

THE EFFECT OF HIGH PRESSURE ON THE FORMATION OF LRu<sub>2</sub> AND LOs<sub>2</sub> (L=LANTHANIDE) COMPOUNDS

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SUMMARY

The compounds SmRu<sub>2</sub>, NdRu<sub>2</sub> and LaOs<sub>2</sub> have the cubic MgCu<sub>2</sub>-type structure when prepared at atmospheric pressure. By application of pressures up to 88 kbar, these compounds were prepared with the hexagonal MgZn<sub>2</sub>-type structure. The hexagonal lattice parameters (*a*, *c*) are (5.298, 8.939), (5.323, 9.004), and (5.42, 9.00), respectively. The formation of these hexagonal polymorphs is attributed to the effect of pressure on the relative atomic size of the lanthanide vs. that of Ru or Os. The amount of 4*f* bonding in these compounds has no influence on the type of polymorph formed.

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INTRODUCTION

Several investigators<sup>1,2,3,4,5,6,7</sup> have reported the preparation and crystal structures of LRu<sub>2</sub> and LOs<sub>2</sub> (L = lanthanide) compounds. In each series the compounds involving the lowest-atomic-number lanthanides crystallize in the cubic MgCu<sub>2</sub>-type structure while those with the higher-atomic-number lanthanides crystallize in the hexagonal MgZn<sub>2</sub>-type structure. The point in a series where the structure changes from cubic to hexagonal will be designated the polymorphic transition point (PTP). In the series under consideration here, the PTP falls at GdRu<sub>2</sub> and PrOs<sub>2</sub>, each of which exists in both cubic and hexagonal structures.

Bandurkin and Dzhurinskii<sup>8</sup>, Gschneidner, *et al.*<sup>9,10,11</sup>, and Pearson<sup>10,12</sup> have suggested that the polymorphic changes seen in certain lanthanide compound series are caused by changes in the amount of 4*f* bonding. Gschneidner and Pearson<sup>10</sup> use the LRu<sub>2</sub> and LOs<sub>2</sub> series (among others) to illustrate this possibility. They show that the value of  $r_L - r_{4f}$  ( $r_L$  = lanthanide atomic radius and  $r_{4f}$  = lanthanide 4*f* shell radius) for these series increases from a minimum at La (excluding Ce) to a maximum near Gd and then remains essentially constant through Lu. This indicates that the amount of 4*f* bonding is at a minimum from Lu to Gd and increases from Gd to a maximum at La. Since an increase in 4*f* bonding is said to favor cubic symmetry<sup>10</sup>, the increase in the amount of 4*f* bonding (from Gd through La) in the LRu<sub>2</sub> and LOs<sub>2</sub> series could be responsible for the observed structure changes at GdRu<sub>2</sub> and PrOs<sub>2</sub>.

Havinga *et al.*<sup>13</sup> have taken issue with this suggestion, claiming instead that volume (size) effects are the cause of polymorphic changes such as those mentioned above. They state that the contribution from 4*f* bonding is too small to have any observable effect. Comments on their paper by Gschneidner<sup>14</sup> and countercomments by Havinga *et al.*<sup>15</sup> have not materially reduced the difference of opinion. These comments did serve, however, to re-expose an earlier suggestion by Gschneidner and Valleta<sup>9</sup> that high-pressure experiments could resolve the question of which factor, volume (size) effect or 4*f* bonding, is predominant.

The application of high pressure will reduce the atomic radius of the lanthanide but have little effect on the size of the 4*f* shell radius<sup>10</sup>. This will increase the amount of 4*f* bonding and should cause more members of the series to crystallize with the cubic structure. The result will be a shift of the PTP toward the heavier lanthanides. On the other hand, because the lanthanides are more compressible than either Ru or Os, the application of pressure should cause the relative atomic size of L vs. that of Ru or Os to decrease, thus causing the larger lanthanides to behave more like the smaller ones. This should cause more members of the series to crystallize in the hexagonal structure and result in a shift of the PTP toward the lighter lanthanides. The effect of pressure on the PTP in the LRu<sub>2</sub> and LOs<sub>2</sub> series therefore provides a test for determining which theory predominates.

## EXPERIMENTAL

A number of experiments were made to determine the effect of high pressure on the formation of the  $\text{LRu}_2$  and  $\text{LOs}_2$  compounds in the vicinity of the PTP. The high pressures required were generated in a tetrahedral press with anvil guides as designed by Hall<sup>16,17</sup>. To increase the internal pressure/applied pressure ratio, each tetrahedral sample holder (containing a 1:2 mixture of the appropriate elements) was painted with a suspension of red iron oxide in methanol. After the methanol had evaporated, the sample holder was placed in the press and brought to the desired pressure. The sample was then heated internally by passing an electric current through a graphite sleeve which contained the reaction mixture (the reactants were insulated from the graphite by boron nitride). After the sample had been heated for the desired period it was quenched and the pressure was released. A detailed description of the experimental procedure, the sample geometry, and the pressure and temperature calibrations may be found in an earlier publication<sup>18</sup> (except that sample holders used in the present work were not baked).

