temperatures in a vacuum. A potential advantage for this process is that selective purifications can be achieved during both the preparation of the carbide and the reduction of the carbide to the metal. Details of the procedure have been published [2,4,11].

Iodide Transport-Thermal Reduction (van Arkel Process)

An iodide transport-thermal reduction procedure can be used to prepare and also refine some of the actinide metals. Requirements are that a volatile iodide of the actinide be readily formed, and that this iodide be thermally degradable to the metal. Both Th and Pa, which form tetraiodides, meet these requirements, whereas for the other actinides, the thermal stabilities of their iodides are too high or their vapor pressures too low for this method. In the procedure the carbides of Th and Pa are formed by carbothermic reduction of their oxides and then their iodides obtained by reacting the carbide with iodine. The preparation can be expressed by the following equations:

$$MO_2 + 2C = MC + 2\,CO \qquad (6)$$

$$MC + 2I_2 = MI_4 + C \qquad (7)$$

$$MI_4 \xrightarrow{\text{hot wire}} M + 2I_2 \qquad (8)$$

Gram-sized samples of Pa metal of excellent quality have been prepared using this procedure [4,11,12]. In the case of Pa metal, an inductively heated tungsten sphere served as the site for deposition of the metal. Decomposition of the iodide to form the metal releases iodine which then can react to form fresh tetraiodide. The temperature necessary for forming the tetraiodide from the carbide is ∿300°C and the tetraiodides decompose ∿1200°C.

Reduction to Metal by Electrolysis

Typically, reductions to the metal using electrolysis is carried out as a refining procedure for large quantities (kg) of impure actinide metals. This electrorefining process essentially consists of oxidizing the metal at an anode and reducing the actinide back to the metal at the cathode in a molten salt at elevated temperatures. The liquid metal generated at the cathode forms a pool in a channel around the anode and the final product is recovered in the form of a large ring after cooling.

Metal obtained in this fashion reaches purities of 99.96%. This procedure is largely used for preparing and refining Np and Pu metal.

The high melting point of thorium metal precludes its preparation by the above technique. However, small quantities of the metal can be prepared by electrolysis of ThF_4 in molten sodium chloride with the metal being obtained as dendrites on a molybdenum cathode [5].

Summary of Some Preparative Methods for Individual Actinide Metals

Actinium

Actinium metal has been prepared on a microgram scale by reducing $AcCl_3$ with K metal vapor [13], on the milligram scale by reducing AcF_3 with Li metal [14], and by reduction of Ac_2O_3 by Th metal [15,16].

Thorium

Thorium metal has been produced by reduction of ThF_4 with Ca metal or $ThCl_4$ with sodium metal [17]. It can also be prepared by electroreducing ThF_4 in molten NaCl [5] and by the iodine transport-thermal reduction technique [2,4].

Proactinium

Proactinium metal has been obtained by alkaline or alkaline earth metal reductions of PaF_4 [18-21]. An excellent method for preparing high quality metal is the iodine transport-thermal reduction procedure [2,4,12].

Uranium

The most common metal for preparing uranium metal is the reduction of UF_4 with calcium metal [22]. Electrorefining may be carried out in a LiCl-KCl salt mixture [23].

Neptunium

The usual procedure is to reduce NpF_4 with Ca metal [24,25]. An alternate approach in electrolysis of a Np halide in LiCl-KCl salt mixture [26]. The metal is also electrorefined in molten salts to improve purity. For preparation on the laboratory scale the reduction of NpC with tantalum and its subsequent distillation has been suggested [4].

Plutonium

Plutonium metal can be prepared by reduction of PuF_4, $PuCl_3$, or PuO_2 with Ca metal [6,10] or by the reduction of PuO_2 with Th metal followed by distillation of the Pu [4]. Tantalothermic reduction of PuC has also been reported [27].

Americium

Americium metal can be prepared by a pressure vessel reduction of AmF_4 with Ca or by metallothermic reduction of AmO_2 with La or Th metal [1-4]. The reductions and distillation of the oxide is a frequently used procedure and is used on the 25 gram scale [28].

Curium

Curium metal has been prepared by reduction of CmF_4 with Li vapor and by reduction of Cm_2O_3 with Th metal [29]. The latter technique is preferred for >100 mg quantities of Cm and the fluoride reduction for <20 mg amounts of ^{248}Cm [2-4].

Berkelium

In principle berkelium metal could be prepared by reduction of BkO_2 with Th metal. Due to the limited quantities of berkelium, the method used is the reduction of BkF_4 by Li vapor [3].

Californium

The higher vapor pressure of californium metal precludes the reduction of CfF_4 or CfF_3 with Li vapor. The usual procedure is to reduce Cf_2O_3 with La metal and then distill the Cf metal [3].

Einsteinium

The vapor pressure of einsteinium metal is even higher than that of Cf metal and makes the preparation of Es metal by reducing EsF_3 with Li vapor even more difficult. The best approach is to reduce Es_2O_3 with La metal and distill the Es metal. Due to the small quantities of Es available, only thin films on a substrate have been prepared [3].

Fermium, Nobelium, and Mendelium

As less than pg of these elements are available, bulk forms of the metal have not been prepared. The metals are expected to have high vapor pressures, which would sugget preparation of their metals by reduction of their oxides with La metal.

