

The Crystal Structure of Nb_8P_5

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The crystal structure of Nb_8P_5 has been determined by X-ray single crystal methods. The symmetry is orthorhombic, and the unit cell, the dimensions of which are $a=26.1998 \text{ \AA}$, $b=9.4652 \text{ \AA}$, $c=3.4641 \text{ \AA}$, contains 32 niobium atoms and 20 phosphorus atoms. In the refinement of the structure the space group symmetry has been assumed to be *Pbam*. The structure can be described as an array of interconnected Nb_8P triangular prisms, with additional niobium atoms inserted between the prisms.

In previous studies of niobium phosphides,¹⁻⁴ several intermediate phases have been prepared by arc-melting mixtures of niobium and NbP. So far, the crystal structures of Nb_3P , Nb_7P_4 , and Nb_5P_3 have been determined by X-ray single crystal methods.²⁻⁴ The results from a crystal structure analysis of a compound denoted Nb_8P_5 are reported in the present paper.

EXPERIMENTAL

Preparation. Niobium (Hermann Stark, Berlin, claimed purity 99.3 %) and red phosphorus (purity higher than 99 %) were reacted at about 800°C in evacuated silica tubes to form NbP. Mixtures of niobium and NbP were then arc-melted under purified argon. Attempts were made to obtain as phosphorus-rich products as possible by successive additions of NbP and re-meltings. Powder diffraction examination of the most phosphorus-rich samples obtained in this manner showed the presence of two new phases not previously characterized. Some very small crystals of one of the phases could be picked from the crushed melts and were subsequently used for the single crystal structure determination.

X-Ray diffraction work. Powder diffraction patterns were recorded in a Guinier-Hägg type focussing camera with monochromatic $\text{CrK}\alpha_1$ radiation. Silicon ($a=5.43054 \text{ \AA}$) was used as internal calibration standard. The single crystal studies were performed with a Weissenberg camera using zirconium-filtered MoK radiation. The crystal used for the structure determination was needle-shaped with a rather uniform cross-section of about 0.03 mm. It was rotated about the needle axis, which coincided with the shortest crystallographic axis (the *c* axis). The small size of the crystal necessitated very long exposures of the Weissenberg films, and the number of reflexions strong enough to be measured

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was rather limited. The reflexions were recorded by the multiple-film technique using thin iron foils as absorbers between successive films. The intensities were estimated visually by comparison with an intensity scale prepared from timed exposures of one reflexion from the crystal. The effects of absorption were estimated to be very small and were neglected in the structure refinement.

Calculations. The numerical calculations were made on a CDC 3600 computer using programmes listed in Table 1, Ref. 2.

Table 1. Structure data (and their standard deviations) for Nb₅P₅. Space group *Pbam*.
 $a = 26.1998(15)$ Å, $b = 9.4652(5)$ Å, $c = 3.4641(2)$ Å.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
2 Nb(1) in <i>2a</i>	0	0	0	0.20(14)
4 Nb(2) in <i>4g</i>	0.2164(2)	0.2505(5)	0	0.33(11)
4 Nb(3) in <i>4g</i>	0.3259(2)	0.4137(6)	0	0.16(11)
2 Nb(4) in <i>4g^a</i>	0.0485(4)	0.5036(10)	0	-0.17(17)
4 Nb(5) in <i>4h</i>	0.4966(2)	0.2444(5)	$\frac{1}{2}$	0.38(11)
4 Nb(6) in <i>4h</i>	0.0841(2)	0.0023(6)	$\frac{1}{2}$	0.33(10)
4 Nb(7) in <i>4h</i>	0.1208(2)	0.3327(5)	$\frac{1}{2}$	0.28(10)
4 Nb(8) in <i>4h</i>	0.2652(2)	0.0029(6)	$\frac{1}{2}$	0.08(10)
4 Nb(9) in <i>4h</i>	0.3762(2)	0.1675(5)	$\frac{1}{2}$	0.35(11)
4 P (1) in <i>4g</i>	0.0655(6)	0.2079(16)	0	0.32(31)
4 P (2) in <i>4g</i>	0.3388(6)	0.9920(13)	0	-0.38(24)
4 P (3) in <i>4g</i>	0.4272(7)	0.3006(15)	0	0.13(27)
4 P (4) in <i>4h</i>	0.1706(6)	0.1044(14)	$\frac{1}{2}$	-0.11(27)
4 P (5) in <i>4h</i>	0.2862(6)	0.2590(15)	$\frac{1}{2}$	0.06(28)

^a Position filled to only 50 %.