Powdered Ru and Os as well as 100-mesh La filings (under oil) were obtained from Research Organic/Inorganic Chemical Corporation, Sun Valley, California. The other elements used in this study (Ce, Pr, Nd, Sm, Gd, Tb) were provided in ingot form by Research Chemicals Incorporated, Phoenix, Arizona.

The ingots were reduced by filing and sieving. Those filings that did not pass a 100-mesh sieve were discarded. Stoichiometric mixtures of the reactants were prepared in small quantities and kept in a desiccator to minimize oxide formation. Lines characteristic of the lanthanide oxides were not observed in the X-ray spectra of the products.

All X-ray work was done on a General Electric XRD-5 powder diffraction unit. Sample products were reduced by crushing and mounted on a 143.2 mm Debye-Scherrer camera by means of 0.5 mm. glass capillaries. Copper ( $\lambda = 1.5418$ ) and chromium ( $\lambda = 2.2909$ ) radiation were used as circumstances dictated. The Nelson-Riley extrapolation method<sup>19</sup> was used to correct for absorption in determining the lattice parameters (except where noted otherwise). A silicon internal standard was used for the hexagonal structures.

## RESULTS

For the  $\text{LRu}_2$  series, syntheses involving six lanthanides (Ce, Pr, Nd, Sm, Gd, Tb) were made. At 65 kbar and 1230°C syntheses with Ce, Pr, Nd, Gd and Tb resulted in compounds with the same structure as obtained at atmospheric pressure ( $\text{GdRu}_2$ , known in both forms at atmospheric pressure<sup>4</sup>, crystallized with the hexagonal structure). Under these same pressure and temperature conditions  $\text{SmRu}_2$  (normally cubic<sup>2</sup>) crystallized with the hexagonal structure. Further experiments revealed that hexagonal  $\text{SmRu}_2$  could be prepared at pressures as low as 6 kbar (the lowest pressure used in this study) and that cubic  $\text{SmRu}_2$  could be prepared at all pressures up to 65 kbar if a high enough temperature was used\*. Work at higher pressures showed that  $\text{NdRu}_2$  (normally cubic<sup>1</sup>) could be prepared in the hexagonal form at 88 kbar and 1300°C. The hexagonal and cubic polymorphs crystallized together down to 78 kbar, and only the cubic polymorph was prepared at pressures less than 78 kbar. Pressures as high as 83 kbar were used in synthesizing  $\text{PrRu}_2$ , but only the cubic polymorph was found.

Work with the  $\text{LOs}_2$  series was complicated by the fact that very little reaction was obtained at high pressures, particularly when the lanthanide was La or Ce. The first attempt (65 kbar and 1230°C) to synthesize  $\text{LaOs}_2$  (normally cubic<sup>1,2</sup>) resulted

TABLE I

## SYNTHESIS RESULTS

<i>Compound</i>	<i>Structure when prepared at</i>	<i>Minimum pressure required for preparation of high pressure structure (bars)</i>
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\* In order of increasing temperature, the result for  $\text{SmRu}_2$  at any pressure up to 65 kbar was (1) no reaction, (2) hexagonal, (3) cubic. The temperature of the hexagonal/cubic boundary was about 1400-1450°C except in the 20-30 kbar region where it dipped to 1200-1250°C. We have no explanation for this unusual behavior.

	<i>atmospheric pressure</i>	<i>high pressure</i>	
CeRu <sub>2</sub>	Cubic	Cubic	1
PrRu <sub>2</sub>	Cubic	Cubic	1
NdRu <sub>2</sub>	Cubic	Hexagonal	78,000
SmRu <sub>2</sub>	Cubic	Cubic and Hexagonal	<6,000
GdRu <sub>2</sub>	Cubic and Hexagonal	Hexagonal	1
TbRu <sub>2</sub>	Hexagonal	Hexagonal	1
LaOs <sub>2</sub>	Cubic	Hexagonal**	?
CeOs <sub>2</sub>	Cubic	Cubic	1
PrOs <sub>2</sub>	Cubic and Hexagonal	Hexagonal	1

\*\*Obtained only once (see section on Results).