REFINING, SINGLE CRYSTAL GROWTH, AND PURITY

Some of the same techniques encountered in preparing the actinide metals are also used for refining them. For the volatile actinide metals, distillation techniques offer additional purification and can be either a single or multiple step process that offers selective separation from contaminants. Melting and casting the metals can remove volatile impurities and concentrate non-volatile contaminants as "slag". This latter technique requires larger quantities of metal and necessitates highly resistant crucible materials to avoid alloying with or being contaminated by the container material. Levitation melting avoids the problems of container material. Electrorefining is a good choice for some of the actinides but also requires larger quantities of the metal. Zone melting and electrotransport techniques are also useful for purifying larger quantities of metal. For small quantities of actinide metals, especially the transamericium metals, refining steps are normally not undertaken. Instead, the highest-purity reactants and the best operating conditions are chosen to produce the quality of metal desired.

The growth of single crystals is an art and normally requires larger quantities of metal. Single crystals have been obtained for Th-Cm metals during their preparation by vaporization, electrorefining, and the van Arkel process. For metals with multiple crystal forms (U, Np, Pu), single crystals have been formed by annealing under pressures. A discussion of growth of single crystals of actinide metals is available [4].

The purity of actinide metals available for study can vary widely. The purity of Th, U, Np, and Pu metals can be ≥99.96%. The purity of proactinium has been stated as ~99.3%. [4]. For the Am-Es metals, the question of purity becomes more difficult. Presumably, purities of 99.5 - 99.9% have been achieved but documentation is often difficult for these metals. Due to limited quantities of the transcurium metals, only cation impurities can be measured and typically these will be <200 ppm. Analyses for oxygen, nitrogen, and hydrogen are not made and the quality of the metal products are often subjectively assessed by their physical properties.

PROPERTIES OF THE ACTINIDE METALS

The actinide metals have widely varying physicochemical proprties unprecedented with regard to other groups of metals, especially in light of being cast as a 5f series of elements. This situation arises in part because of the extended wave functions and diffuse nature of the 5f electrons of the early members. Thus, the solid state properties of the actinide metals reflect a dualism of localized and itinerant 5f electrons for the series. Detailed explanations of the electronic nature and its ramifications on solid state properties of the actinides have been published [30-33]. The net result of this dual nature of the 5f electrons is the generation of two groups in the actinide series. The first group contains the Pa to Pu metals, and its members have their 5f electrons in an itinerant state. The remaining actinide metals are characterized by localized, non-bonding 5f electrons. This first group of metals is characterized by smaller atomic volumes, crystal structures with lower symmetries, higher cohesive energies, and very low or zero magnetic moments. In contrast, the transplutonium metals are characterized by high crystal symmetries, and have cohesive energy values and magnetic moments similar to those of the lanthanide metals. With the transplutonium metals, a complication arises in the series about the position of Es, where stabilization of the divalent metallic state is encountered. Because of such complexities, the properties of the actinide metals show both interesting parallels and contrasts when compared to the lanthanide metals.

The complex nature of the actinide metals can be seen in Figure 2, where their crystal structures, phase transformations, and melting points are summarized. The melting points of the metals range from 1133 to 2023 K. Even for the metals of Pa, U, Np, and Pu, where 5f electron participation in bonding is acknowledged, the melting points vary from 1840 down to 913 K. The decrease in melting points observed after curium has been explained by the onset of divalency which is achieved at Es. In contrast, the melting points of the lanthanide metals gradually increase across the series, except for the divalent metals Eu and Yb. Low-symmetry crystal structures, for which the lanthanides have no counterparts at ambient pressures, are observed for the light actinide metals, and plutonium is known to display six different phases between 298 and 913 K.

The crystal structures for the transplutonium metals, where the 5f electrons are localized, are more in accord with the structures observed for the lanthanide metals if differences between dhcp and hcp, and between fcc and bcc forms are neglected. However, there are distinct differences between the atomic volumes of the transplutonium and lanthanide metals as seen in Figure 3. Except for divalent Es metal, the actinide atomic volumes are all smaller than those for the Ln metals and an actinide metal can not be "matched" with a lanthanide metal as can be done with ionic compounds or semimetallic compounds of these elements. In ionic compounds of the transplutonium elements, their behavior, structure, and even lattice parameter can often be inferred from comparable lanthanide compounds. From the plot of lattice parameters for the sesquioxides (Figure 3) it can be seen that a relationship in structure-type, lattice parameter, and the metal ion's radius is established with a lanthanide located to the left of the actinide's electronic homolog. With the mononitrides (Figure 3), such a relationship is found with the transplutonium compound's electronic homolog. Such differences in behavior in part reflects differences in metal-metal spacings and interactions for the different materials. Johansson [34] has suggested correlating the transplutonium metals with lighter lanthanide metals (setting Am below Pr which places Es below Eu) rather than as electronic homologs. There are some merits to this shift, as structures are similar (both dhcp) and heats of vaporization and chemical properties are also similar. However, in this approach differences in atomic volume and metallic radii become even greater and the correlation in magnetic moments is lost due to a change in the ion configuration.

