JOURNAL OF SOLID STATE CHEMISTRY 3, 112–124 (1971)

Investigations into the Eu–Eu_2O_3, the Eu–Pt–Eu_2O_3, the Sm–Sm_2O_3, and the Yb–Yb_2O_3 Systems*

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Received May 1, 1970

The binary system Eu–Eu_2O_3 has been examined in detail over the composition range EuO to Eu_2O_3 at 1500°C. Only three oxide phases were found: EuO, Eu_3O_4, and Eu_2O_3. Both EuO and Eu_3O_4 exhibit very narrow composition limits, while the monoclinic sesquioxide is stable over the composition range $EuO_{1.45}$ to $EuO_{1.50}$ at 1500°C. The melting points found for the three phases were 1900°C for EuO, 2000°C for Eu_3O_4 and 2300°C for Eu_2O_3. Europium was quantitatively extracted from EuO by reaction with platinum in sealed capsules at 1500°C, which resulted in the formation of an intermetallic phase plus a higher oxide of europium. The most europium-rich intermetallic phase found in these studies, $EuPt_{2+x}$, has the fcc $MgCu_2$ structure and is stable over the composition range $EuPt_{2.0}$ to $EuPt_{2.8}$ at 1500°C. Besides $EuPt_2$, two phases were encountered in the Eu–Pt alloys which contained more than 75 at.% Pt. These are tentatively designated as Eu_2Pt_7 and $EuPt_5$. No crystalline phases other than the sesquioxides were found in the Sm–Sm_2O_3 or the Yb–Yb_2O_3 systems.

1. Introduction

Brauer (*1*) has reviewed the structural and solid state chemistry of the lanthanon oxides, and Westrum (*2*) has reviewed the thermodynamics and magnetic properties of the oxides and other chalcogenides.

When the work reported here began, the Eu–Eu_2O_3 system had not been clearly defined. Although the oxides Eu_2O_3, Eu_3O_4, and EuO had been reported and their structures described, the possibility of other intermediate phases in the system still remained (*3–7*). However, it has since been established (*8*) that no other phases exist in this system. Significant ranges of stoichiometry have been reported for EuO (*9*) and Eu_2O_3 (cubic) (*10*). The results reported here confirm the findings of Ref. (*8*) and present new data on the composition ranges of these oxides.

Optical and X-ray examination of samples prepared by metathetical synthesis in sealed containers indicated that EuO, Eu_3O_4, and Eu_2O_3 were the only stable oxides in the Eu–Eu_2O_3 system. However, there had been some uncertainty about this conclusion due to interference by tantalum contamination in some of our early experiments. An investigation involving controlled quantitative extraction of Eu from EuO single crystals was devised which unambiguously established the number of phases present in the range EuO–Eu_2O_3 and provided data on the stoichiometries of these phases. Europium was removed from EuO through the vapour phase by equilibration with platinum in sealed containers at 1500°C. These experiments also provided new information on the Eu–Pt system.

We applied the techniques and facilities previously used in studying the reduced europium oxides to investigate the possible stability of divalent or other reduced oxidation states of samarium or ytterbium in oxide systems. SmO, Sm_2O, and YbO had all been reported (*11–15*). We were interested in characterizing these phases if possible and in comparing the samarium, europium, and ytterbium systems. Brauer et al. have reported that reduced oxidation states of Sm and Yb could not be prepared in binary oxides at temperatures up to 800°C and that the divalent ions could not be stabilized even in solution with SrO or CaO (*16*). Felmlee and Eyring have reported that the substances previously identified as Sm_2O and SmO were actually SmH_2 and $SmN_{1-x}O_x$ (*17*). McCarthy et al. have also reported that divalent Sm cannot be formed in titanates and is probably not stable in any oxide

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* Work performed under the auspices of the U.S. Atomic Energy Commission.

system (*18*). Fishel et al. have reported the preparation of mixtures of YbO plus Yb_2O_3 by the reaction of oxygen with Yb dissolved in liquid ammonia at −33° to −78°C (*19*). Our results, which include observations from reactions carried out at temperatures up to 2100°C, confirm that, in the binary oxide systems, reducing conditions at high temperatures lead to no new phases in which Sm or Yb are in reduced oxidation states. Reduced sesquioxides Sm_2O_{3-x} and Yb_2O_{3-x} were found. Similar reduced lanthanon sesquioxides have been reported and the oxygen deficiencies shown to be due to vacancies in the oxygen sublattice (*19*). Our measurements show that the oxygen deficiency in Yb_2O_{3-x} is approximately the same as that reported for the other reduced lanthanon sesquioxides.

2. Melting of Eu_2O_3

Eu_2O_3 was melted in both tungsten and iridium crucibles. We used an induction furnace with a shielded tungsten susceptor. Temperatures were measured with a disappearing-filament optical pyrometer sighted through a prism and window into a hole of 1-mm diam in the lid and upper shields. Prism and window corrections were applied. The crucibles were not sealed, but they had close-fitting covers, and an argon atmosphere was used to repress vaporization. The starting material was nominally 99.9% Eu_2O_3 which had been previously heated in air for several hours at about 1200°C in a platinum crucible and then stored in a desiccator. The oxide is monoclinic, colorless, and highly birefringent.

On heating to 2270°C in a tungsten container, the sample melted and reacted with the crucible, producing a noticeable recess in the wall at the meniscus. This behavior is typical for reactions involving a gaseous product of the container material such as WO_3. The europium oxide product appeared dark in color and contained small red crystals of Eu_3O_4 uniformly dispersed throughout. A sample heated to 2280°C in an iridium crucible also melted. There was no evidence of reaction with the container; however, enough oxygen was lost (presumably by vaporization to yield a product which contained a significant amount of Eu_3O_4. Another sample heated in iridium to 2300°C appeared to have been only partly melted. Samples heated to 2250°C showed evidence of liquid formation only around the Eu_3O_4 inclusions. We maintained the samples at maximum temperature only for a few minutes because of rapid vaporization losses. This and the temperature gradients which were unavoidable even in the well-shielded crucible used for a susceptor leave some doubt about the accuracy of the melting point measurements. We can only estimate the melting point to be in the range 2250–2350°C.

Our observations of the melting of Eu_2O_3 were therefore not precise enough to confirm either the value of 2240 ± 10°C given by Schneider (*21*) or of 2330°C by Foex (*22*), but agree with the values near 2300°C as opposed to 2000°C reported by Mordovin (*23*). Schneider determined the melting point in air using an iridium container. Foex's measurement was also in air, using a solar furnace and Mordovin's measurement was in argon under a pressure of 3 atm.