STRUCTURE DETERMINATION

The oscillation and Weissenberg films indicated that the symmetry of the new niobium phosphide is orthorhombic. The approximate unit cell dimensions as obtained from the single crystal films were used for indexing the reflexions on the powder films, and accurate cell dimensions were then obtained by a least squares refinement of the powder diffraction data. No significant changes in the unit cell dimensions were observed for different samples. Since the synthetic technique employed makes it very difficult to obtain singlephase samples suitable for chemical analysis (*cf.* Refs. 2 and 4), the composition of the new phosphide could not be determined by ordinary phase-analytical methods. It could only be inferred that the phosphide was intermediate in composition between Nb₅P₃ and NbP. A comparison of the unit cell volume with those for Nb₇P₄, Nb₅P₃, and NbP indicated a cell content of 52–54 atoms.

Inspection of the Weissenberg films showed that (*h*0*l*) reflexions with $h = 2n + 1$ and (0*kl*) reflexions with $k = 2n + 1$ were not visible. If these extinctions are systematic the space group symmetry is either *Pba*2 or *Pbam*. In space group *Pbam*, occupation of positions 8*i*, 4*e*, and 4*f* would lead to unreasonably short interatomic distances, since the *c* axis is only 3.464 Å. Further inspection of the Weissenberg films showed that the intensity ratio between (*hkl*) and (*hkl* + 2) reflexions was constant, allowing for the influence

of the Lorentz-polarization factor. This observation indicates that the atoms are confined to two planes perpendicular to the c axis and spaced $c/2$ apart.

It thus seemed reasonable to assume that the structure, at least to a first approximation, should conform to $Pbam$ symmetry, with atoms occupying only $4g$, $4h$, and $2a-d$ positions. In the Patterson function, all maxima should then appear in the sections $P(uv0)$ and $P(uv\frac{1}{2})$. Accordingly, the Patterson sections mentioned were computed, using the intensity material from the two layer lines ($hk0$) and ($hk1$). Analysis of the Patterson sections by simple superposition methods yielded a partial structure proposal, consisting of one twofold set of niobium atoms in $2a$, two fourfold sets of niobium atoms in $4g$, and five fourfold sets of niobium atoms in $4h$. Signs of the structure factors were calculated on the basis of this partial structure, and the electron density sections $\rho_o(xy0)$ and $\rho_o(xy\frac{1}{2})$ were computed. In addition to the expected niobium maxima, new maxima appeared in these sections. Five of these maxima could readily be interpreted as arising from three fourfold sets of phosphorus atoms in $4g$ positions and two fourfold phosphorus sets in $4h$ positions. At this stage only one maximum corresponding to a $4g$ position remained to be interpreted. This maximum was appreciably higher than the maxima corresponding to the phosphorus atoms but had only half the height of the niobium atom maxima. An atom occupying this position would have a coordination, which seemed abnormal for a phosphorus atom but much more reasonable for a niobium atom. However, if the $4g$ position were filled with niobium atoms, one very short interatomic distance would occur between each atom and another atom belonging to the same fourfold set. Such short contacts may be avoided if the fourfold position is occupied to only 50 % or less.

Following these observations it was tentatively assumed that the crucial $4g$ position is occupied by only two niobium atoms. This structure proposal gives a unit cell content of 32 niobium atoms and 20 phosphorus atoms, and accordingly the composition lies between Nb_5P_3 and NbP as required by the phase-analytical results.

