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**PREPARATION OF ^{147}Pm METAL
AND DETERMINATION
OF THE DENSITY AND MELTING POINT**

JANUARY 1969

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PREPARATION OF ^{147}Pm METAL AND DETERMINATION
OF THE DENSITY AND MELTING POINT

By

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ABSTRACT

Four 30 g buttons of ^{147}Pm metal were prepared by Ca reduction of anhydrous PmCl_3 . Additional purification was obtained by vacuum distillation of Ca and Mg impurities. The density of the metal was found to be $7.22 \pm 0.03 \text{ g/cm}^3$ and the melting point, $1168 \pm 6 \text{ }^\circ\text{C}$.

Promethium metal was found to be highly reactive toward impurities in the protective argon atmosphere. The equipment used within the glove-box was designed for evacuation and backfill with protective argon, but rapid radiation damage or radiation-induced ozone damage of nonmetal tubing, gaskets and other sealants used in the equipment created continuous atmospheric containment problems.

The Pm metal obtained in this work does not represent the optimum obtainable by the method. Promethium metal containing less than 200 ppm total impurities could reasonably be anticipated.

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PREPARATION OF ^{147}Pm METAL AND DETERMINATION
OF THE DENSITY AND MELTING POINT

E. J Wheelwright

INTRODUCTION

In 1963, Fritz Weigel reported the preparation of approximately 50 mg of promethium metal by the reduction of anhydrous PmF_3 with Li vapor.^(1,2) He obtained approximately 50 Ci ^{147}Pm contaminated by 50 mg Sm, 40 mg Nd and 7 mg ^{241}Am from the Isotopes Division of Oak Ridge National Laboratory, removed the Sm and Nd by alpha hydroxyisobutyrate elution from Dowex 50, X-12 resin, and removed the ^{241}Am by selective elution from Dowex 1, X10 resin with 8M ammonium thiocyanate. The ^{147}Pm was precipitated with HF, washed with distilled water, centrifuged and dried over P_2O_5 . Reduction was performed in tantalum at 2.7×10^{-6} mm Hg pressure by induction heating. Purity of the metal was not given but the melting point was reported to be 1080 ± 10 °C. Two years later, Weigel reported additional work with similar quantities of Pm. The method of preparation was the same, but again the purity of the metal product was not reported. The melting point was revised to 865 ± 40 °C.⁽³⁾ The Pm metal was perhaps impure and the revised melting point, observed by means of McWhan's "solder-rupture" method, might have resulted from a rupture of the Pm bead at the solid-solid phase transition temperature rather than from true melting. Consideration should be given to the problems encountered in the purification, reduction and measurement steps performed with only 0.05 g of Pm when evaluating the results obtained by Weigel.

Under AEC sponsorship, efficient separation processes have been recently developed at Battelle-Northwest Laboratory and more than 4 kg of high purity ^{147}Pm have been obtained.⁽⁴⁻⁶⁾ Programs are now in progress to study the

chemistry of this heat generating radioisotope and to carefully measure specific physical and chemical properties. The density and melting point of the metal, paramount values required for proper evaluation of ^{147}Pm metal for remote or portable energy-source applications, were among the first physical property measurements made.

CONCLUSIONS

Four 30 g buttons of ^{147}Pm metal were prepared by Ca reduction of anhydrous PmCl_3 . Additional purification was obtained by vacuum distillation of Ca and Mg impurities. The density of the metal was found to be $7.22 \pm 0.03 \text{ g/cm}^3$ and the melting point, $1168 \pm 6 \text{ }^\circ\text{C}$.

Promethium metal was found to be highly reactive toward impurities in the protective argon atmosphere. Funding did not permit identification of the specific reactants or reaction mechanism. Self heating and the intense beta decay could contribute toward an "activated" surface whereon reaction rates are accelerated and normally prohibited reactions become energetically possible. The equipment used within the glove-box was designed for evacuation and backfill with protective argon, but rapid radiation damage or radiation-induced ozone damage of nonmetal tubing, gaskets and other sealants used in the equipment created continuous atmospheric containment problems.