The heat of vaporization can be derived from experimental measurements of the actinide metal's vapor pressure as a function of temperature. The heat of vaporization is essentially a measure of the material's cohesive energy, when the electronic structure of the vapor species and solid phase are identical, and from the cohesive energy the thermodynamics of the substance can be derived. Ward and Hill [35] have established correlations which allow calculations of reliable entroy values for the metals, and together with available enrgy level data [36], the thermodynamics of the metals can be produced. The vapor pressures of the metals have been determined for actinide metals through Es and the results summarized [37,38]. In addition, extrapolations by Samhoun [39] and tracer experiments [40] have suggested values of 30-33 kcal$\cdot$mol^{-1} for the next three transeinsteinium metals. In Figure 4 are summarized the heats of vaporization for the An and Ln metals. Johansson et al [41] have given values for energy gained for the solid relative to the free atom for different metallic valences. For divalent metals the value is close to 40 kcal•mol^{-1}; for trivalent metals it is 100 kcal•mol^{-1}, and for tetravalent metals about 145 kcal•mol^{-1}. It is evident from Figure 4 that the lanthanide and transplutonium metals qualify as trivalent metals except for the divalent metals, Eu, Yb, Es, Fm, Md, and No. The higher heats for the earlier actinide metals reflect the effect of partial 5f bonding, where the concept of metallic valence is not applicable. The good correlation of heats for Gd and Cm metals reflects the similarities in properties and stabilization of the trivalent state brought about by a half-filled f shell ($f^7d^1s^2$) configuration. Shifting the first five transplutonium metals to the left to place Am under Pr [34] does improve the correlations between the heats of vaporization for these metals, except for the case of Cm metal which has a half-filled 5f shell.

The compressibility of the actinide metals also reflects the nature of their 5f electrons. The early members of the series have low compressibilities (high bulk moduli) which bear some resemblance to the d-transition metals' compressibilities [42]. The first four transplutonium metals have compressibilities of the same order as those of the lanthanide metals [43].

Magnetism and superconductivity are also related to the degree of delocalization of 5f electrons in the actinide metals. Metals with highly localized 5f electrons are characterized by temprature dependent magnetism and the absence of superconductivity. Their magnetic moments agree well with moments calculated by simple L-S coupling or intermediate coupling, and with moments of the lanthanide metals having the same ion configuration. Metals with itinerant 5f electrons show small temperature-independent magnetic moments and are conducive to superconductivity. The metals Pa, U, and Am are superconducting; NP and Pu metals are anamalous in their behavior. Discussions on magnetism in the actinide metals has been published [30,31,44-46]. Magnetic measurements on Cf metal, the highest member of the series on which measurements have been made, have recently reported [47].

RECENT STUDIES OF THE ACTINIDE METALS

Einsteinium Metal

In the absence of direct structural correlations of atomic volumes or metallic radii between the lanthanide and actinide metals, it is difficult to use the lanthanide metals for predicting actinide metal structures. The atomic volumes of the actinide metals are all smaller, except for divalent Es metal (see Figure 3). Neither the smarium rhomohedral structure nor the hcp (as opposed to the dhcp) structure known for the second half of the lanthanide series, have been established for the actinide metals. Recently, a hcp-type structure with $a_0 = \sim 0.398$ and $c_0 = \sim 0.650$ nm has been observed in thin films of Es metal formed by distilling the metal and analyzing the condensed phase by electron diffraction [48]. Previously, only a fcc structure with $a_0 = 0.575$ nm has been reported for Es metal [49]. A hcp and a fcc form for Es metal are comparable to two structure forms known for Yb metal [50,51]. However, because of potential difficulties associated with analyzing thin metal films and the possibilities of forming impurity stabilized phases, caution must be exercised in assigning this hcp structure to Es metal. If Es metal does indeed exhibit a true hcp phase, it is expected that the phase arises because of the divalent nature of the metal, rather than reflecting a change in structural sequence as observed at Gd metal in the lanthanide elements.

Studies of the Metals Under High Pressure

Both temperature and pressure are thermodynamic variables which can affect interatomic distances. Based on the magnitudes of pressure and temperature that can be achieved experimentally in laboratories, a greater change in interatomic distances in the metals can be brought about by applying pressure. A review of high pressure studies on the lighter actinide has been published [42]. Dramatic changes with pressure have not been observed for the metals through Pu. The alpha phases of these metals are retained up to moderately high pressures and very high pressures are needed to bring about a phase transition. The application of pressure can reduce the number of phase transitions these metals will undergo as a function of temperature and such studies provide information about their bulk modului.

A significant change in behavior with pressure has been noted with the first four transplutonium metals. By applying pressure on these metals the normally localized 5f electrons can be forced to participate in the metallic bond; that is, they can become itinerant like the 5f electrons in the lighter actinide metals. Such a transition with prssure was observed first with Am metal [52] and more recently with Cm [53], Bk, and Cf [54] metals. Additional studies on Am metal [55-57] have also been carried out.