Except for the presence of Eu_3O_4 inclusions, the optical properties and X-ray diffraction results for the melted Eu_2O_3 were identical to those for the starting material. The X-ray powder patterns corresponded to the ASTM data (*24*).

3. Synthesis and Melting of EuO

The starting materials were Eu_2O_3 (described above) and nominally 99% europium metal in ingot form. The europium ingot was handled in a steel glove box which could be evacuated to 3×10^{-6} Torr and filled with dry argon. A steel chisel was used to cut pieces of europium from the ingot as required after scraping off the surface coating. Normally, a clean europium surface would retain its shiny metallic appearance for several hours in the glove box before developing a noticeable tarnish.

Although a number of procedures have been reported for preparing EuO, most of them yield a product of questionable purity (*6*, *12*, *25*). We avoided methods which used a metal other than europium as a reducing agent, methods for which the stoichiometry could not be closely predetermined (such as reduction by carbon), and methods requiring difficult procedures or specialized equipment.

We prepared EuO by reducing Eu_2O_3 with europium metal in sealed, evacuated molybdenum crucibles. Reactions carried out even at moderately low temperatures in silica yielded products contaminated with silicate [see also Ref. (*6*)]. Reactions carried out in tantalum containers at temperatures high enough to melt EuO (~1800°C) resulted in products which were contaminated by tantalum. The tantalum was found in two different forms. One was as an unidentified crystalline material thought to be a complex oxide, which was transparent, red or brownish in color, and birefringent.

Tantalum was also found (by electron microprobe X-ray analysis) to be finely dispersed in the EuO probably as precipitated metal which may have been in solution at higher temperatures. The occurrence of dispersed tantalum in EuO prepared in tantalum containers has also been reported by Guerci and Shafer (*26*). Samples of EuO which had been heated to 1880°C in tantalum were found to have melted. Of two samples heated to 1800°C one melted and one did not.

EuO was prepared without troublesome side reactions in molybdenum capsules using an excess of europium metal. Samples were prepared by weighing the desired amounts of sesquioxide from the desiccator into capsules and transferring them into the glove box. The appropriate amount of metal was weighed on a torsion balance of ±10 mg accuracy and added to each of the capsules. After the lids were pressed on, the capsules were placed in previously weighed bottles which were capped and removed from the box. The final weights of the filled capsules were then determined on an analytical balance without exposing the samples to the ambient environment. After weighing, the capsules were placed in a vacuum system which was then pumped out to 10^{-5} Torr. The capsules were left in the vacuum overnight to allow evacuation and then were sealed by electron beam welding (EBW).

A sample heated to 1870°C resulted in a compact product of EuO which had not melted. The excess europium metal was found primarily at the bottom and sides of the capsules. Samples heated above 1990°C and cooled at about 70°C per hr resulted in EuO boules containing large crystals which had grown from a melt. Excess metal was found at the bottom and sides of the boule and in the grain boundaries.

Most of the EuO taken from several such preparations was then crushed, remelted in a sealed molybdenum container, and cooled slowly. About 1.5% Eu was added to ensure that the overall composition would remain on the metal-rich side of EuO. The europium excess in the final product is estimated to have been from 1–5% by weight. From this preparation we obtained single crystals of approximately 1 cm^3. There was no visible excess europium metal in this sample, but the surfaces of uncleaved crystals tarnished in air over a period of several months, probably due to the presence of europium metal in the grain boundaries.

These results are consistent with those of Guerci and Shafer (*26*). However, we believe that as yet there is not enough evidence to conclude that EuO melts peritectically, as they suggest, rather than congruently. We estimate the melting point of EuO to be 1900 ± 50°C, in agreement with the value suggested by Shafer (*9*). X-Ray powder diffraction analysis of this material gives a lattice parameter, $a = 5.14_4 \pm 0.005$ Å for the NaCl type structure, in agreement with prior reports.

EuO crystals are dark reddish-violet in color and are opaque to visible light even in thin sections with the most intense illumination available on our microscope (a mercury discharge lamp).

4. Synthesis and Melting of Eu_3O_4

Attempts to prepare pure Eu_3O_4 from mixtures of EuO and Eu_2O_3 in sealed tantalum containers were unsuccessful. Extensive reduction occurred due to loss of oxygen by solution into the tantalum. This reduction resulted in products containing large excesses of EuO. A preparation heated to 1820°C had completely melted. The product was principally EuO, containing some Eu_3O_4 with minor amounts of two or three other unidentified phases. The latter were lightly colored, transparent, and birefringent. They were coprecipitated with the Eu_3O_4 in banded eutectic-like structures. These materials may have been complex europium–tantalum oxides.

A small sample of Eu_3O_4 (0.4 g) was prepared by heating an equimolar mixture of EuO and Eu_2O_3 (actual O/Eu = 1.331) to 2135°C in a sealed (by EBW) iridium crucible. The uncertainty in the initial oxygen–europium ratio is estimated to be about 1 ppt, due primarily to the uncertain composition of starting materials. The product had melted completely. Examination with a polarizing microscope showed the product to consist primarily of transparent, very dark-red crystals which were birefringent, appearing bright red under crossed polarizers. Very few bright, white, birefringent crystals were also seen in the sample, indicating the presence of a trace of Eu_2O_3. X-Ray powder diffraction patterns agreed with the results reported by Bärnighausen and Brauer (*5*) and Rau (*6*, *27*) for Eu_3O_4 (orthorhombic).

A larger preparation (15 g) was made by heating a mixture of EuO and Eu_2O_3 (O/Eu = 1.333) to 2050°C in an iridium container and cooling at 40°C per hr. We were unable to make a leak-tight weld on this container, but the heating was done in an argon atmosphere to retard vaporization of the sample. The product completely melted. It consisted of relatively large Eu_3O_4 grains (~1 mm^3) with traces of Eu_2O_3 concentrated at the grain boundaries. Although there was no visible sign of reaction between the sample and the container, there may have been some loss of europium by vaporization, yielding a product slightly more oxygen-rich than the starting material. Part of the product was ground and reheated to 1920°C in a sealed iridium capsule; no sign of melting was observed. A portion of the product was heated to 2140°C in a sealed molybdenum capsule and cooled rapidly. The product, which had completely melted, consisted of Eu_3O_4 with traces of Eu_2O_3, and was identical in appearance to the original material that had been cooled slowly. We could detect no sign of reaction with the container. Reheating in a sealed molybdenum container for 8 hr at 1625°C had no detectable effect on the sample. These observations indicate that the Eu_2O_3 resulted from a slight excess of oxygen in the sample rather than from disproportion by a peritectic reaction.

