

SHORT COMMUNICATION

The effect of high pressure on the crystal structure of LaOs₂ and CeOs₂

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A short time ago the results of experiments on the effect of pressure on the formation of LRu₂ and LOs₂ compounds (L= Lanthanide) were reported¹. Compounds in the LOs₂ series did not readily form under high pressure and temperature conditions. Because of this difficulty no definite conclusion could be drawn concerning the shift of the LOs₂ PTP‡ with the application of pressure.

TABLE I

LATTICE PARAMETERS*

Compound	Structure	Lattice Parameters (Å)			
		This work	Literature		
			2	7	8
LaOs ₂	Cubic	7.743(2)	7.737	7.736	
CeOs ₂	Cubic	7.593(1)	7.593		
PrOs ₂	Cubic	7.660(1)	7.663		
LaOs ₂	Hexagonal	5.419(1)			
		9.083(2)			
CeOs ₂	Hexagonal	5.355(1)			
		8.816(2)			
PrOs ₂	Hexagonal	5.370(1)	5.368	5.370	
		8.978(1)	8.945	8.960	

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

Copper radiation ($\lambda = 1.5418 \text{ \AA}$) used.

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‡ PTP= polymorphic transition point, the point in a lanthanide compound series where the crystal structure changes. At atmospheric pressure the LOs₂ PTP falls at PrOs₂, a compound which exists in both the cubic MgCu₂-type structure (characteristic of lighter LOs₂ compounds) and the hexagonal MgZn₂-type structure (characteristic of the heavier LOs₂ compounds)².

Further experiments utilizing the MgCu₂-type LOs₂ compounds as starting material (rather than a 1: 2 mixture of the elements) have now been completed.

The MgCu₂-type compounds (for L= La, Ce, Pr) were prepared by arc-melting stoichiometric mixtures of the elements. X-ray powder patterns of the unannealed products revealed the MgCu₂-type structure in each case. The lattice parameters were determined and compared favorably with literature values (see Table 1).

TABLE II

X-RAY DATA FOR HEXAGONAL LaOs₂ AND CeOs₂

<i>h k l</i>	<i>LaOs₂</i>		<i>CeOs₂</i>	
	<i>d(obs.)</i>	<i>d(calc.)</i>	<i>d(obs.)</i>	<i>d(calc.)</i>
1 1 0	2.709	2.710	2.678	2.678
1 0 3	2.545	2.544	2.481	2.482
2 0 0	n.o.	--	2.312	2.318
1 1 2	2.327	2.327	2.289	2.288
2 0 1	2.271	2.272	2.243	2.243
0 0 4	2.271	2.271	2.203	2.204
2 0 2	2.081	2.085	2.049	2.052
1 0 4	2.047	2.044	1.990	1.991
2 0 3	1.844*	1.855	1.819	1.820
2 1 0	1.784*	1.774	1.751	1.753
3 0 0	1.562	1.564	1.544	1.546
2 1 3	1.528	1.530	1.505	1.505
3 0 2	1.478	1.479	1.458	1.459
2 0 5	1.437	1.436	1.403	1.404
2 1 4	1.397	1.398	1.373	1.372
2 2 0	Si	--	1.338	1.339
1 1 6	1.322	1.322	n.o.	--
2 2 2	1.299	1.298	n.o.	--
2 0 6	1.272	1.272	Si	--
3 1 3	1.194*	1.196	1.178	1.178
2 2 4	1.163	1.163	1.146*	1.144
2 0 7	1.135	1.136	Si	--
3 2 3	1.012*	1.014	1.000	1.000
2 2 6	n.o.	--	0.990	0.990
4 1 2	0.998	0.999	0.986	0.986
4 0 5	0.985	0.986	0.968	0.969
3 2 4	0.973	0.973	Si	--
2 1 8	Si	--	0.932	0.933
4 0 6	0.927	0.927	0.909	0.910
3 3 2	0.886	0.886	0.875	0.875
4 2 1	0.883	0.883	0.872	0.872
4 2 2	0.871	0.871	Si	--
4 0 7	n.o.	--	0.853	0.853
3 1 8	Si	--	0.837	0.837
2 0 10	n.o.	--	0.824	0.824
5 1 3	n.o.	--	0.801	0.801
4 2 5	0.797	0.797	Si	--

* Not used in lattice constant determination.

n.o.= not observed, Si= interference from silicon internal standard.

The high pressure experiments were carried out in a tetrahedral press with anvil guides as designed by Hall^{3,4}. Experimental details have been given in previous papers^{1,5}.

X-ray work was done on a G.E. XRD-5 powder diffraction unit. Immediately following each high pressure run the sample was crushed and X-rayed without further preparation. The Nelson-Riley extrapolation⁶ was used to correct for absorption. A silicon internal standard was used with the non-cubic structures.

Experiments conducted at 70 kbar and 1000°C resulted in the conversion of the cubic starting materials (LaOs₂, CeOs₂ and PrOs₂) to the hexagonal form. Further experiments revealed that hexagonal CeOs₂ could be prepared at pressures as low as 6 kbar (the lowest pressure used in this work) and that the lowest synthesis pressure for hexagonal LaOs₂ is between 6 and 14 kbar. It was also noted that at temperatures above 1050-1100°C the cubic structure was retained regardless of the pressure. X-ray data are given in Table I (lattice parameters) and Table II (observed and calculated *d*-values for hexagonal LaOs₂ and CeOs₂)

It is clear that the LOs₂ PTP shifts toward the lighter lanthanides with the application of high pressures at temperatures less than 1050-1100°C. This further supports the tentative conclusion of the previous paper¹ that changes in the amount of 4*f* bonding are not responsible for the polymorphic changes in lanthanide compound series.

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