Applying pressure on the transplutonium metals can bring about at least three changes: (1) dynamic compression; (2) structural changes;

and (3) collapse in volume. These changes can occur either sequentially or in combination. Dynamic compression reflects adjustment of packing volume in the metal's structure(s). From such data a bulk modulus can be extracted which is a quantitative measure of the change and can be used for a group classification of the metal. Structural changes with pressure can either represent slight modifications to give more favorable packing arrangements, or represent the participation of f electrons in the metallic bonding. The pressure at which the transplutonium metal's 5f electrons begin to participate in metallic bonding is termed the delocalization pressure.

For the Am-Cf metals, in progressing across the series toward Cf it would be expected that: (1) the density of the 5f electrons near the bonding orbitals diminishes, requiring higher pressure to force delocalization; and (2) the electronic configuration of a particular metal would have an affect on the delocalization process. This is exactly what is observed for the transplutonium metals, as can be seen from Figure 5 where their phase behavior as a function of pressure is summarized. The dashed line in Figure 5 ties together the pressures at which the α-uranium-type structure appears (delocalization pressure). It is apparent that Cm metal has both the highest dhcp-fcc transition pressure as well as the highest delocalization pressure. These higher pressures required for Cm metal reflect the added stability resulting from its half-filled 5f state (ground state - [RN] $5f^7 6d^1 7s^2$). It has also been observed that the change in volume accompanying delocalization is the largest for Cm metal among these four metals [53].

It can be noted from Figure 5 that both Am and Cf metals have an additional transition as compared to Cm and Bk metals. One study on Am metal [57] has questioned whether the Am-III phase is monoclinic [57]. Recent examinations of Bk-Cf alloys under pressure have explored the existence of the Cf-III phase in Bk-Cf alloys [43]. The formation of low-symmetry crystal phases under pressure has also been observed for some lanthanide metals (Ce, Pr, Nd, and Sm) [59]. For Ce and Pr metal the phases has also been identified as the α-uranium-type structure.

The next transplutonium metal, divalent Es metal, would be an interesting metal to study under pressure as it may be possible to induce a change of valence (two to three) with pressure. Such experiments would be extremely difficult due to the radioactivity of Es isotopes. Studies of the divalent metals, Eu and Yb, under pressure have not observed the formation of trivalent metals but rather an intermediate valence for the metals [59]. Johansson et al [41] have suggested Es metal under pressure may even form the Sm-type metal structure.

One other useful finding has come from the high pressure studies of the transplutonium metals. Although two metallic phases (α=dhcp; β=fcc) have been known for the transplutonium metals under normal pressure, the atomic volumes or radii obtained from the lattice parameters for the fcc forms for Cm, Bk, and Cf metals were considerably larger than these values calculated for the dhcp forms. In contrast, parameters for both structural forms of Am metal yielded the same atomic volume or metallic radius. The lattice parameters reported for the fcc form of Cm and Bk metals were also very similar to lattice parameters reported for the mononitrides of these elements, causing some concern about the parameters of the high temperature phases reported for the metal.

Recently, the lattice parameter of CfN has been determined [60] and its lattice parameter is also nearly identical to the literature value previously reported for the fcc form of Cf metal.

It appears such the problems have been resolved by data obtained during pressure studies of these metals. In Table I are listed the lattice parameters, radii and atomic volumes for the different forms of the transplutonium metals obtained under normal pressure. The high temperature forms were obtained at room temperature by quenching the metals from elevated temperatures. The "pressure quenched" lattice parameters were obtained from the fcc forms of these metals which were retained after pressure on the metals was released [62,63]. From Table I it is apparent that the radii and atomic volumes for the fcc phases from the pressure studies are nearly identical to those reported in the literature for the dhcp forms of Cm, Bk, and Cf metals. Thus, it appears that the fcc forms of these metals obtained from elevated temperatures retained an expanded lattice at room temperature, and in reality each transplutonium metals exhibits the same atomic volume for each of its two crystal forms.

ACKNOWLEDGMENT

This work was sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under contracts DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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FIGURE AND TABLE CAPTIONS

Figure 1. Vapor Pressures of the actinide metals as a function of temperature.