A second set of ρ_o and ρ_c maps was computed. Since a comparison between the observed and calculated electron densities revealed no further abnormal features it was decided to complete the refinement by the least squares method. The observed 190 ($hk0$) and 176 ($hk1$) reflexions were all included in the refinement. Atomic scattering factors, including dispersion corrections, were taken from the appropriate tables in Ref. 5. Weights of the reflexions were assigned according to the formula $w = 1/(A + |F_o|^2 + C|F_o|^4 + D|F_o|^6)$ as suggested by Cruickshank *et al.*⁶ The constants were adjusted on the basis of weight analyses calculated between each cycle of refinement and were finally given the values $A = 80$, $C = 0.1$ and $D = 0.01$. The following 42 parameters were refined: two scale factors, one for each of the two layer lines, 26 positional parameters and 14 isotropic temperature factors. The refinement converged rapidly, and it was stopped when the parameter shifts were less than one tenth of the calculated standard deviations. The conventional R value for the 366 observed reflexions was then 0.119. The temperature factor values returned by the program were close to zero and even negative for the partially occupied niobium position and for four of the phosphorus positions. The small values of the temperature factors could be a consequence of neglecting absorption correc-

tions, but in the present case the absorption errors were estimated to be much too small for any appreciable influence on the temperature factor values. Extinction errors might be a more likely explanation, and a comparison between observed and calculated structure factors for the strongest low-angle reflexions showed that the observed values were consistently smaller than the calculated ones. It cannot be excluded that this effect might be produced by a systematic error in the visual intensity estimation, but nevertheless a final refinement was made in which the 42 strongest low-angle reflexions were omitted. The *R* value dropped to 0.109, the temperature factor values increased on average by 0.07 Å², while the positional parameters remained practically unchanged.

The results of the refinement indicate that the proposed structure is substantially correct. There are, however, at least two possible ways in which the true space group symmetry might deviate from *Pbam*.

Firstly, the lower space group *Pba2* leaves the *z* coordinates as free parameters, and small deviations from the values 0 and $\frac{1}{2}$ cannot be excluded. Previous experience in similar situations (see, *e.g.*, Ref. 7), where only a moderately accurate intensity material is available, shows, however, that it is very difficult to obtain conclusive evidence for minor symmetry deviations by means of ordinary refinement procedures. No attempt to refine the structure assuming *Pba2* symmetry was therefore made.

Secondly, the assumption of a nearly random partial occupation of one of the niobium positions might be wrong, and a different space group symmetry with fully ordered positions might represent the correct alternative. However, within the accuracy of the available intensity material no violation of the *mmm* Laue symmetry or the *b* or *a* glide plane symmetries could be detected, and no superstructure reflexions (as for instance indicating a larger *c* axis) were observed.

The crystal structure of Nb₈P₅ is accordingly reported with *Pbam* symmetry, and the final structure data are presented in Table 1. Powder data for identification purposes are given in Table 2, and a list of observed and calculated structure factors is given in Table 3.

Table 2. Powder diffraction data for Nb₈P₅. (Guinier-Hägg camera, CrK_{α1} radiation, internal calibration standard silicon: *a* = 5.43054 Å.) The sample contained, in addition to Nb₈P₅, an uncharacterized niobium phosphide phase, the diffraction lines of which are not included in the table.

<i>h k l</i>	sin ² θ × 10 ⁴		<i>I</i> obs	<i>p F </i> ² × 10 ⁻⁴	<i>h k l</i>	sin ² θ × 10 ⁴		<i>I</i> obs	<i>p F </i> ² × 10 ⁻⁴
	obs	calc				obs	calc		
2 0 0		76.4		0.3	2 2 0		661.4		0.5
1 1 0	164.5	165.4	w-	3.0	6 0 0		687.3		0.0
2 1 0		222.7		0.0	3 2 0		757.0		0.0
4 0 0		305.5		0.1	6 1 0	833.9	833.6	w-	1.4
3 1 0		318.1		1.1	4 2 0		890.6		0.1
4 1 0		451.8		0.3	5 2 0		1062.5		1.1
0 2 0		585.2		0.0	7 1 0		1081.8		0.7
1 2 0	603.4	604.2	w-	2.0	0 0 1	1092.2	1092.2	m	9.4
5 1 0		623.6		1.3	2 0 1		1168.6		0.7

Table 2. Continued.

