Unit Cell Dimensions of CeP_2 and PrP_2

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An X-ray crystallographic investigation of rare earth metal phosphides has been started at this institute. In the present paper, X-ray powder diffraction data are given for CeP_2 and PrP_2. These compounds are found to be isostructural, and belong to the $NdAs_2$ structure type,[1] which also includes $LaAs_2$ (below 750°C), $CeAs_2$ and $PrAs_2$. The existence of these diphosphides has earlier been discussed in the literature. By X-ray investigations Olcese [2] has shown the occurrence of CeP_2. Schmid and Hahn,[3] who have studied the system Ce-P report a phase, which probably is CeP_2. The occurrence of PrP_2 has been suggested by Franceschi and Olcese,[4] but unsuccessful attempts to prepare PrP_2 have also been reported.[5]

The starting materials for the preparations were a cerium metal ingot (Koch-Light Laboratories, Ltd., claimed purity 99.95 %), a praseodymium metal ingot (Rare Earth Products, Ltd., claimed purity 99.9 %) and red phosphorus of purity higher than 99 %. Powders of the metals were prepared by filing, fragments of the file being removed from the powders by a magnet. Appropriate amounts of the metals and phosphorus were thoroughly mixed and transferred to silica ampoules. All the above mentioned operations were performed in an argon-filled glove box. The silica ampoules were evacuated, sealed off and heated for various periods of time at temperatures below 1000°C.

Praseodymium diphosphide was obtained by heating a mixture of the elements for a week at 750°C. Cerium diphosphide has also been obtained by direct reaction between the elements. The sample used for the cell dimension determination was, however, prepared by heating arc-melted monophosphide and red phosphorus

Table 1. Powder diffraction data for CeP_2 and PrP_2. Hägg-Guinier camera (Philips XDC 700) with $CrK\alpha_1$ radiation.