The Pm metal purity obtained in this work does not represent the optimum obtainable by the method. Development of agitated bed chlorination equipment would eliminate fused particles from the PmCl_3 product, and thereby allow more intimate mixing of the reduction reactants and contribute to both higher button yields and purity. The vacuum purification step could be improved by use of more radiation resistant equipment and by continuing the outgasing for several hours at a lower pressure. Promethium metal containing less than 200 ppm total impurities could reasonably be anticipated.

The inclusion of the Pm metal melting point with those of the other lanthanide elements in Figure 10 provides an interesting correlation of the melting points of these elements.

Engineers conducting comparative evaluations of the various radioisotopic heat sources need to consider three new facts about ^{147}Pm .

1. Technology is in hand to produce ^{147}Pm metal sources in gram to kilogram sizes. The metal can be machined to any desired configuration or can be cast directly into the primary containment capsule.
2. The maximum operating temperature (without melting) of ^{147}Pm metal is at least 100 °C higher than previously considered.
3. Theoretical densities of 7.62, 7.43 and 6.84 g/cm³, respectively, are given for the A, B and C crystal forms of Pm_2O_3 .⁽⁷⁾ Apparent nonreversible phase transitions occur at 950 °C for the C → B transition and at >1600 °C for the B → A transition. However, the engineer must consider the "practical" density that can be achieved within the inside dimensions of the primary capsule, not the theoretical density of heat source material. The maximum density demonstrated to date is 6.6 g/cm³ — obtained by pressing and sintering a series of pellets and dropping them into the primary container. Since Pm metal can be machined to exact tolerances or cast directly into the primary container, the "practical" density for Pm metal approaches very closely to 7.22 g/cm³. The power density of pure Pm metal and of pure oxide at a series of densities are:

- Pm Metal

$$7.22 \text{ g/cm}^3 = 2.40 \text{ W/cm}^3$$

- Pm Oxide

$$6.6 \text{ g/cm}^3 = 1.89 \text{ W/cm}^3$$

$$6.8 \text{ g/cm}^3 = 1.95 \text{ W/cm}^3$$

$$7.0 \text{ g/cm}^3 = 2.00 \text{ W/cm}^3$$

$$7.2 \text{ g/cm}^3 = 2.06 \text{ W/cm}^3$$

$$7.4 \text{ g/cm}^3 = 2.12 \text{ W/cm}^3$$

Applying demonstrated technology, Pm metal sources would have approximately 0.5 W/cm^3 higher power densities than oxide sources. Even with improved technology yielding oxide sources in the 7.0 to 7.2 g/cm^3 range, the metal would retain an advantage of 0.3 to 0.4 W/cm^3 .

PREPARATION OF METAL

Because of requirements of absolute containment and minimization of personnel exposure, all work with Pm was performed in a stainless steel glove-box covered with 1/2 in. of lead and equipped with both lead impregnated gloves and 1 in. thick lead-glass viewing windows. This glove-box facility, shown in Figure 1, is routinely used as a Pm_2O_3 conversion facility. In anticipation of the high reactivity of Pm metal in air, the smaller module of the glove-box was isolated by activation of the interconnecting air-lock and purged continually with dry argon. However, the box could not be made completely leak-tight and the required negative differential pressure in the box resulted in continuous contamination of the box argon atmosphere by air.

Two alternate methods were considered for the preparation of the metal:

1. Conversion of Pm_2O_3 to an anhydrous halide followed by a "bomb" reduction to the metal with calcium plus an iodine booster.
2. Direct reduction of Pm_2O_3 with La metal followed by distillation of the Pm metal.

The first method has been used to prepare metallic plutonium as well as all of the light lanthanide metals (except Sm) and represents in-house technology. The second method has been used to prepare both Sm and Am metal, has greater promise to yield ultra high purity metal, but requires

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FIGURE 1. Lead-Shielded Glove-Box Facility Utilized for the Pm Metal Work

some moderately expensive tantalum equipment and does not represent in-house technology. As a result of these limitations, work on Method No. 2 was deferred and a strong effort initiated to develop Method No. 1. Nd was used as a stand-in for Pm during process development and equipment testing.