8 0 0	1222.5	1221.9	w	6.3	8 2 1		2899.3		{40.1
1 1 1		1257.6		0.8	10 0 1	2900.0	3001.4	m	{10.5
6 2 0 ^a		1272.5	w-	2.3	6 4 0	3027.9	3027.9	w+	11.1
2 1 1		1314.8		0.0	6 3 1	3096.2	3096.1	m	32.5
1 3 0 ^b		1335.7		15.9	10 1 1	3147.0	3147.7	m+	44.9
8 1 0	1368.5	1368.2	w+	6.4	9 2 1		3223.8		1.3
2 3 0		1393.0		{3.3	10 3 0		3225.9		0.2
4 0 1	1395.3	1397.7	m	{9.1	7 4 0 ^a		3276.2	w-	4.3
3 1 1	1409.4	1410.3	m	9.5	12 2 0	3334.1	3334.5	m+	48.0
3 3 0	1487.1	1488.4	w-	0.7	7 3 1		3344.3		0.1
7 2 0	1521.4	1520.7	w-	1.3	13 1 0 ^a		3372.9	w	8.9
4 1 1	1545.0	1544.0	w-	1.6	0 4 1		3432.8		0.0
4 3 0	1622.9	1622.1	w+	8.1	1 4 1 ^c		3451.9	(m+)	10.6
0 2 1		1677.3		1.6	2 4 1		3509.2		0.0
9 1 0		1692.8		{12.5	11 1 1		3548.7		5.3
1 2 1	1696.1	1696.4	m+	{16.7	8 4 0		3562.5		1.2
5 1 1	1714.9	1715.8	m	19.4	10 2 1 ^a		3586.6	w-	6.1
2 2 1	1753.6	1753.7	st	63.8	3 4 1		3604.6		0.5
6 0 1	1778.8	1779.5	m	15.1	11 3 0	3628.3	3626.8	w	10.9
5 3 0	1794.5	1793.9	m+	31.1	8 3 1		3630.7		0.6
8 2 0	1805.5	1807.1	m	11.5	1 5 0		3676.3		0.4
3 2 1		1849.2		0.2	2 5 0		3733.6		0.0
10 0 0 ^a		1909.3	w-	5.3	4 4 1	3739.4	3738.3	w+	18.2
6 1 1	1927.4	1925.8	m	20.4	14 0 0		3742.2		6.6
4 2 1	1983.3	1982.8	w-	2.4	13 2 0		3811.8		2.5
6 3 0	2005.1	2003.9	w-	4.4	3 5 0	3828.7	3829.0	m	32.5
10 1 0 ^a		2055.5	w-	2.6	12 0 1		3841.5		0.4
9 2 0 ^a		2131.7	w-	1.5	9 4 0		3887.1		0.0
5 2 1	2154.8	2154.7	m	11.2	14 1 0		3888.4		0.4
7 1 1 ^c		2174.0	(st)	19.2	5 4 1		3910.1		4.0
7 3 0	2251.8	2252.1	m	26.0	9 3 1 ^a		3955.3	w-	4.0
8 0 1	2314.6	2314.1	st	108.2	4 5 0		3962.7		0.1
0 4 0	2340.9	2340.6	m+	46.6	11 2 1		3987.5		{7.0
1 4 0		2359.7		1.0	12 1 1	3988.6	3987.8	w+	{10.6
6 2 1	2364.1	2364.7	st	224.6	12 3 0		4065.9		0.6
2 4 0		2417.0		2.5	6 4 1		4120.1		5.3
1 3 1	2427.4	2427.9	st	91.3	5 5 0 ^a		4134.5	w-	9.7
11 1 0		2456.5		{94.6	10 4 0 ^a		4249.9	w-	6.2
8 1 1	2457.9	2460.4	st	{20.8	10 3 1		4318.0		0.0
2 3 1	2484.3	2485.1	m	31.5	14 2 0 ^a		4327.3	w	28.3
10 2 0	2495.6	2494.4	m	22.4	6 5 0		4344.5		0.4
3 4 0		2512.4		0.1	7 4 1		4368.3		6.9
8 3 0		2538.5		0.9	0 0 2	4369.7	4368.7	st+	199.3
3 3 1 ^c	2581.2	2580.6	(st)	16.5	12 2 1		4426.7		2.1
7 2 1	2612.3	2612.9	w+	14.7	15 1 0		4442.1		1.3
4 4 0	2646.3	2646.1	st	83.0	2 0 2		4445.1		0.2
4 3 1	2714.2	2714.3	m+	41.3	13 1 1		4465.1		0.1
12 0 0 ^a		2749.3	w-	3.6	1 1 2		4534.1		2.5
9 1 1	2784.8	2785.0	m+	49.3	13 3 0 ^a		4543.2	w-	10.2
5 4 0 ^a		2817.9	w-	2.9	7 5 0 ^a		4591.4		0.0
9 3 0	2862.2	2863.1	m	39.8	11 4 0		4592.7	w-	9.5
5 3 1	2886.4	2886.1	st	125.5	8 4 1		4650.8		0.7
11 2 0		2895.4		0.1			4654.7		0.8
12 1 0		2895.6		3.0					