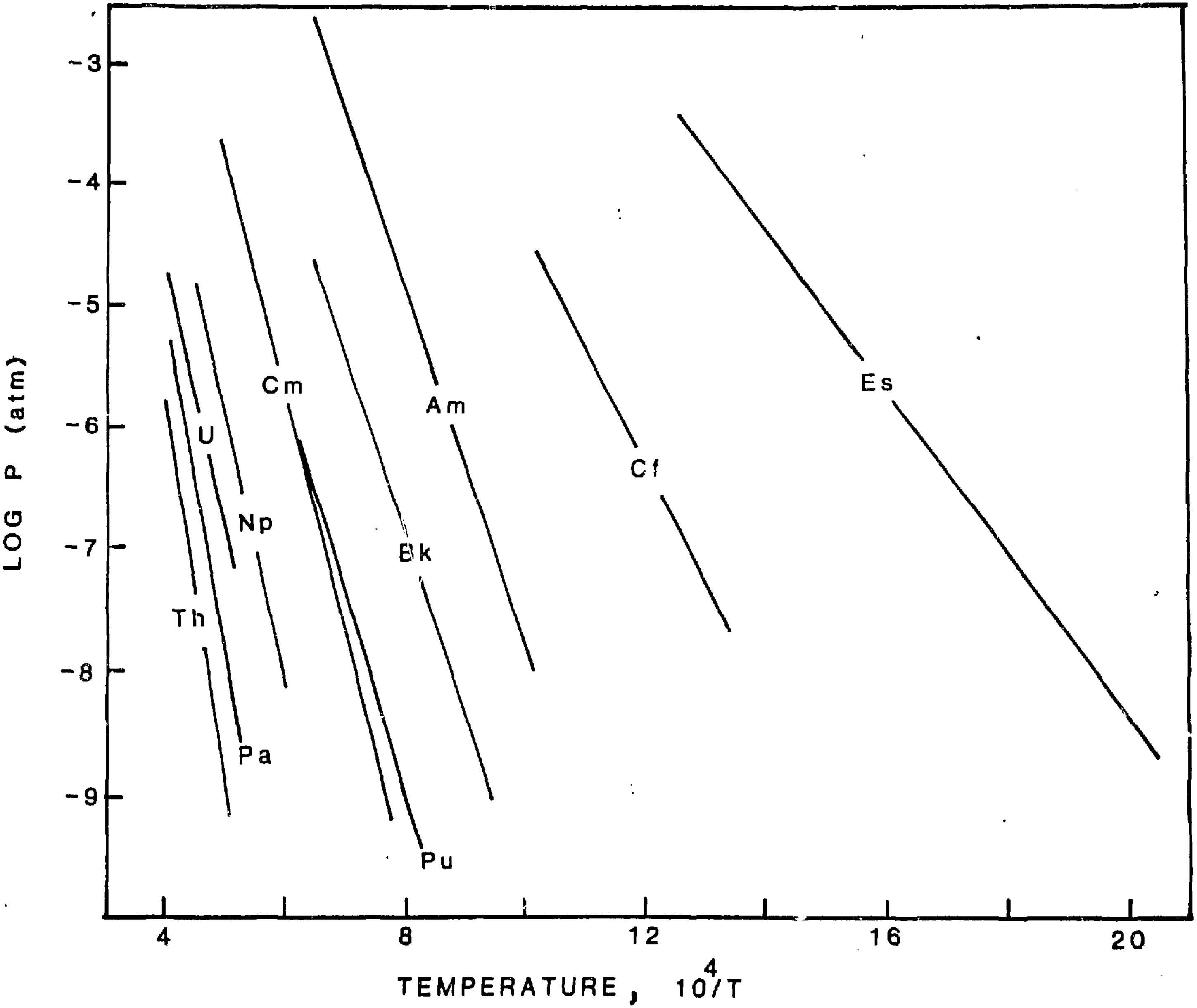
Figure 2. The melting points and phases of the actinide metals.

Figure 3. Lattice parameters of the lanthanide and actinde sesquioxides and mononitrides and the atomic volumes of the actinide and lanthanide metals.

Figure 4. The enthalpy of vaporization for the lanthanide and actinide metals.

Figure 5. Metallic phases of the first four transplutonium metals as a function of pressure.

Table 1. Lattice parameters, radii, and atomic voulmes of selected transplutonium metals prepared by thermal and pressure treatment.


-3
-4
-5
-6
-7
-8
-9
LOG P (atm)
4
8
12
16
20
TEMPERATURE, 10⁴/T
Th
Pa
U
Np
Cm
Pu
Bk
Am
Cf
Es