PREPARATION OF ANHYDROUS HALIDE

The anhydrous fluoride has been the halide of choice for the preparation of lanthanide metals.⁽⁸⁾ Good yields are reported for the fluorination of the sesquioxide with $\text{NH}_4\text{F} \cdot \text{HF}$ or HF directly, and the salts are reasonably stable in air. However, the utilization of either fluorinating agent in a highly contaminated stainless steel glove-box, containing pyrex glass equipment used for other work and glass viewing windows, did seem to present problems that might not exist in the chloride system. Chlorination of metal oxide with CCl_4 at elevated temperatures is reported to give good results.^(9, 10)

Initial attempts to prepare anhydrous NdCl_3 by pumping CCl_4 directly into the bottom of a heated vertical quartz tube containing Nd_2O_3 , supported at midpoint of the furnace by a fritted disc, failed to yield satisfactory results. The CCl_4 vaporized properly and passed through the frit as a vapor, but the heat of reaction fused the charge and prevented complete conversion. At lower furnace temperatures, the reaction could not be initiated. When an argon carrier gas was used to transport CCl_4 vapor into the furnace tube, dilution and much slower addition of the chlorinating agent controlled the reaction rate and prevented sintering of the charge. This was accomplished by bubbling argon through a flask containing CCl_4 and hence into the bottom of the furnace tube. The flask was maintained at 65 °C by electrical heating to increase the flow of CCl_4 . When the furnace temperature was increased from 450 to 600 °C in 50 degree increments spaced 8 hr apart, the

reaction reached completion in approximately 30 hr and produced a free-flowing crystalline powder. The reaction is reported to proceed as:⁽¹⁰⁾

and/or

Care must be exercised to hold the furnace temperature below approximately 620 °C or the charge will start to sinter. Sintering is deleterious when unchlorinated oxide particles become coated with fused chloride and protected from complete chlorination. Unfortunately, the sintering temperature must be approached to ensure complete chlorination. Complete chlorination was verified by placing a few milligrams of the chloride powder in 5 ml of water. Unreacted oxide or oxychloride does not dissolve in water

Off-gas from the chlorination contains phosgene and, near the end of the reaction, chlorobenzene species. The off-gas was scrubbed with caustic to remove reaction products which might be corrosive to stainless steel. In addition, it was necessary to periodically examine the off-gas system to ensure against sufficient condensation and solidification of chlorobenzene species to block the flow of argon.

Only one problem was encountered when Pm_2O_3 was chlorinated. Self-heating, coupled with poor thermal conductivity, caused some sintering in the center of the charge. The sintered lumps proved difficult to pulverize in preparation for subsequent processing and conceivably contributed to lower than optimum yield and purity. This problem is not serious and could be eliminated by procurement of equipment which would continuously mix the charge during the chlorination step.

METAL PREPARATION

Several active metals could be used to reduce PmCl_3 or the NdCl_3 stand-in to metal. Calcium was chosen because high purity metal, as small granules, is available at this laboratory and the technology is in hand. Preparation for the reduction is made by mixing the proper quantities of the metal chloride with granular calcium and iodine, tamping the mix into a domed-bottom magnesia crucible, and sealing the crucible inside a small pressure bomb. In the initial reductions with stand-in Nd, the annular space between the crucible and bomb was filled with fine sand. When the loaded bomb is heated to a surface temperature of 600 to 800 °C, two reactions take place:

The exothermic Ca-I_2 reaction takes place first and yields sufficient heat to initiate the second reaction and to keep the mixture molten long enough for the metal to properly separate from the slag and collect in a pool at the bottom of the container. Initiation of the reaction or "firing" of the bomb can be detected by a sharp increase in temperature if the bomb is equipped with a thermocouple well, or by a sharp decrease in the pressure (exhaustion of vaporized I_2) if the bomb has a pressure gauge.