^a Reflexion too weak for accurate measurement of diffraction angle.^b Reflexion overlapped by the silicon (111) reflexion.^c Reflexion overlapped by reflexion from uncharacterized niobium phosphide.

Table 3. Observed and calculated structure factors for Nb₅P₅. ^a Reflexion omitted in the final refinement.

h,k,l	F _o		F _c		F _o		F _c		F _o		F _c		F _o		F _c					
	•10	•10	•10	•10	•10	•10	•10	•10	•10	•10	•10	•10	•10	•10	•10					
8 0 0	1484	772	15	3	8	2095	2486	9	7	1068	1003	4	15	922	753	24	3			
10 0 0	1390	1628	16	3	10	1444	1044	10	7	628	674	4	15	1093	1292	25	3			
12 0 0	1335	1348	21	3	11	1138	1250	11	7	2226	2256	16	0	1840	1808	11	4			
14 0 0	1739	1810	22	3	12	7	1139	1002	12	7	1139	1002	15	15	1789	1775	29	3		
16 0 0	1974	1983	23	3	13	2121	2196	13	7	1061	769	15	15	1485	1455	30	3			
18 0 0	2293	2569	24	3	14	125	744	15	7	1300	1751	4	4	1385	1509	4	4			
20 0 0	1874	1983	25	3	15	1469	1432	17	7	2232	2330	5	4	745	710	5	4			
22 0 0	2320	2534	26	3	16	1268	1040	19	7	721	594	6	4	829	817	6	4			
24 0 0	1947	1983	27	3	17	1671	1560	21	7	912	1055	7	4	928	927	7	4			
26 0 0	1835	1413	28	3	18	1659	1878	23	7	862	820	8	0	3897	5202	9	4			
28 0 0	3947	3803	29	3	19	962	852	27	7	926	1051	10	0	1388	1618	10	4			
30 0 0	1260	886	30	3	20	4276	4829	28	0	8	770	895	16	0	1640	1608	11	4		
32 0 0	1885	1746	31	3	21	1578	787	33	3	704	653	18	0	1532	1293	12	4			
34 0 0	1274	1265	32	3	22	3704	4556	34	0	2963	3103	20	0	1088	1004	13	4			
36 0 0	1675	1767	33	3	23	786	866	35	0	8	770	895	26	0	2136	2060	14	4		
38 0 0	786	814	34	3	24	1578	1666	36	0	1527	1623	28	0	2462	2081	17	4			
40 0 0	4332	4864	35	3	25	4	1497	1035	37	0	1655	1846	28	0	2589	2504	18	4		
42 0 0	862	870	36	3	26	4	786	866	38	0	1366	1410	34	0	1582	1427	19	4		
44 0 0	1740	1490	37	3	27	4	954	1241	39	0	1308	1250	37	0	1384	1547	22	4		
46 0 0	810	567	38	3	28	4	4	426	40	0	1485	1405	38	0	1394	1611	24	4		
48 0 0	1279	1326	39	3	29	4	1583	1853	40	0	1871	1961	39	0	1284	2482	25	4		
50 0 0	1065	1017	40	3	30	4	2831	3683	41	0	1941	1891	40	0	2094	2369	26	4		
52 0 0	886	627	41	3	31	4	4959	512	42	0	1446	1139	41	0	858	813	3	5		
54 0 0	505	523	42	3	32	4	1185	1224	43	0	1354	1666	42	0	1177	1149	4	5		
56 0 0	2115	2007	43	3	33	4	1917	1101	44	0	960	985	43	0	1521	1394	6	5		
58 0 0	1146	1066	44	3	34	4	1107	1797	45	0	1250	977	44	0	2872	3426	7	5		
60 0 0	1188	825	45	3	35	4	2042	175	46	0	1145	1001	45	0	924	808	9	5		
62 0 0	783	892	46	3	36	4	910	872	47	0	7	960	885	46	0	1265	1136	10	5	