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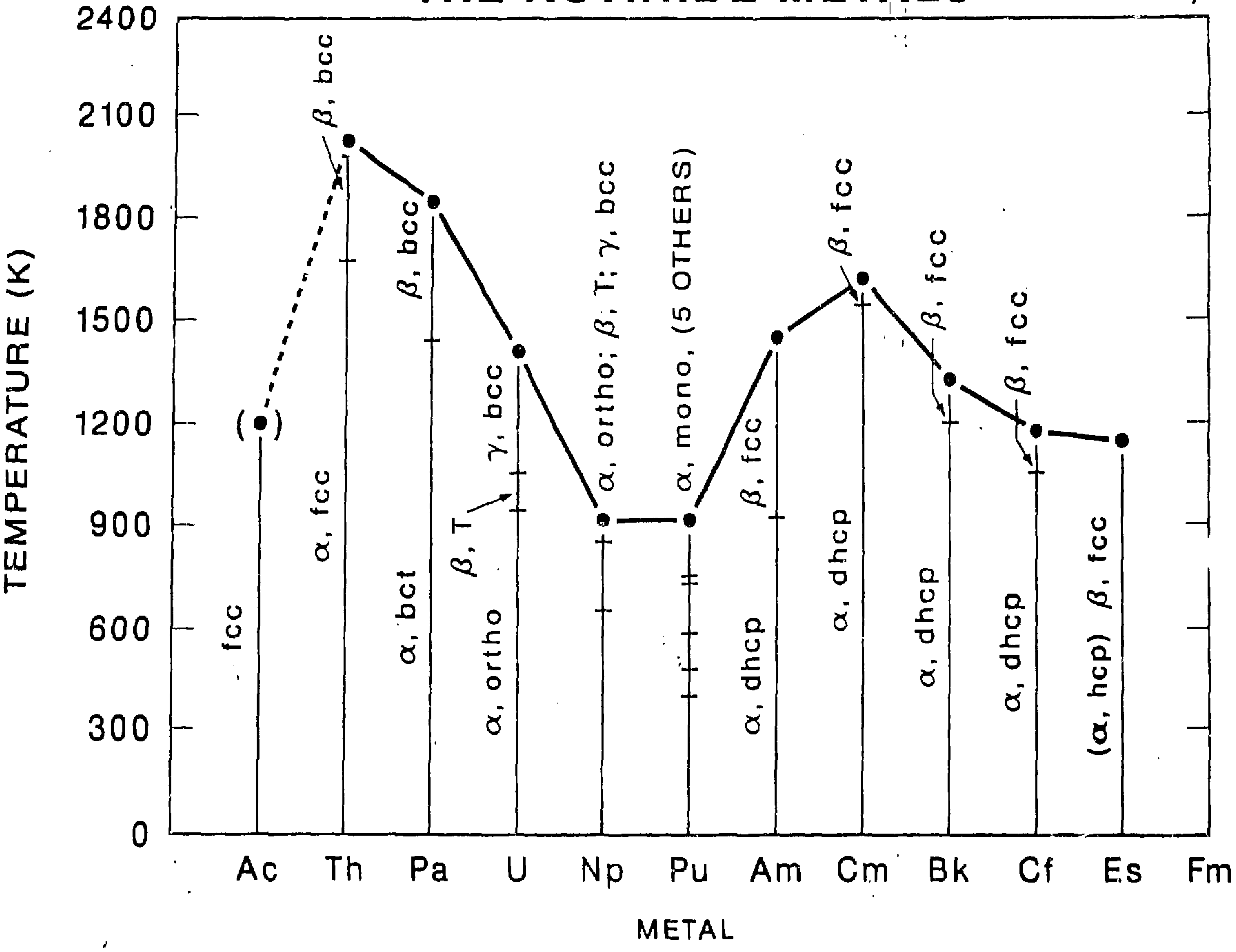