Only one problem was encountered in the development of the reduction process. Because of relatively low viscosity and/or melting point, the chloride slag was able to penetrate through the magnesia crucible and solidify in the surrounding sand, producing a concrete-like mass frozen in the bottom one-third of the bomb. Recovery of the button could be accomplished only after considerable hand work with a hammer and chisel. The button recovery problem was solved by employment

of a thin-wall stainless steel can designed to contain the crucible plus surrounding sand and slip, with close tolerances, into the pressure vessel. After the charge had "fired" and the bomb had been cooled and opened, the can was withdrawn from the bomb by use of a pair of needle-nose pliers. A few hammer blows deformed the can wall and fractured the contents sufficiently that they could be poured out of the can. The button was then easily identified and recovered.

Figure 2 shows a sealed bomb after it has been fired and the pressure decreased from approximately 40 psi to near zero. The screw jack holder on the right is used to raise or lower the induction coil. The glowing bomb rests upon an alumina cylinder which stands erect in the groved face of a water-cooled metal base. As a result of subsequent testing, the 14-turn induction coil was replaced by an 8-turn inductor; achieving improved load coupling within the range of the 15 kW, 10 kc motor generator power unit.

Following the development of the equipment and procedure but prior to any Pm reductions, three test reductions were made using NdCl_3 prepared as previously described. In each test, the charge containing 60 g NdCl_3 , 24 g Ca and 40 g I_2 was mixed, tamped into the MgO crucible, and sealed within the bomb. The bomb was twice evacuated and backfilled with argon, then inductively heated to initiate the reaction. The recovered metal buttons were smooth hemispheres, free of slag inclusions, and weighed 33.7 g, 34.1 g and 33.9 g, respectively. Button yields were approximately 92% and purity, 96%. The principle impurities were approximately equal amounts of Ca and Mg.

METAL PURIFICATION AND CASTING

The equipment used for remelting the recovered metal buttons is shown in Figures 3, 4 and 5. One to three buttons

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FIGURE 2. Induction Firing of a Pressure Bomb
to Initiate the Metallothermic
Reduction of Anhydrous NdCl_3

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FIGURE 3. Exploded View of the Button Melter and Magnesia Cone

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FIGURE 4. Button Melter With Protective Cone in Place

Neg 0682058-1

FIGURE 5. Assembled Button Melting Equipment
as Power is Applied to the Inductor

were placed in the small open-top tantalum bucket and the magnesia cone positioned as a lid. The cone served to vent the bucket and to prevent loss of product metal by splattering. The tantalum collar added physical stability to the cone and heated the lower portion of the cone during the melting step; thereby, preventing deposition of product metal or impurities in the bottom part of the cone. With the cone installed, the assembly was then placed on the alumina cylinder and a quartz bell-jar lowered over the assembly. The bell-jar sealed against a neoprene "O" ring positioned by a recess in the face of the metal base. The base was water cooled for the protection of the "O" ring and contained a port in the center of the alumina cylinder for evacuation and back-fill of the bell-jar. Figure 5 views the assembled equipment as power is applied to the induction coil.

After the button or buttons had been melted and the purification step (described later) completed, the equipment was allowed to cool and the bell-jar removed. The cone was removed and the tantalum melter, containing a frozen melt, was inverted into a magnesia casting mold as shown in Figure 6. A graphite susceptor was positioned around the magnesia mold, the assembly placed on the alumina hearth, and the bell-jar lowered into place. By use of the susceptor, the casting mold could be preheated to avoid thermal shock and the cast metal held molten, briefly, for removal of voids.

Several preliminary attempts were made to melt Nd buttons under vacuum conditions. In each instance, dissolved gas caused a violent disruption as the melting point was reached, and Nd was splattered out of the container. This problem was corrected by pumping a vacuum on the bell-jar as the temperature was slowly increased to 800 °C (over a period of 2 hr) and then backfilling the bell-jar with pure argon prior to increasing the temperature to affect melting of the button.