64 0 0	1104	1335	47	3	37	4	675	636	48	0	1174	664	47	0	1339	1135	11	5		
66 0 0	799	805	48	3	38	4	1296	1416	49	0	1205	899	48	0	1212	1159	12	5		
68 0 0	505	523	49	3	39	4	3504	3504	50	0	1700	1619	49	0	1578	1445	13	5		
70 0 0	863	611	50	3	40	4	2543	2882	51	0	1339	1433	50	0	1042	1181	14	5		
72 0 0	609	576	51	3	41	4	1564	1557	52	0	754	814	51	0	3587	5299	16	5		
74 0 0	1714	1676	52	3	42	4	1276	1538	53	0	1609	1604	52	0	1144	1233	17	5		
76 0 0	665	632	53	3	43	4	1426	939	54	0	1917	1015	53	0	1572	2239	18	5		
78 0 0	2356	2365	54	3	44	4	485	362	55	0	1605	1401	54	0	399	409	19	5		
80 0 0	2683	3464	55	3	45	4	1249	1964	56	0	1628	1530	55	0	843	876	20	5		
82 0 0	811	797	56	3	46	4	2149	1944	57	0	1597	1393	56	0	995	935	23	5		
84 0 0	2495	2661	57	3	47	4	1009	1025	58	0	758	734	57	0	450	517	25	5		
86 0 0	438	412	58	3	48	4	1590	1499	59	0	1830	1772	58	0	1269	1223	26	5		
88 0 0	1044	1144	59	3	49	4	691	304	60	0	1700	1619	59	0	1578	1445	28	5		
90 0 0	1372	1343	60	3	50	4	2510	2984	61	0	1210	1250	60	0	2396	2751	30	5		
92 0 0	531	548	61	3	51	4	1249	773	62	0	1053	1080	61	0	2319	2465	32	5		
94 0 0	1819	2063	62	3	52	4	895	658	63	0	891	956	62	0	1843	878	34	5		
96 0 0	1500	1581	63	3	53	4	1503	1623	64	0	757	687	63	0	1947	1788	36	5		
98 0 0	707	633	64	3	54	4	2044	1890	65	0	835	854	64	0	1356	1098	38	5		
100 0 0	1819	2063	65	3	55	4	1420	1393	66	0	1522	1315	65	0	1733	2038	40	5		
102 0 0	806	606	66	3	56	4	2942	3400	67	0	824	923	66	0	1415	968	42	5		
104 0 0	2630	2594	67	3	57	4	1938	2150	68	0	1415	4475	67	0	38254	3378	44	5		
106 0 0	951	838	68	3	58	4	1420	1393	69	0	1812	1495	68	0	1607	1985	46	5		
108 0 0	1321	1992	69	3	59	4	1010	1010	70	0	885	859	69	0	1615	1436	48	5		
110 0 0	973	913	70	3	60	4	1946	824	71	0	1609	1676	70	0	1799	2272	50	5		
112 0 0	687	423	71	3	61	4	1149	806	72	0	876	801	71	0	32915	3960	52	5		
114 0 0	1216	1425	72	3	62	4	1396	1470	73	0	1315	1315	72	0	1615	2014	54	5		
116 0 0	2370	2789	73	3	63	4	1362	1394	74	0	1460	1541	73	0	816	705	56	5		
118 0 0	972	1053	74	3	64	4	2233	2586	75	0	968	702	74	0	1607	1817	58	5		
120 0 0	2293	2543	75	3	65	4	5163	3581	76	0	681	702	75	0	1613	1527	60	5		
122 0 0	435	478	76	3	66	4	1794	2136	77	0	14	989	785	76	0	1504	1607	62	5	
124 0 0	2934	3153	77	3	67	4	1724	1652	78	0	14	982	1013	77	0	2226	2360	64	5	
126 0 0	416	395	78	3	68	4	1214	459	79	0	12	14	1013	1330	78	0	1515	1475	66	5
128 0 0	1272	1595	79	3	69	4	937	816	80	0	12	14	920	1072	79	0	1636	1331	68	5