We estimate the melting point of Eu_3O_4 to be 2000 ± 100°C. Part of the uncertainty in this figure is due to the fact that in some of the heatings the shielding was deliberately rearranged to establish a large temperature gradient (~80° from top to bottom) to facilitate crystal growth. Results from preparations in tantalum indicate the possibility of peritectic melting. The experiments in iridium and molybdenum do not support this conclusion but neither do they provide direct contradictory evidence.

5. Investigation of Other Compositions Between EuO and Eu_2O_3

Several compositions between EuO and Eu_2O_3 were heated in sealed iridium or molybdenum containers in conjunction with the preparation and study of Eu_3O_4.

Mixtures with oxygen–europium ratios of 1.051, 1.093, and 1.401 which were prepared from EuO and Eu_2O_3 and then heated to 1970°C in EBW-sealed iridium capsules had completely melted. The samples with $O/Eu = 1.051$ and 1.093 showed evidence of reaction with the containers. The metallic reaction product was not identified. The major oxide phase in the products was Eu_3O_4, with some opaque material (probably EuO) detectable by microscopic examination. X-Ray diffraction analysis showed only Eu_3O_4. The sample with $O/Eu = 1.401$ apparently did not react with the container. The product in this case consisted of approximately equal amounts of Eu_2O_3 and Eu_3O_4 with no other phase detectable either by X-ray or optical analysis.

Samples with oxygen–europium ratios of 1.17 and 1.25, prepared from Eu_3O_4 and EuO, were heated to 2140°C in sealed molybdenum capsules and cooled rapidly. There was no indication of container reaction; Eu_3O_4 and EuO were the only phases detectable in the products by X-ray and optical analysis. The samples had been completely melted. The products were resealed in molybdenum capsules and heated to 1800°C for 8 hr without effect.

The X-ray powder diffraction patterns of Eu_3O_4 were identical within our precision for samples prepared with either excess oxygen or excess europium, as were the qualitative optical properties. The existence of Eu_3O_4 in the presence of either EuO or Eu_2O_3 and the failure to observe any other phases is in agreement with other recent reports on this system (*6–8*).

The presence of Eu_2O_3 in samples very close to the ideal composition for Eu_3O_4, and the concentration of the Eu_2O_3 in the grain boundaries of Eu_3O_4 preparations, indicate that the deviation from stoichiometry of Eu_3O_4 is very small on the oxygen-rich side. The appearance of the crystallized samples indicated that the stable composition range for Eu_3O_4 is probably narrow even near the melting point. Even in rapidly cooled samples, the Eu_3O_4 crystals did not appear to contain inclusions of EuO or Eu_2O_3.

6. Study of the EuO–Eu_2O_3 System by the Removal of Eu from EuO at 1500°C by Platinum

In order to confirm the absence of compounds other than Eu_3O_4 between EuO and Eu_2O_3, as well as to investigate in more detail the stoichiometry of these three oxides, we studied the distribution of europium between the oxide phases and intermetallic phases in the Eu–Pt system at 1500°C.

EuO single crystals weighing from 100–400 mg were sealed by EBW into molybdenum capsules, along with pieces of chemically pure platinum wire weighing 6 mg to 1 g. In the first experiments, the platinum wire was suspended from molybdenum wire holders to avoid physical contact between the platinum and the oxide. Subsequently, several runs were made in which a tungsten-lined molybdenum cup was used instead of the molybdenum wire to contain the platinum. This is the configuration shown in Fig. 1. Unfortunately, we did not have enough single crystals for the later runs. Therefore, we used dense pieces of polycrystalline EuO from the same preparation used for the previous work. The sealed capsules were heated at 1500°C for about 5 hr and cooled quickly. About 1.5 min were required for the temperature to fall below 700°C. In the second series we did not use a quench gas and the

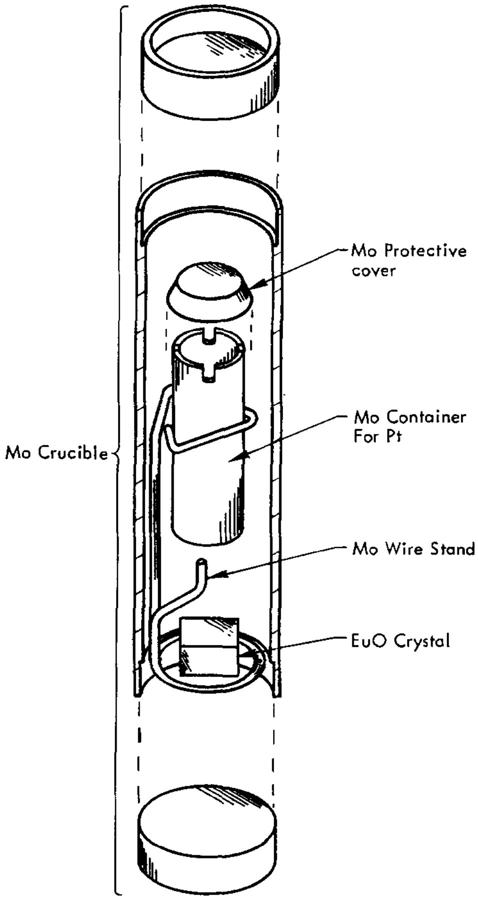

FIG. 1. Sample configuration for extraction of europium from EuO by platinum. The protective cover prevents molybdenum particles from falling into the container when the capsule is opened. Early runs were made with Pt wire hung directly on the Mo wire stand.

samples cooled more slowly, falling below incandescence in 5–10 min. After cooling, the capsules were broken open to recover the oxide and platinum samples. Both the oxide and metallic products were weighed to determine their final compositions.

The product oxide phases were recovered intact and had the same size and shape as the starting EuO crystals. There was no evidence of vapor transport of oxide within the capsules nor of mechanical losses of oxide in transfers or recovery. After examination with a low-power microscope, the oxide products were cleaved and examined further. The two-phase oxide products consisted of a central core of the lower oxidation state phase surrounded by an outer shell of the higher oxidation state phase. The boundaries were very sharp with no gradation in properties detectable. Samples were taken from the inner and outer phases for X-ray diffraction and examination with the polarizing microscope. The X-ray and optical properties of the products of these experiments were identical to those described above for EuO, Eu_3O_4 and Eu_2O_3. The results showed unambiguously that the only stable oxides in this system at 1500°C are the three mentioned above.