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FIGURE 6. *Button Melter Inverted into MgO Casting Mold*

An absolute pressure of 500 mm Hg was maintained during the melting step to ensure a seal of the bell-jar to the base. A similar procedure was followed when casting the melted buttons into MgO molds. Unfortunately, most of the Mg and Ca impurities remained with the Nd metal and the purity of the cast metal was not satisfactory. Final resolution of the problem was achieved by slowly pumping the argon from the bell-jar after the button had been melted and while the metal was maintained in a molten condition. As the argon pressure was decreased, Ca and Mg evaporated from the surface of the molten Nd metal and condensed on the colder surface of the bell-jar. Twenty minutes were required to reduce the absolute pressure from 500 to 100 mm Hg and an additional 25 min to reach 200 μ Hg pressure.

As a final demonstration, two of the three Nd buttons described previously were melted, the impurities distilled and the metal cast into 1/2 in. diameter rods. One of the rods was machined to expose virgin metal (see Figure 7) and then sampled. Analysis by spark source mass spectroscopy revealed the following impurities:

Sm	<1	ppm	Mn	4	ppm	Mg	160	ppm
Pr	0.1	ppm	Cr	80	ppm	Na	3	ppm
I	<0.3	ppm	Ca	3	ppm	F	4	ppm
Y	6	ppm	K	0.8	ppm	O	0.10%	
Ni	16	ppm						

With the exception of oxygen, the purity is very good. A prolonged distillation at lower pressure would probably lower both the Mg and O impurity levels, but would result in some loss of product metal since both Nd and Pm have significant vapor pressures at these temperatures.

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FIGURE 7. *Machined Ingot of Purified Nd Metal*

PREPARATION OF ^{147}Pm METAL

A special "heart cut" product fraction was segregated from the promethium chromatographic ion-exchange purification run completed on August 14, 1968 and was converted to Pm_2O_3 . The purity was determined by emission spectroscopy to be 99.95% with respect to all impurities except the ^{147}Sm daughter. Two batches of oxide, totaling 159 g, were converted to anhydrous chloride by the CCl_4 process. As stated previously, small lumps of fused chloride were found in the core of the first charge, apparently the result of self-heating and poor thermal conductivity. Sintering was more severe in the second batch, and it was necessary to dissolve the chloride, reprecipitate as the oxalate, convert to oxide and again chlorinate to obtain an acceptable PmCl_3 . The chlorination product weighed 238 g. Theoretical conversion would yield 236 grams, indicating acceptable conversion. Only slight turbidity could be observed when small samples were dissolved in water.

The total amount of PmCl_3 was converted into four metal buttons by use of the Ca-I_2 metallothermic reaction. Figure 8 shows the first two buttons and Table 1 summarizes some of the significant information.

TABLE 1. PmCl_3 Reduction Data

<u>Button No.</u>	<u>PmCl_3, g</u>	<u>I_2, g</u>	<u>Ca, g</u>	<u>Recovered Button, g</u>	<u>Theoretical Recovery, g</u>
1	60.0	40	24	33.1	34.5
2	64.0	40	25	35.2	36.8
3	53.0	40	24	26.1	30.7
4	61.0	40	24	32.3	35.1
Total	238			126.7	137.1

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FIGURE 8. First Two Buttons of ^{147}Pm Metal

Each button was pickled in water for a few minutes and dried, prior to weighing, to remove traces of adherent slag. The metal surface was smooth and symmetrical. No analyses were made. Each button was remelted, the volatile impurities removed by distillation, and the melt cast into a cylindrical MgO mold. The Mg and Ca contamination in buttons 1 and 2 was deduced to be 3.6 and 3.4 wt%, respectively, by weighing the tantalum melter plus Pm charge between the purification and casting steps.

The surface of each cast ingot was removed by use of a small lathe, see Figure 9, to expose virgin metal. Then turnings were removed from each for chemical analysis. The analytical results obtained by emission spectroscopy are shown in Table 2.