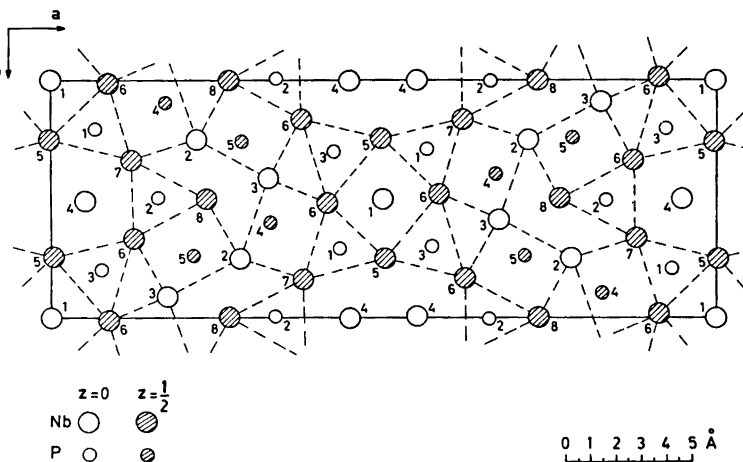


Fig. 1. The structure of Nb₅P₅ projected on (001).

Table 4. Interatomic distances (Å) and their standard deviations ($\times 10^3$) in Nb_8P_5 . Distances shorter than 4.0 Å are listed.