TABLE II  
LATTICE PARAMETERS\*

<i>Compound</i>	<i>Structure</i>	<i>Lattice parameters(Å)</i>				
		<i>This work</i>	<i>Literature</i>			
			1	2	3	5
CeRu <sub>2</sub>	Cubic	7.536(3)	7.535		7.5364	
PrRu <sub>2</sub>	Cubic	7.623(7)	7.624		7.6223	
NdRu <sub>2</sub>	Cubic	7.612(1)	7.614			
NdRu <sub>2</sub>	Hexagonal	5.323(4) 9.004(7)				
SmRu <sub>2</sub>	Cubic	7.577(3)		7.580		
SmRu <sub>2</sub>	Hexagonal	5.298(4) 8.939(7)				
GdRu <sub>2</sub>	Hexagonal	5.277(6) 8.886(11)	5.271 8.904			5.276 8.904
TbRu <sub>2</sub>	Hexagonal	5.265(5) 8.853(8)			5.254 8.831	5.263 8.867
LaOs <sub>2</sub>	Hexagonal	5.42(2) 9.00(4)**				
CeOs <sub>2</sub>	Cubic	7.576(10)	7.593			
PrOs <sub>2</sub>	Hexagonal	5.359(6) 8.938(11)**	5.368 8.945		5.370 8.960	

\*The number in ( ) refers to the standard deviation in the last significant figure.

\*\*Not corrected for absorption.

TABLE III  
X-RAY DATA FOR HEXAGONAL SmRu<sub>2</sub> AND NdRu<sub>2</sub>

<i>hkl</i>	<i>SmRu<sub>2</sub></i>		<i>NdRu<sub>2</sub></i>	
	<i>d(obs.)</i>	<i>d(calc.)</i>	<i>d(obs.)</i>	<i>d(calc.)</i>
110	2.647	2.649	2.662	2.661
103	2.504	2.499	2.512	2.515
112	2.281	2.279	2.290	2.291
201	2.223	2.222	2.235	2.233
202	2.049	2.041	2.057	2.052
104	2.007	2.009	N.O.	---
213	1.499	1.499	1.506	1.507
302	1.447	1.447	1.456	1.454
205	1.410	1.410	1.419	1.419
220	1.324	1.325	1.331	1.331

313	1.170	1.170	1.172*	1.176
401	1.138	1.138	1.143	1.143
412	0.976	0.977	0.981	0.982
332	0.867	0.866	N.O.	---
241	0.863	0.863	N.O.	---
243	0.834	0.833	N.O.	---

\*Not used in lattice constant determination.

N.O. = not observed.

Copper radiation ( $\lambda = 1.5418$ ) was used; the 214 reflection was obscured by the Si internal standard.

TABLE IV  
X-RAY DATA FOR HEXAGONAL  $\text{LaOs}_2$

<i>hkl</i>	$\text{LaOs}_2$	
	<i>d(obs.)</i>	<i>d(calc.)</i>
103	2.492	2.528
112	2.310	2.322
201	2.255	2.272
202	2.070	2.081
203	1.836	1.849
213	1.522	1.527
302	1.472	1.478
205	1.430	1.428
214	1.392	1.393
220	1.365	1.356
206	1.267	1.264

Chromium radiation ( $\lambda = 2.2909$ ) was used.

in partial reaction to the hexagonal polymorph. Although several other syntheses were attempted under presumably the same conditions, this run could not be duplicated. All following runs produced no reaction. The situation was similar for  $\text{CeOs}_2$ . Several synthesis attempts were made but little or no reaction occurred. When  $\text{CeOs}_2$  was obtained it always had the cubic structure. Each attempt to prepare  $\text{PrOs}_2$  (normally both cubic and hexagonal) resulted in partial reaction to the hexagonal polymorph. The maximum pressure used in work with the  $\text{LOs}_2$  series was 65 kbar.

A summary of the synthesis results is shown in Table I. The lattice parameters of compounds prepared during this study are shown in Table II along with those obtained from the literature. The calculated and observed *d*-values for the previously unknown polymorphs are shown in Tables III and IV.

## DISCUSSION

The results for the  $\text{LRu}_2$  series clearly show that an applied pressure of 88 kbar causes the PTP to shift from  $\text{GdRu}_2$  to a point between  $\text{NdRu}_2$  and  $\text{PrRu}_2$ . Unfortunately the results for the  $\text{LOs}_2$  series do not allow a definite conclusion. The fact that  $\text{PrOs}_2$  is found only in the hexagonal form when prepared at high pressure, indicates that any high pressure shift of the PTP is toward the lighter lanthanides. This conclusion is far from proved for the  $\text{LOs}_2$  series, however, and further work needs to be done.

The only adequate explanation for the high-pressure shift of the PTP in the  $\text{LRu}_2$  series is based on the volume (size) effect. If it is true that pressure reduces  $r_L$  to a greater extent than  $r_{4f}$ , then it is clear that the change in amount of  $4f$  bonding is not responsible for the polymorphic change observed at  $\text{GdRu}_2$  in the  $\text{LRu}_2$  series. It is probable, therefore, that  $4f$  bonding does not have an observable effect on any of the lanthanide compound series, although further high pressure experiments must be carried out to establish this unequivocally.

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