The samples changed as the initial ratio of platinum to EuO was progressively increased. At lower ratios ($Pt/EuO < 0.5$), not enough europium was extracted to increase the overall oxygen–europium ratio in the product oxide phase to 4/3. In these samples a dense layer of polycrystalline Eu_3O_4 was formed on the external surfaces of the EuO crystal. When the platinum–EuO ratio was further increased so that more than one-fourth of the europium was extracted from the oxide, the product was a homogeneous, dense, polycrystalline core of Eu_3O_4 with an outer layer of Eu_2O_3. With continued Eu extraction from the oxide, the outer layer of Eu_2O_3 became progressively thicker. However, the outer layers were not pure Eu_2O_3. Small red crystals of Eu_3O_4 were uniformly dispersed in these layers. When enough platinum was added to give an oxide product with an oxygen–europium ratio of 1.45 ± 0.01 or more, the Eu_3O_4 core was absent and the product was Eu_2O_3 containing small crystals of Eu_3O_4 uniformly dispersed throughout.

The metallic phase products were examined with a microscope and by X-ray diffraction. For runs in which the platinum–europium ratio of the product was 3.45:1 or less, the surfaces of the products were very rough, and relatively large (0.05 mm) plate-like crystals had developed. There was no evidence of liquid formation and the platinum phase-molybdenum or tungsten interfaces were sharp with the interaction confined to very small regions at the points of contact between the sample and holder. In most cases there was no mechanical bond or a very weak one between sample and holder. The samples with Pt:Eu of 3.69 and 5.21 had completely melted. The platinum phase wetted the molybdenum and was strongly bound to it; however, the boundary observed under the microscope was very sharp with no evidence of reaction or corrosion of the original molybdenum surfaces. The samples with higher platinum–europium ratios were similar but had only partly melted. They retained the basic form of the original wire, and were smooth with coils stuck together by the crystallized liquid phase. The liquid phase is probably due to a eutectic reaction below 1500°C between platinum and the platinum-rich intermetallic compound.

Although the solubility of molybdenum in platinum at 1500°C is high, and intermetallic compounds of molybdenum and platinum are known (*28*), we believe the interactions of platinum with the containers did not have an important effect in this experiment except for the samples where a liquid phase was formed. This judgment is reinforced by the agreement between the first runs and the later runs in which tungsten-lined containers were used for the platinum. The solubility of tungsten in platinum is high at 1500°C, but there are no platinum–tungsten intermetallic compounds. The solubility of platinum in either molybdenum or tungsten is small (*28*). Spectroscopic analysis of the $EuPt_{5.21}$ sample indicated that it was contaminated with about 200 ppm molybdenum. The presence of molybdenum may have influenced the form and structure of the platinum phases that were melted or partly melted, but we think that even in these samples the platinum–europium ratios are essentially the same as they would be in the pure equilibrium Eu–Pt phases. The molybdenum concentration in the products of runs for which tungsten-lined containers were used was about 30 ppm. Tungsten was not detected by either spectroscopic or X-ray fluorescence analysis in any of the products.

X-Ray powder diffraction analysis of the platinum-phase products gave additional information. The most europium-rich phase formed in these experiments has the fcc $MgCu_2$ structure. The apparent compositions of the products in equilibrium with two-phase mixtures of $EuO + Eu_3O_4$, determined by weight losses of the oxide crystals, ranged from $EuPt_{1.87}$ to $EuPt_{2.08}$. The lattice parameters of these samples were identical within the precision of our measurements (±0.005 Å), with a value of 7.72_3 Å. This indicates that they were all of the same composition as required by the fact that they were all in equilibrium with the same two oxide phases at the same temperature. The variation in the measured compositions of the samples is significantly greater than can be explained by the uncertainties in weighing (±0.1%–±1%). The weighted average of the compositions of the intermetallic phase in equilibrium with $EuO + Eu_3O_4$ is $EuPt_{2.02\pm0.04}$. The experimental compositions were weighted by the sample masses to account for differences in weighing precision. The lattice parameter reported for $EuPt_2$ by Elliott (*29*) is 7.731 Å. The lattice parameter of $EuPt_{2+x}$ decreases linearly with increasing Pt concentration to a value of 7.62_0 Å for $EuPt_{2.8}$. The dependence of lattice parameter on composition for $EuPt_{2+x}$ is shown in Fig. 2. The results of Harris (*30*) for $EuPt_3$ ($MgCu_2$ structure type) are inconsistent with ours, which show that the $EuPt_{2+x}$ solid solution extends only to $\sim EuPt_{2.8\pm0.1}$. The lattice parameter data indicate that the material Harris prepared by arc melting had a composition of about 68 at.% platinum ($EuPt_{2.17}$).

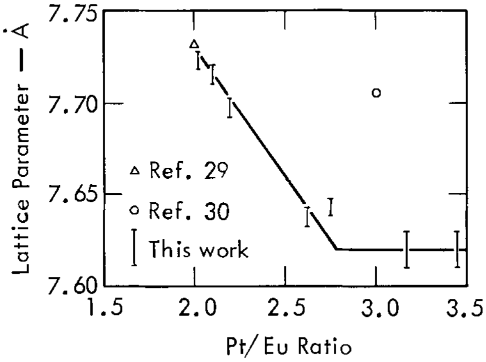

FIG. 2. The fcc lattice parameter of $EuPt_{2+x}$ versus composition. Data obtained from measurements of black reflection lines of Debye–Scherrer powder patterns taken with CuK_α radiation.

X-Ray diffraction results for samples with Pt:Eu ratios higher than 2.8 are inconclusive. The powder diagrams were either too poor in quality or too complicated for complete analysis. Compositions with Pt:Eu ratios of 3.17 and 3.45 appeared to be two-phase mixtures of $EuPt_{2.8}$ and another phase whose structure and stoichiometry are undetermined. Of the possible candidates for this phase, Eu_2Pt_7 seems to be the most reasonable. It is in agreement with our equilibrium results, and preliminary single-crystal results on specimens from the $EuPt_{3.45}$ sample appear to be consistent with one of the Ln_2Ni_7 structure-types (*31–34*).