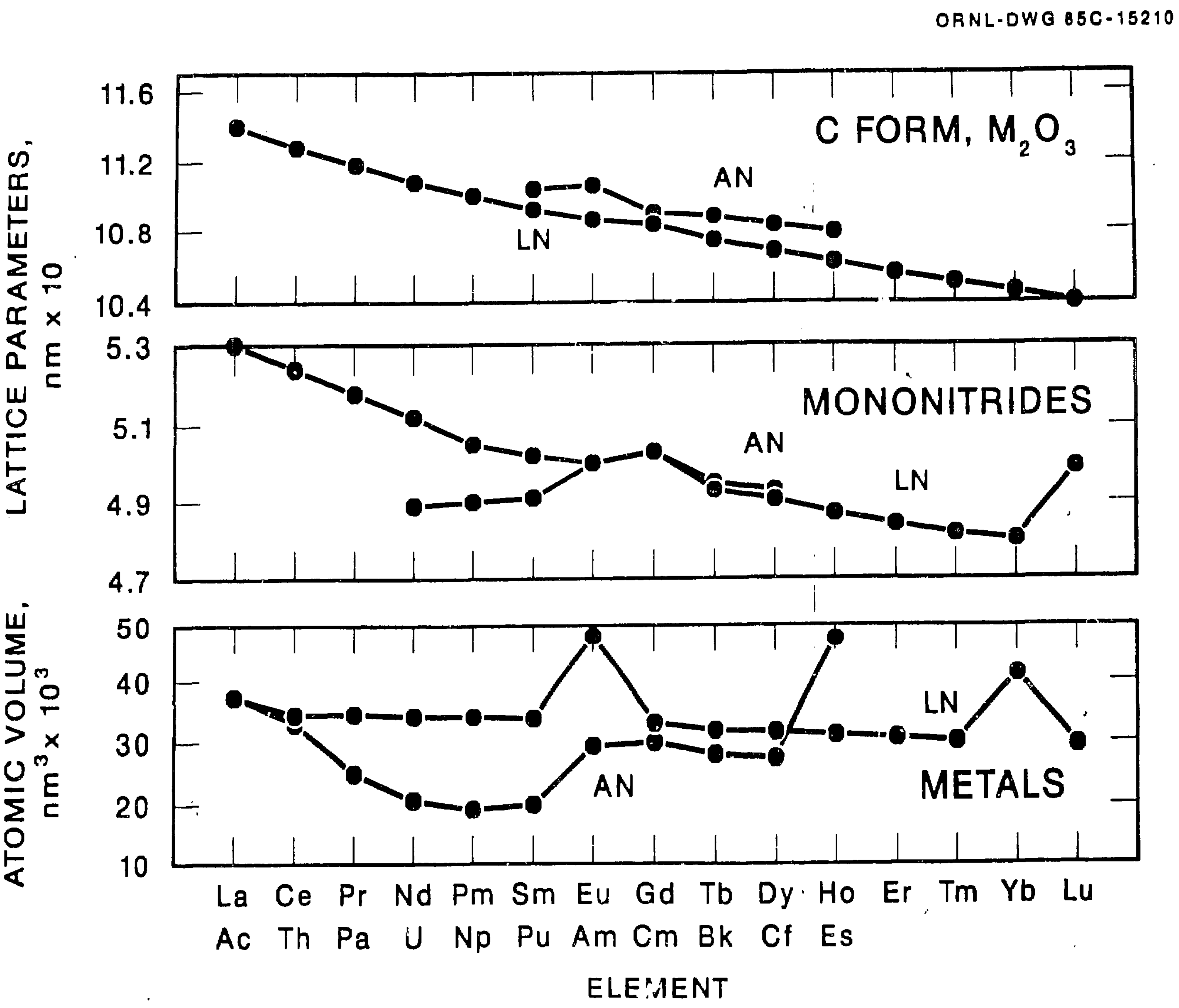
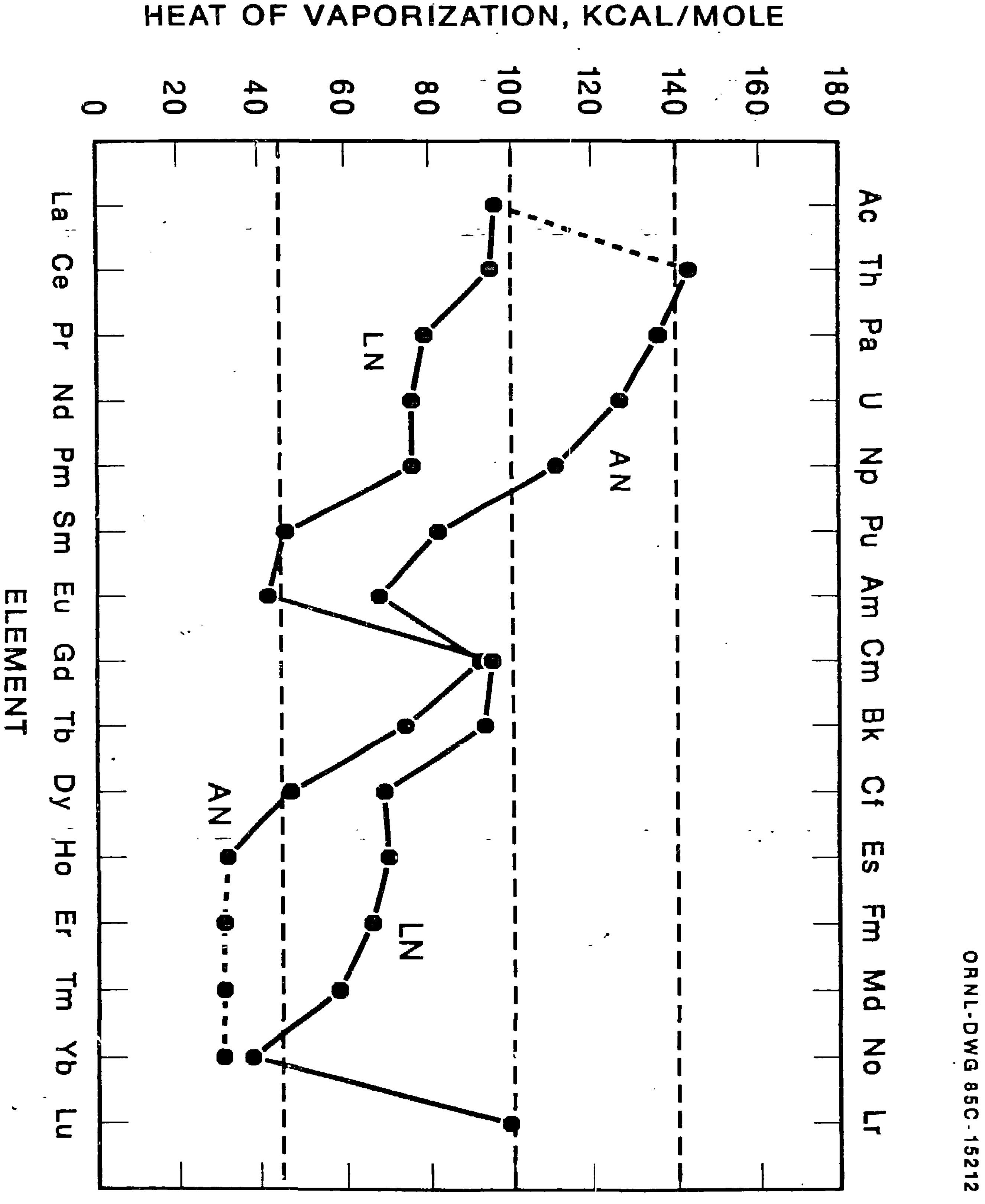
MELTING POINTS AND PHASES OF THE ACTINIDE METALS