h k l	CeP_2 $\sin^2\theta \times 10^5$ obs	CeP_2 $\sin^2\theta \times 10^5$ calc	CeP_2 d calc	CeP_2 I obs	PrP_2 $\sin^2\theta \times 10^5$ obs	PrP_2 $\sin^2\theta \times 10^5$ calc	PrP_2 d calc	PrP_2 I obs
0 0 1		1370	9.7808		1316	1385	9.7277	w-
0 1 0		3025	6.5826			3050	6.5553	
0 1 1	4383	4395	5.4610	w+	4433	4435	5.4362	w+
0 0 2	5462	5480	4.8904	w-	5533	5540	4.8638	w-
-1 0 1		8079	4.0277			8207	3.9961	
0 1 2	8494	8505	3.9256	s-	8590	8590	3.9061	s-
1 0 0	8550	8561	3.9128	w+	8703	8701	3.8811	m
-1 0 2	10326	10337	3.5607	m+	10482	10484	3.5357	m+
-1 1 1	11104[a]	11103	3.4356	w	11256[a]	11257	3.4121	w-
1 1 0	11576	11585	3.3634	w+	11750	11751	3.3397	w
1 0 1		11782	3.3352			11964	3.3097	
0 2 0	12095	12099	3.2913	m	12197	12200	3.2776	m
0 0 3		12330	3.2603			12465	3.2426	
-1 1 2	b	13362	3.1319		13533	13534	3.1119	s
0 2 1	13461	13469	3.1194	w+		13585	3.1061	
1 1 1	14818[a]	14807	2.9751	w+	15017[a]	15014	2.9545	w+
-1 0 3	15346	15335	2.9234	s-	15516	15530	2.9050	m+
0 1 3		15355	2.9216			15515	2.9064	
0 2 2	17570	17579	2.7305	w-	17734	17740	2.7181	w-
1 0 2	17734	17744	2.7177	w	17997	17998	2.6985	w
-1 1 3		18360	2.6718		18596	18580	2.6559	w-
-1 2 1	20175	20177	2.5486	s	20410	20407	2.5342	s
1 2 0		20659	2.5187		20899	20900	2.5041	w
1 1 2	20767	20769	2.5121	s-	21050	21047	2.4954	s
0 0 4	21917	21920	2.4452	m-	22167	22160	2.4319	w+
-1 2 2	22440	22436	2.4169	w-	22679	22683	2.4037	w
-1 0 4	23068	23073	2.3833	w	23343	23347	2.3693	w+
1 2 1	23867	23881	2.3427	w-	24154	24164	2.3289	w-
0 2 3	24427	24429	2.3162	w+	24669	24664	2.3051	w+
0 1 4	24944	24944	2.2922	w-	25213	25210	2.2801	w
-1 1 4	26098	26098	2.2409	m	26401	26397	2.2282	m+
1 0 3		26446	2.2262			26801	2.2114	
0 3 0	27215	27222	2.1942	w-		27449	2.1851	
-1 2 3		27434	2.1857			27730	2.1740	
0 3 1	28599[a]	28592	2.1410	w+	28833	28834	2.1320	w+
1 1 3	29460[a]	29470	2.1088	w-	29856	29851	2.0953	w-
1 2 2	29834	29843	2.0956	w-	30172[a]	30197	2.0833	w-
-2 0 1		31909	2.0266			32431	2.0103	
-2 0 2	32315	32315	2.0139	m-	32829	32829	1.9980	w+
0 3 2	32694	32702	2.0019	w-	32988	32989	1.9932	w-
-1 0 5		33552	1.9764			33933	1.9653	
0 2 4	34022	34018	1.9628	w	34361	34359	1.9530	w+
2 0 0	34230	34242	1.9564	w-	34803	34803	1.9406	w-
0 0 5		34250	1.9562			34625	1.9455	
-2 2 1		34933	1.9369		b	35481	1.9219	w-
-1 2 4	35172	35172	1.9303	w-		35546	1.9202	
-1 3 1	35296	35301	1.9268	w-		35656	1.9172	
-2 1 2		35340	1.9258		35872	35879	1.9112	w-
-2 0 3	b	35462	1.9224			35997	1.9081	
1 3 0	35750	35782	1.9138	w-	36150	36150	1.9041	w-
-1 1 5		36576	1.8929			36983	1.8825	
2 1 0	37274	37267	1.8753	w+	37867	37853	1.8607	m-
0 1 5		37274	1.8751			37675	1.8651	
-1 3 2	37564	37559	1.8680	w-		37933	1.8588	
1 0 4	37888	37887	1.8599	w-	38381	38374	1.8480	w
-2 1 3	38514	38486	1.8454	w	39043	39047	1.8321	w+
1 2 3		38544	1.8440			39001	1.8332	
1 3 1	39020	39004	1.8331	w	39408	39413	1.8235	w+
2 0 1		39316	1.8258		39921	39945	1.8114	m
0 3 3	39562	39552	1.8203	m-		39914	1.8121	
1 1 4		40912	1.7898			41424	1.7787	
-2 0 4		41348	1.7804			41935	1.7679	
2 1 1	42351	42340	1.7594	w	43002	42994	1.7459	
-1 3 3	42569	42557	1.7549	w-		42979	1.7462	w+
-2 2 1		44007	1.7257		44627	44630	1.7136	w-
-2 1 4	44406[a]	44373	1.7186	w+	45015	44985	1.7069	w+
-2 2 2		44414	1.7178			45028	1.7060	
1 3 2		44966	1.7072			45446	1.6982	
-1 2 5	45653	45650	1.6944	m-	46145	46133	1.6855	m-
2 2 0	46335	46341	1.6817	w-	47007	47002	1.6698	w-
0 2 5		46348	1.6816			46824	1.6730	
-1 0 6		46770	1.6740			47290	1.6648	
2 0 2	47117	47129	1.6676	w-	47875	47856	1.6549	w-
-2 2 3	47561	47560	1.6600	w-	48200	48196	1.6490	w-
0 4 0	48400	48394	1.6456	w-	b	48798	1.6388	w-
0 3 4	49119	49142	1.6331	w-		49609	1.6254	
0 0 6	49318	49320	1.6301	w-	49843	49860	1.6213	w-
0 4 1	49778	49764	1.6228	w-				
-1 1 6		49794	1.6223					
-2 0 5	49973	49975	1.6194	w-				
1 2 4		49986	1.6192					

[a] Overlapped by a monophosphide line. [b] Overlapped by a silicon line.

at 700°C for a week.

X-Ray powder diffraction data were recorded in a Hägg-Guinier-type camera (Philips XDC 700) using $CrK\alpha_1$ radiation and silicon (a= 5.43054 Å) as internal calibration standard.

Comparison of the diffraction data for the diphosphides with those reported for $CeAs_2$ ($NdAs_2$-type) by Ono *et al.*[1] indicated that all these compounds are isostructural. The symmetry is monoclinic, but a determination of the crystal structure has not yet been reported. The unit cell dimensions were refined by the least squares method using the local program CELNE [6] on an IBM 1800 computer.

The following values were obtained (numbers in parenthesis are the calculated standard deviations referring to the last significant digits):
CeP_2: a=4.0641(2) Å; b=6.5826(3) Å; c= 10.1591(6) Å; β=105.686(5)°.
PrP_2: a=4.0315(2) Å; b=6.5553(3) Å; c= 10.1046(5) Å; β=105.698(5)°.
For identification purposes, powder diffraction data are presented in Table 1.

Acknowledgement. The work has been financially supported by the Swedish Natural Science Research Council.

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Received December 4, 1973.