Powder patterns from samples of products with Pt:Eu ratios of 3.69 and 5.21 were identical except for a very weak Pt line in the $EuPt_{5.21}$ pattern. The structure or stoichiometry of the phase producing these patterns was not determined in this study but is tentatively identified as $EuPt_5$. Results from single-crystal studies of material from samples with Pt:Eu ratios of 3.69 and 17.29 were consistent with single-crystal results for $EuPt_5$ reported by Bronger (*35*). We were unable to find crystals in our samples that were good enough for unambiguous structure determinations. Professor Bronger has kindly furnished a list of *d*-spacings for $EuPt_5$ to be compared with the unresolved patterns of this study. Patterns from samples of $EuPt_{3.69}$ and $EuPt_{5.21}$ agreed with Professor Bronger's results for $EuPt_5$ down to a *d*-spacing of 1.25 Å, with the exception of five very weak lines observed in our patterns. X-Ray powder diffraction analysis of samples from

TABLE I

d-SPACINGS FOR UNIDENTIFIED PHASES FOUND IN $EuPt_{3.45}$ AND $EuPt_{5.21}$

Pt:Eu = 3.45		Pt:Eu = 5.21	
d	I/I_0	*d*	I/I_0
4.53_4	15	4.57_1	10
4.40_7[a]	10	2.64_7	15
2.83_7	5	2.52	<5
2.69_1[a]	10	2.45	<5
2.53_4	5	2.27_0	65
2.40	<5	2.19_5	100
2.30_8	60	2.13_5	<5
2.28_6	100	2.09_5	<5
2.21_8	15	2.01_5	<5
2.17_7[a]	70	1.96[b]	<5
2.15_0	75	1.74	<5
2.11	<5	1.69_7	5
2.01	<5	1.65	<5
1.94_8	10	1.58	<5
1.92[a]	<5	1.52	<5
1.75_5[a]	7	1.44_6	10
1.69_6	5	1.38_5[b]	5
1.52	<5	1.32_7	10
1.50	<5	1.28_3	35
1.47_4	7	1.27_2	5
1.46_3	35	1.26_0	<5
1.43_2	10	1.18[b]	<5
1.42	<5	1.13_6[b]	10
1.35_8	7	1.10_0	15
1.34_3[a]	30		
1.30_3	20		
1.28_1[a]	15		
1.17_4	7		
1.14_4	40		

[a] Spacings corresponding to fcc $EuPt_{2.8}$.

[b] Spacings corresponding to Pt.

products with Pt:Eu ratios of 9.13 and 17.29 showed that they were mixtures of the phase identified above as $EuPt_5$ plus platinum. The platinum lines in these patterns were identical to those for pure Pt, with no detectable change in lattice parameter. Since the only difference between the powder patterns of $EuPt_{3.69}$ and $EuPt_{5.21}$ samples was the presence of a very weak Pt line in the $EuPt_{5.21}$ pattern, it would appear that $EuPt_{3.69}$ is monophasic. A possible explanation is that a $EuPt_{5-x}$ solid solution is stable to substantially platinum-deficient compositions, and the concentration of Eu_2Pt_7 in the $EuPt_{3.69}$ sample was too low to detect by X-ray diffraction. Table I gives *d*-spacings measured from patterns of sample products with Pt:Eu ratios of 3.45 and 5.21.

The results of the oxide–platinum equilibration experiments are summarized in Table II. The product compositions were calculated assuming that the weight loss of the oxide phase resulted only from europium loss and that all of this europium was transferred to the platinum phase. Under the conditions of our experiments, the europium gas pressures were in the range 2×10^{-5}–10^{-3} atm (*36*, *37*), which were sufficiently high to allow the systems to reach equilibrium in relatively short times. The correction for the amount of europium in the vapor phase in our capsules (~2 cc) at 1773°K was negligible compared to the total amount transferred. In the first run listed in Table II (the worst case), the correction would have been about 0.1 at.%; in all but the first three runs, the corrections would have amounted to less than 0.02 at.%.

Ideally, the europium transfer could be measured both by the weight loss of the oxide and the weight gain of the platinum which should be identical, but in our early experiments we were unable to accomplish this ideal mass balance. In many runs the platinum came in contact with the capsule and could not be quantitatively recovered. Even in those runs for which the recovery of the platinum phase seemed to be quantitative, and in the runs in which the platinum was placed in tungsten-lined cups, the weight gain of the platinum was always slightly less than the weight loss of the oxide. The discrepancy seemed to be the largest for the samples which contained the most platinum. Since the errors amounted to only 0.05–0.5 mg (a few tenths of a per cent or less of the platinum weights) the discrepancies will not significantly alter the conclusions from these experiments. In the later runs the results indicated that the polycrystalline EuO starting material may have contained excess Eu. For several of these runs the composition of the oxide phase product was determined by igniting the sample in air to constant weight (about 60 hr at 1200 to 1300°C) and measuring the weight gained on oxidizing to Eu_2O_3. Weighings were made to ± 2 μg.

The quantitative results of the equilibrations are illustrated in Fig. 3, where the oxygen–europium ratios for the oxide phases are plotted against the platinum–europium ratios for the equilibrium metallic phases. The lines in Fig. 3 are drawn using the information from optical and structural (X-ray) examinations of the samples as well as the composition data. The graph represents the locus of the endpoint compositions of tie lines in the ternary diagram and facilitates finding the compositions of the binary compounds. Such a graph for a pair of binary systems with a common component, which