TABLE 2. Pm Metal Impurities

<u>Ingot No.</u>	<u>Ca, ppm</u>	<u>Mg, ppm</u>	<u>Fe, ppm</u>	<u>Cr, ppm</u>	<u>Al, ppm</u>	<u>Pb, ppm</u>	<u>Na, ppm</u>
1	100	450	ND	ND	ND	ND	ND
2	480	350	ND	ND	ND	ND	ND
3	55	700	ND	ND	ND	ND	ND
4	175	400	ND	ND	ND	ND	ND

The detection limits for the impurities shown as "not detected" (ND) range up to 100 ppm. The list of impurities is not complete and precision is less than desired, but only one analytical instrument is currently equipped to contain the off-gas from the vaporization of 10 to 100 Ci samples of ^{147}Pm . With respect to all impurities except daughter Sm, the Pm metal purity appears to be >99.8%.

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FIGURE 9. Machining of Pm Metal Ingot

^{147}Pm METAL DENSITY

Ingot 1 was machined into a right cylinder, cooled to ambient temperature (25 to 30 °C) on a chill-block, measured with a dial micrometer and weighed. Successive independent measurements gave volumes of 2.204 and 2.199 cm³. From a weight of 15.90 g, the density was calculated to be 7.22 ± 0.01 g/cm³.

A 1/8 in. long section was then removed from the end of the ingot, suspended from an analytical balance by a fine tungsten wire and the weight determined in air and submerged in a fluorocarbon liquid.* The weights were 1.9928 g in air and 1.5063 g in the liquid. Using 1.7593 g/cm³ as the liquid density at the measured temperature of 27 °C, the Pm metal density was calculated to be 7.206 g/cm³.

The metal was bright and free from corrosion or surface voids when the measurements were made. Considering both measurements, the probable density is reported as 7.22 ± 0.02 g/cm³ at 25 to 30 °C.

^{147}Pm METAL MELTING POINT

Since 50 g of Pm metal was available, the thermal arrest method was chosen for the melting point measurement. A resistance-heated pot furnace was fabricated, incorporating provision for evacuation of the furnace atmosphere and replacement with argon at 2 to 3 atm pressure. A 1.1 in. diameter by 1.5 in. high tantalum cup was positioned inside the heating elements by a Lavite** holder and the annular space between the elements and the steel outer wall was filled with Fiberfrax[†]

* Minnesota Mining and Manufacturing Company product FC-75.

** Trade name of American Lava Corporation.

† Trade name of Carborundum Corporation.

insulation. Primary temperature measurement was made by a Pt:Pt, 10% Rh thermocouple penetrating the bottom of the furnace and extending up into a 0.35 in. deep vertical well in the bottom of the tantalum cup. Constant contact was maintained between the thermocouple and the end of the well. The accuracy of the thermocouple was checked against a certified Cu freeze standard using a certified Leeds and Northrup K-3 potentiometer prior to installation in the furnace and was found to deviate less than 1 °C. After installation in the furnace, a Honeywell stripchart recorder with a 1 mV range and chart speed of 3/4 in./min was used for thermocouple readout. A thermostated bucking-voltage source permitted a broad range of zero suppression. Frequent range and zero point checks were made with a Technique potentiometer, standardized against the certified Leeds and Northrup K-3 potentiometer. The PT to Cu wire junctions were made through Hg maintained at ice-bath temperature.

The furnace was installed in the glove box, held at 1000 °C under vacuum conditions for 48 hr and then tested by observing the freeze point of 55 g of electrolytic Cu (verified to be 99.999% pure). Five cycles through the freeze point yielded the following thermal arrest data:

Freeze Point, °C

1080.4

1080.4

1079.6

1078.9

1078.9

Average = 1079.6

Thermal arrests several inches long could be obtained by careful control of the furnace power input. The listed freeze point for pure Cu is 1083.3 ± 0.3 °C so these values were 4 °C low.