ORNL-DWG 85C-15210
LATTICE PARAMETERS, nm x 10
11.6
11.2
10.8
10.4
C FORM, M_2O_3
AN
LN
5.3
5.1
4.9
4.7
MONONITRIDES
AN
LN
ATOMIC VOLUME, $nm^3 x 10^3$
50
40
30
20
10
LN
AN
METALS
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Ac Th Pa U Np Pu Am Cm Bk Cf Es
ELEMENT


ORNL-DWG 85C-15212
HEAT OF VAPORIZATION, KCAL/MOLE
0
20
40
60
80
100
120
140
160
180
Ac
Th
Pa
U
Np
Pu
Am
Cm
Bk
Cf
Es
Fm
Md
No
Lr
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
ELEMENT
AN
LN
AN
LN

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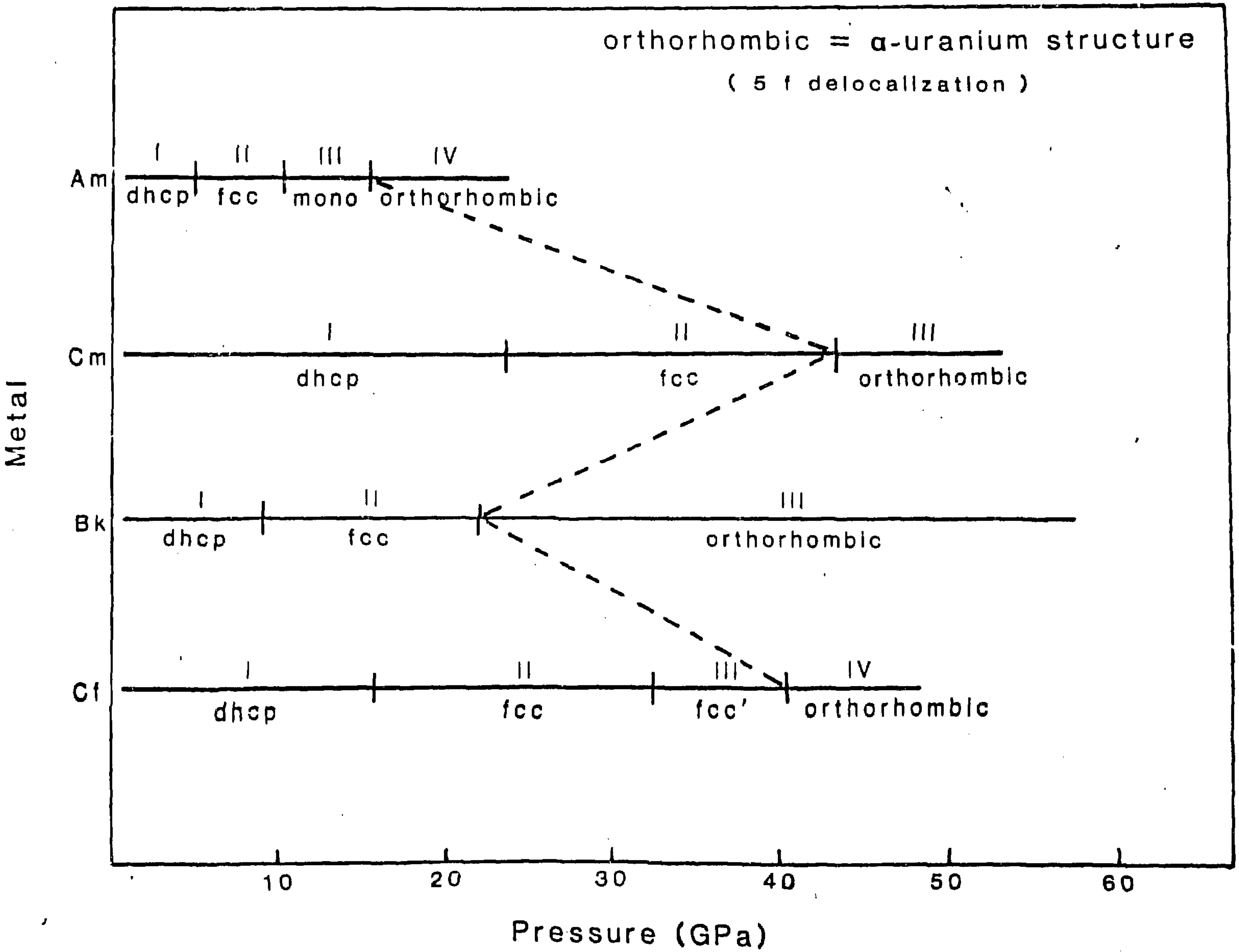
Metal Phases as a Function of Pressure



LATTICE PARAMETERS AND RADII OF TRANSPLUTONIUM METALS

Metal	L.P. dhcp*	Radius*	Atomic Vol.*	L.P. fcc*	Radius*	Atomic Vol.*
					"<u>Thermal Quench</u>"	
Am	a_0 = 3.474 c_0 = 11.250	1.732	29.30	4.804	1.730	29.30
Cm	a_0 = 3.492 c_0 = 11.338	1.742	29.93	5.07	1.79	32.6
Bk	a_0 = 3.416 c_0 = 11.069	1.704	27.96	4.997	1.767	31.19
Cf	a_0 = 3.384 c_0 = 11.040	1.694	27.37	4.94	1.75	30.1
					"<u>Pressure Quench</u>"	
Cm				4.93	1.74	30.0
Bk				4.82	1.70	28.0
Cf				4.78	1.69	27.4

*L.P. = lattice parameter(s) nm x 10; radius in nm x 10; atomic volume in $nm^3 \times 10^3$.