TABLE II

RESULTS FROM EQUILIBRATION OF SAMPLES IN THE Eu–Pt–Eu_2O_3 TERNARY SYSTEM AT 1500°C

Composition of starting EuO-Pt mixture		Metallic phase product				Oxide phase product					
		X-ray analysis				Composition		X-ray analysis			
Mole fraction platinum	Composition Pt/Eu	Structure	Lattice parameters (Å)	Identification	Notes	Experimental O/Eu	Analysis O/Eu	Structure	Lattice parameters (Å)	Identification	Notes
0.019_7	1.97_6 (1)	fcc	7.72_3	$EuPt_{2+x}$	(6)	1.01_0		fcc	5.14_4	EuO	(10)
$.040_4$	1.86_5 (2)	fcc	7.72_3	$EuPt_{2+x}$	(6)	1.02_3					(10)
$.060_3$	1.95_6 (2)	fcc	7.72_3	$EuPt_{2+x}$	(6)	1.03_4					(10)
$.102_3$	(2.59_0) (2,3)	fcc	7.72_4	$EuPt_{2+x}$	(6)	1.04_6					(10)
$.143_7$	1.95_3 (2)	fcc	7.72_4	$EuPt_{2+x}$	(6)	1.09_4		fcc orthorhombic	5.14_4	EuO (inner) Eu_3O_4 (outer)	(10)
$.180_9$	2.05_2 (2)	fcc	7.72_3	$EuPt_{2+x}$	(6)	1.12_1					(10)
$.212_5$	2.04_9 (2)	fcc	7.72_3	$EuPt_{2+x}$	(7)	1.15_2					(10)
$.252_0$	2.03_0 (2)	fcc	7.72_3	$EuPt_{2+x}$	(6)	1.20_0		orthorhombic		Eu_3O_4 (outer)	(10)
$.295_6$	2.05_1 (2)	fcc	7.72_3	$EuPt_{2+x}$	(7)	1.25_7					(10)
$.317_9$	2.07_8 (2)	fcc	7.72_3	$EuPt_{2+x}$	(7)						(10)
$.318_6$ (4)	1.98_8 (1)	fcc	7.72_3	$EuPt_{2+x}$	(6)	1.30_7 (5)					(10)
$.355_7$	2.12_5 (2)	fcc	7.71_5	$EuPt_{2+x}$	(6)	1.35_1					(11)
$.356_1$ (4)	2.06_0 (1)	fcc	7.71_6	$EuPt_{2+x}$	(6)	1.36_7 (5)					(11)
$.382_4$	2.13_1 (2)	fcc	7.71_4	$EuPt_{2+x}$	(7)	1.41_0		monoclinic		Eu_2O_3 (outer)	(11)
$.396_8$ (4)	2.08_7 (1)	fcc	7.71_8	$EuPt_{2+x}$	(6)	1.46_0 (5)					(11)
$.417_3$ (4)	2.19_1 (1)	fcc	7.69_8	$EuPt_{2+x}$	(6)	1.48_5 (5)	1.46_8				(12)
$.452_7$ (4)	2.62_4 (1)	fcc	7.63_8	$EuPt_{2+x}$	(6)	1.46_0 (5)	1.46_0				(12)
$.467_4$	2.75_2 (2)	fcc	7.64_3	$EuPt_{2+x}$	(7)	1.46_8		monoclinic		Eu_2O_3	(12)
$.484_1$ (4)	2.81_9 (1)	fcc + wk. lines	Pattern too poor to measure		(6)	1.50_7 (5)	1.47_0				(12)
$.504_5$ (4)	3.16_9 (1)	fcc + wk. lines	7.62	$EuPt_{2+x}$ (Eu_2Pt_7)?	(6)	1.47_3 (5)	1.47_4				(12)
$.531_2$ (4)	3.44_5 (1)	(fcc)? + unidentified	(7.62)?	$(EuPt_{2+x})$? (Eu_2Pt_7)?	(6)	1.49_0 (5)	1.47_4				(12)
$.545_0$	3.68_7 (2)	unidentified		$(EuPt_5)$?	(8)	1.48_1					(12)
$.626_8$	5.20_6 (2)	unidentified		$(EuPt_5)$?	(8)	1.47_6					(12)
$.748_0$	9.13_4 (2)	unidentified + fcc	2.265	$(EuPt_5)$? Pt	(9)	1.48_1		monoclinic		Eu_2O_3	(12)
0.848_4	17.29_3 (2)	unidentified + fcc	2.265	$(EuPt_5)$? Pt	(9)	1.47_8					(12)

NOTES:

(1) Calculated from weight loss of oxide and weight gain of platinum phase.

(2) Calculated from weight loss of oxide.

(3) Value rejected, inconsistency between initial and final weights indicates weighing error.

(4) *Equilibrations done with configuration in Fig. 1, using tungsten liner in container for Pt.*

(5) EuO starting material was not single crystal and may have contained excess Eu, which would result in a high calculated experimental O:Eu ratio.

(6) Wire intact, no melting, no container reaction, extensive recrystallization.

(7) Wire stuck to capsule wall.

(8) Completely melted, wet Mo capsule and formed strong bond. Boundary sharp with no evidence of extensive reaction. Analysis showed 200 ppm Mo.

(9) Partly melted.

(10) Inner core of EuO with dense outer layer of Eu_3O_4 which increases in thickness as the O:Eu ratio increases.

(11) Inner core of dense polycrystalline Eu_3O_4 with outer layer of yellow material which increases in thickness with increasing O:Eu ratio. Yellow material is Eu_2O_3 with a small amount of Eu_3O_4 uniformly dispersed in it.

(12) Eu_2O_3 with uniformly dispersed second phase of Eu_3O_4, identical to outer layer described in Note (11).

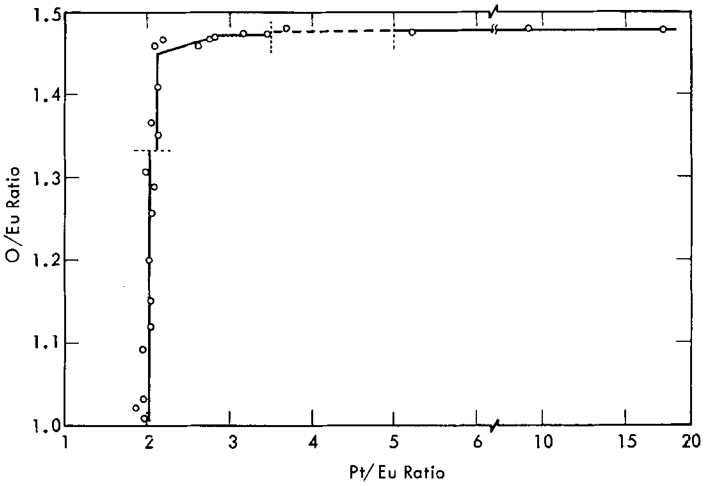

FIG. 3. Oxygen-europium ratios versus platinum-europium ratios for samples equilibrated at 1500°C.

form only binary compounds and no solid solutions or ternary compounds, would consist of vertical and horizontal line segments. Curved or sloped lines might be obtained where the equilibria involved solutions. These characteristics may be seen by comparing Fig. 3 with the derived ternary diagram shown in Fig. 4. The interpretation of results presented here is based on the following assumptions:

(1) compounds and solid solutions may exist in either binary system but there are no ternary phases;

(2) the solubility of either of the noncommon components in any phase of the other binary system is negligible, i.e., there is negligible solubility of platinum in any of the oxide phases or of oxygen in any of the platinum-containing phases.