Four freshly machined cylindrical ingots of ^{147}Pm metal (totaling 53 g) were placed on end around the thermocouple well in the tantalum cup and the cup covered with a tantalum lid. Insulation was put in place and the furnace sealed, outgassed, and filled with argon at 2 atm pressure. The furnace temperature was increased at a rate of approximately 5 °C/min until 800 °C was reached. The rate of climb was then decreased to approximately 3 °C/min. No thermal arrest was observed below 1100 °C as had been anticipated from the work of Weigel. As 1160 °C was passed with no indication of a thermal arrest, apprehension became strong that the equipment was in error and the furnace was turned off. The temperature reached a plateau at 1169 °C and then decreased. When cooled, the furnace was opened, revealing that three of the ingots had melted, but about half of one ingot protruded erect from the frozen melt. The thermocouple well was covered, indicating a valid temperature determination. The furnace was sealed, outgassed, backfilled with argon and heated to 1200 °C at the same rate. The temperature was cooled to 1000 °C at 2 °C/min with no indication of a thermal arrest. Repeated cycling between these temperatures at rates ranging from 1 to 10 °C/min gave no arrest. When the furnace was cooled and opened, the protruding ingot was found to have melted.

The Pm loaded cup was removed from the furnace and replaced with an identical cup containing approximately 65 g of 99.999% pure Cu. The melting point of Cu was again measured, following the same procedure used with Pm, and found to agree within 1 °C with the previous measurement.

A 1/8 in. diameter by approximately 1/4 in. deep hole was drilled into the Pm metal and the Pm-loaded cup resealed in the furnace. Following outgassing and replacement with argon, the temperature was carefully brought up to 1148 °C and held constant for 15 minutes. When the furnace was cooled and

opened, the hole was observed to be intact and the metal drillings were unaltered. This test was repeated at 1163 °C with similar results. When repeated at 1173 °C, the drillings were fused to the metal surface and the hole was almost closed. Partial oxidation on the surface of the metal had prevented complete closure of the hole. These observations indicate the Pm metal melting point is about 1168 ± 6 °C. At the time the measurement was made, the metal contained 2.5 wt% Sm as a result of ^{147}Pm decay.

DISCUSSION

Reason for the failure of the thermal arrest determination is not known. The melting points of other rare earth metals have been measured by this method.⁽⁸⁾ Perhaps it is significant that these measurements were made with 100 g or more of metal. The failure may have resulted from a combination of low heat of fusion, insufficient amount of metal, self-heating of the sample, or poor furnace design. In an initial experiment, using an insulated tantalum cup of identical design supported in the bell-jar and heated by induction, a 50 g sample of Sm metal gave a distinctive thermal arrest. The equipment was not used for Pm because a positive pressure of argon could not be used without rupture of the bell-jar seal. A positive pressure was deemed necessary to suppress the partial pressure of Pm metal vapor in order to avoid contamination of the thermocouple. Plans were made to measure the melting point of pure Sm metal following the completion of the Pm work, but the thermocouple bead was destroyed during the removal of the tantalum bucket containing the Pm metal and funding limitations precluded further work.

The addition of the melting point obtained in this work with those of the other lanthanide metals⁽⁸⁾ (see Figure 10) suggests some relationships not previously discernable. As with such other properties as the boiling point, heat of vaporization and atomic volume,⁽¹¹⁾ the melting points of La,

MELTING POINTS OF RARE EARTH METALS

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FIGURE 10. Melting Points of Rare Earth Metals

Sm, Eu and Yb metal are not "normal," but the behavior can, perhaps, be related to the occupancy of the 4f and 5d energy levels. With both Eu and Yb, the 5d bonding electron vacates that level and moves into the 4f level. As a result, Eu and Yb melt 590 and 768 °C lower than they would if they retained the "normal" $6S^25d^1$ configuration. Sm and to a lesser degree La exhibit a statistical tendency to yield to a similar shift and they melt 223 and 65 °C lower, respectively, than they would without such a transition.

Assuming all the lanthanides were "normal," there appear to be two linear related series, Ce through Eu and Gd through Lu. Perhaps as the first 6 unpaired 4f electrons are added, the shielding of the bonding electrons varies in a linear fashion and melting points reflect this change. At Gd, the final unpaired electron completes the level and initiates a new series with a different shielding pattern for the bonding electrons. This does not explain the behavior of La. The crystal field effects upon the bonding electrons may be more pronounced in the absence of a 4f electron. These thoughts are summarized in Figure 10. The measured values are shown as solid data points and the shifts to hypothetical "normal" positions are shown by the dashed lines.

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