A vertical line is drawn in Fig. 3 at Pt:Eu = 2.02 corresponding to the composition of the platinum phase in equilibrium with two-phase mixtures of EuO and Eu_3O_4. A limit to the range of stoichiometry for single-phase EuO at 1500°C can be established from the run with the lowest platinum–EuO ratio. The EuO sample for the first run in Table II

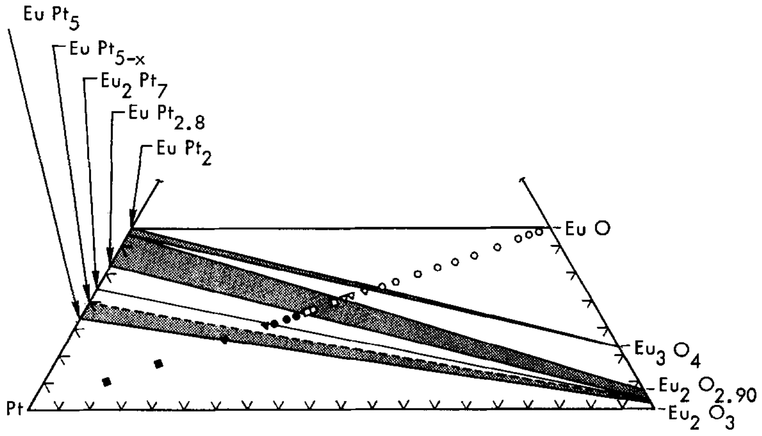

FIG. 4. A portion of the Eu-Pt-Eu_2O_3 ternary diagram at 1500°C.

○ = EuO + Eu_3O_4 + $EuPt_{2.02}$
▽ = Eu_3O_4 + $Eu_2O_{2.90}$ + $EuPt_{2.10}$
□ = Eu_2O_{3-y} + $EuPt_{2+x}$
● = $Eu_2O_{2.94}$ + $EuPt_{2.8}$ + Eu_2Pt_7
▼ = Eu_2O_{3-y} + $EuPt_{5-x}$
■ = $Eu_2O_{2.96}$ + $EuPt_5$ + Pt

initially weighed 272.26 ± 0.03 mg; it lost 2.51 ± 0.05 mg during equilibration and gave a product with a uniform layer of Eu_3O_4 covering the EuO crystal. The calculated overall composition of the oxide product (assuming a starting composition of $EuO_{1.000}$) is $EuO_{1.010}$. The starting material was europium-rich and the product was two-phase EuO plus Eu_3O_4, so the composition range for EuO at 1500°C must be <0.01. We are not able to set more accurate composition limits because we do not know how much free europium was contained in the starting crystal and we did not remove and weigh the Eu_3O_4 from the crystal after the run. The narrow composition range found here is contradictory to the findings of Shafer (*9*). The lattice parameter of EuO in the equilibration products which were oxygen-rich was 5.14_4, identical to the parameter for europium-rich products. The color and appearance in bulk and under the microscope were also the same for hypo- and hyperstoichiometric EuO. The identity of lattice parameters and optical properties of hypo- and hyperstoichiometric material shows only that these properties are consistent with a narrow composition range. Wide ranges in composition are possible without corresponding changes in lattice parameters or optical properties large enough for us to have observed them.

Another vertical line at Pt:Eu = 2.10 corresponds to the intermetallic phase in equilibrium with two-phase mixtures of Eu_3O_4 and oxygen-deficient Eu_2O_{3-x}. The limits for the stoichiometry of Eu_3O_4 provided by the samples with oxide products of O:Eu = 1.31 and 1.35 are far beyond the actual values. Both of the above samples contained substantial amounts of second-phase material (either EuO or Eu_2O_{3-x}). The range on the oxygen-rich side was shown to be very small by the synthetic work discussed previously. The absence of dispersed second-phase precipitates in the bulk material, after quenching from equilibrations at 1500°C either with EuO or with oxygen-deficient Eu_2O_{3-x}, indicates that the composition range is not significantly greater at temperatures up to 1500°C than it is at room temperatures. As with EuO, the hypo- and hyperstoichiometric materials have identical X-ray and optical properties. We conclude that at 1500°C the range of stoichiometry in Eu_3O_4 is very small, and a horizontal line is drawn at O:Eu = 1.333.

The sloped line from Pt:Eu = 2.10–2.8 corresponds to equilibria between $EuPt_{2+x}$ and Eu_2O_{3-x}. Additional dashed lines are drawn to represent equilibria involving the unidentified phase found in this study (taken to be Eu_2Pt_7) and $EuPt_5$. The final horizontal line is drawn through the data at O:Eu = 1.48, which corresponds to the composition of oxide in equilibrium with two-phase mixtures of the platinum-rich intermetallic (assumed to be $EuPt_5$) and platinum saturated with europium.

The ternary diagram for part of the system, Pt–Eu_2O_3–Eu at 1500°C, constructed using the above information and assumptions, is shown in Fig. 4.

Limiting values for the free energies of formation at 1773°K of $EuPt_{2+x}$ can be derived from observed equilibria with the europium oxides. We can get the partial molal free energy of europium in an intermetallic compound at a given temperature if we know the Eu(g) pressure in equilibrium with the compound. This gives a limiting value for the free energy of formation. Consider the following reactions:

$$4EuO(s) + 2.02Pt(s) = Eu_3O_4(s) + EuPt_{2.02}(s), \tag{1}$$

$$Eu_3O_4(s) + Eu(g) = 4EuO(s), \tag{2}$$

$$Eu(l) = Eu(g), \tag{3}$$

$$2.02Pt(s) + Eu(l) = EuPt_{2.02}(s). \tag{4}$$

Equation (4) defines the formation of $EuPt_{2.02}(s)$ from the elements in their standard states. For $EuPt_{2.02}(s)$, $\Delta G^\circ_{f,1773} = \Delta G(1) + \Delta G(2) + \Delta G(3)$. Observed equilibria between the intermetallic compounds and the oxides show $\Delta G(1) < 0$. References (*36*) and (*38*) give free energies for Eqs. (2) and (3) of $\Delta G(2) = -25.1$ kcal and $\Delta G(3) = 1.8$ kcal. Therefore for $EuPt_{2.02}(s)$, $\Delta G^\circ_{f,1773} < -23.3$ kcal/gfw. The value −23.3 kcal/g-at. also corresponds to the partial molal free energy of Eu in the intermetallic compound, with Eu(l) as the standard state. We also know how the partial molal free energy of europium in the intermetallic compound is changing with increasing platinum content. We have determined that $EuPt_{2.10}(s)$ is in equilibrium with $Eu_3O_4(s) + Eu_2O_{3-x}(s)$ at 1773°K. Haschke and Eick (*37*) have determined the Eu(g) pressures for the coexistence of these two oxides. Consideration of a set of reactions similar to those above gives a value of −34.4 kcal/g-at. for the partial molal free energy of Eu in $EuPt_{2.10}(s)$ at 1773°K.

7. The Sm–Sm_2O_3 and Yb–Yb_2O_3 Systems

Attempts were made to prepare Sm_2O, SmO, Yb_2O, YbO, and other reduced oxides of Sm and Yb. The starting materials were nominally 99.9% Sm_2O_3 and Yb_2O_3 which had been fired in air at 1200°C, and corresponding metal chips which had been cut from ingots of nominal 99% purity with a tungsten carbide tool. The ingots were cut under dry hexane and the material from the first cut was discarded to reduce oxide contamination. The chips were transferred into the steel glove box and mixtures were prepared in the same way described above for EuO. The samples were sealed in molybdenum capsules by EBW.

The Sm samples were heated to 2100°C and cooled quickly, using helium gas as a quenching aid. The capsules were broken open and the products recovered without the use of the glove box. All samples had been completely melted and cooled to a uniformly dark gray product. X-Ray powder diffraction and microscopic analysis showed that the products, in all cases, were Sm_2O_3 with finely dispersed samarium metal. In order to check for the possible existence of Sm compounds stable only at lower temperatures, the samples were again sealed in molybdenum capsules and heated for 8 hr at 1500°C. The products of this run were identical to the starting material.

The results indicate that at temperatures above 2100°C, the system is one liquid phase for compositions from Sm metal to ones with O:Sm ratios of 1.33 or higher, and that at high temperatures no crystalline oxide of samarium other than Sm_2O_3 exists.

The Yb samples were heated for several hours at 1800°C in sealed molybdenum capsules and allowed to cool in the furnace under vacuum (about 5 min to cool to 700°C). The composition Yb_2O had completely melted and appeared to consist of a mixture of dark red crystals and excess metal. With the other two compositions, only the metal phase melted. In these samples the oxide sintered and consisted of very dark red crystals about 0.01 mm across.

Examination with the polarizing microscope showed the material to contain a mixture of dark red crystals and colorless crystals in addition to the excess metal. There was no birefringence. X-Ray powder diffraction analysis showed only Yb_2O_3 (bcc) and Yb (fcc). Using spectrographic analysis, the only metallic impurities detected in the products at levels greater than 15 ppm were La (3000 ppm) and Lu (2000 ppm).

The excess metal was dissolved from one sample with HCl as described by Miller and Daane (*20*). The loose crystalline powder from this treatment was washed in distilled water, transferred to a platinum dish, and dried in a vacuum oven at about 50°C. The weight gain of this sample, on ignition in air at 1200°C, was measured to assess the oxygen deficiency of Yb_2O_{3-x} in equilibrium with Yb metal at 1800°C. The sample of 0.296211 g gained 112 μg on ignition. The composition of the reduced sesquioxide calculated from this data is $YbO_{1.495}$, which agrees well with the compositions of reduced sesquioxides of other rare-earth elements reported by Miller and Daane (*20*).

Since our products were obviously two-phase at room temperature, the reduced sesquioxide apparently disproportionated into $Yb_2O_3 + Yb$ as it cooled from 1800°C. We have assumed that the metal from this reaction is dispersed within the crystalline material and is not dissolved when the bulk excess metal is removed. If some of this metal was lost in the HCl treatment, then the oxygen deficiency in Yb_2O_{3-x} at 1800°C is somewhat greater than the value we have reported.

Another sample of composition YbO was heated to 1450°C for 3 hr and cooled slowly (3 hr to 1000°C). The reaction temperature for this sample was in the range used by Achard for preparations of YbO (*15*). The product was a sintered pellet of oxide similar to the previous samples, but the excess metal was concentrated at the bottom of the capsule rather than dispersed through the oxide pellet.

We conclude that Yb_2O_3 is the only stable oxide of ytterbium at high temperatures and that the material Achard reported as YbO was probably a solid solution of oxygen in YbN similar to the samarium oxide–nitride which had been confused with SmO (*17*). Since Achard's preparations were made by reducing the sesquioxide with carbon, an oxide–carbide is also a possibility.

8. Conclusions

We have established that EuO and Eu_3O_4 are the only stable reduced oxides of europium and that they both have very narrow ranges of stoichiometry. We have also shown that oxygen-deficient Eu_2O_{3-x} is stable to $Eu_2O_{2.90\pm0.02}$ at 1500°C. In the Eu–Pt system, the range of stoichiometry for the fcc ($MgCu_2$) phase $EuPt_{2+x}$ has been determined to be $EuPt_2$ to $EuPt_{2.8\pm0.1}$ at 1500°C and two additional intermetallic phases were observed.

In contrast to the fluorides, for which there is rather close correspondence between the samarium, europium, and ytterbium systems (*39*, *40*), there are no stable oxides of samarium or ytterbium corresponding to EuO or Eu_3O_4. This is a manifestation of the enhanced stability of the divalent oxidation states in the fluoride systems compared to the oxide systems. Results from two related investigations also show greater stability for divalent europium in the fluoride than in the oxides. In products from a study of the Eu–O–F ternary system we found $EuF_{2.0}$ in equilibrium with oxygen-deficient Eu_2O_{3-x} (*41*). An investigation involving the equilibration of europium fluorides with platinum–europium phases was carried out at a lower temperature than that used for the oxide equilibrations, so the results cannot be compared directly. However, the fact that EuF_2 is in equilibrium with $EuPt_5$ at 1260°C (*39*), while EuO is in equilibrium with $EuPt_2$ at 1500°C, indicates that the divalent state of europium is much more stable in the fluoride since the activity ratio of europium between $EuPt_2$ and $EuPt_5$ is not expected to change much from 1260 to 1500°C. The factors that lead to the marked differences in stability of the divalent oxidation states of the lanthanon elements between the fluoride and the oxide systems are still not understood.

Acknowledgments

We wish to thank Mrs. Bettie Shroyer for help in the preparatory work, V. Silveira for the X-ray powder work, E. Wrenn and R. Reiss for aid in the encapsulation of samples, J. Stevens and E. Peck for spectrographic analyses, and D. McCoy and Dr. R. Gutmacher for X-ray fluoresence and microprobe analyses. We are also grateful to Dr. Q. Johnson for the single-crystal X-ray work and for helpful discussions. Special thanks are due to Dr. Leo Brewer who predicted for us in 1965, before any Sm or Eu intermetallic with Pt or Ir had to our knowledge been reported, the stability and structures of LnM_2 and LnM_5, for Ln = Sm and Eu and M = Pt and Ir. The time and effort of the people who reviewed early versions of the manuscript are appreciated. The comments of Dr. R. Taylor, Dr. L. Himmel, and Dr. A. W. Searcy were particularly helpful.

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