Nb(1)–	Nb(6)–	P(1)–
2 P (1) 2.611(16)	1 P (4) 2.465(16)	2 Nb(5) 2.543(13)
2 P (3) 2.683(16)	2 P (3) 2.594(12)	2 Nb(7) 2.548(12)
4 Nb(6) 2.803(5)	2 P (1) 2.651(12)	1 Nb(1) 2.611(16)
4 Nb(5) 2.977(4)	2 Nb(1) 2.803(5)	2 Nb(6) 2.651(12)
2 Nb(1) 3.464(0)	2 Nb(3) 2.044(7)	1 Nb(4) 2.834(18)
	1 Nb(5) 3.229(8)	2 P (4) 3.398(19)
Nb(2)–	1 Nb(7) 3.272(8)	2 P (1) 3.464(0)
2 P (5) 2.519(13)	1 Nb(5) 3.318(8)	1 P (3) 3.625(24)
2 P (4) 2.520(11)	1 Nb(9) 3.335(8)	1 P (2) 3.677(21)
1 P (2) 2.704(14)	2 Nb(6) 3.464(0)	1 P (3) 3.860(21)
2 Nb(8) 2.990(6)		1 Nb(2) 3.974(17)
2 Nb(7) 3.144(7)	Nb(7)–	1 Nb(3) 3.981(17)
2 Nb(8) 3.181(6)	1 P (4) 2.526(15)	
1 Nb(3) 3.257(8)	2 P (2) 2.529(10)	P(2)–
1 Nb(3) 3.375(7)	2 P (1) 2.548(12)	2 Nb(7) 2.529(10)
2 Nb(2) 3.464(0)	2 Nb(4) 3.033(10)	2 Nb(9) 2.593(10)
1 P (1) 3.974(17)	2 Nb(2) 3.144(7)	2 Nb(8) 2.594(12)
	1 Nb(9) 3.170(7)	1 Nb(2) 2.704(14)
Nb(3)–	1 Nb(6) 3.272(8)	1 Nb(4) 2.955(19)
2 P (5) 2.495(11)	1 Nb(5) 3.334(8)	2 P (5) 3.360(16)
2 P (4) 2.503(10)	1 Nb(8) 3.395(9)	2 P (2) 3.464(0)
1 P (3) 2.862(18)	2 Nb(7) 3.464(0)	1 P (1) 3.677(21)
2 Nb(6) 3.044(7)		1 P (3) 3.729(20)
2 Nb(8) 3.067(7)	Nb(8)–	
2 Nb(9) 3.188(6)	1 P (5) 2.485(15)	P(3)–
1 Nb(2) 3.257(8)	2 P (2) 2.594(12)	2 Nb(9) 2.525(12)
1 Nb(2) 3.375(7)	1 P (4) 2.656(16)	2 Nb(5) 2.566(13)
2 Nb(3) 3.464(0)	1 P (5) 2.672(15)	2 Nb(6) 2.594(12)
1 P (1) 3.981(17)	2 Nb(2) 2.990(6)	1 Nb(1) 2.683(16)
	2 Nb(3) 3.067(7)	1 Nb(3) 2.862(18)
Nb(4)–	2 Nb(2) 3.181(6)	1 Nb(4) 2.882(18)
1 Nb(4) 2.544(23)	1 Nb(9) 3.299(8)	2 P (3) 3.464(0)
1 P (1) 2.834(18)	1 Nb(7) 3.395(9)	1 P (1) 3.625(24)
1 P (3) 2.882(18)	2 Nb(8) 3.464(0)	1 P (2) 3.729(20)
1 P (2) 2.955(19)		1 P (1) 3.860(21)
2 Nb(7) 3.033(10)	Nb(9)–	
2 Nb(9) 3.049(10)	1 P (5) 2.513(17)	P(4)–
2 Nb(5) 3.097(9)	2 P (3) 2.525(12)	1 Nb(6) 2.465(16)
2 Nb(5) 3.219(10)	2 P (2) 2.593(10)	2 Nb(3) 2.503(10)
2 Nb(4) 3.464(0)	2 Nb(4) 3.049(10)	2 Nb(2) 2.520(11)
	1 Nb(7) 3.170(7)	1 Nb(7) 2.526(15)
Nb(5)–	2 Nb(3) 3.188(6)	1 Nb(8) 2.656(16)
2 P (1) 2.543(13)	1 Nb(5) 3.238(8)	1 P (5) 3.362(22)
2 P (3) 2.566(13)	1 Nb(8) 3.299(8)	2 P (1) 3.398(19)
2 Nb(1) 2.977(4)	1 Nb(6) 3.335(8)	1 P (5) 3.460(19)
2 Nb(4) 3.097(9)	2 Nb(9) 3.464(0)	2 P (4) 3.464(0)
2 Nb(4) 3.219(10)		
1 Nb(6) 3.229(8)		P(5)–
1 Nb(9) 3.238(8)		1 Nb(8) 2.485(15)
1 Nb(6) 3.318(8)		2 Nb(3) 2.495(11)
1 Nb(7) 3.334(8)		1 Nb(9) 2.513(17)
2 Nb(5) 3.464(0)		2 Nb(2) 2.519(13)
		1 Nb(8) 2.672(15)
		2 P (2) 3.360(16)
		1 P (4) 3.362(22)
		1 P (4) 3.460(19)
		2 P (5) 3.464(0)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A projection of the structure on the (001) plane is shown in Fig. 1. Interatomic distances are listed in Table 4. Each phosphorus atom is surrounded by six niobium atoms in a triangular prismatic configuration and 1 to 3 additional niobium neighbours situated outside the four-sided faces of the prisms. The Nb_6P prisms are linked into a three-dimensional arrangement in much the same way as in numerous other transition metal phosphide, arsenide, sulphide, and selenide structures. The triangular prisms are indicated by broken lines in Fig. 1.

A feature of particular interest is the coordination about the partially occupied Nb(4) position. Two $\text{Nb}_6\text{P}(1)$, two $\text{Nb}_6\text{P}(2)$ and two $\text{Nb}_6\text{P}(3)$ triangular prisms share edges to form a six-membered ring enclosing a central void. These rings are stacked on top of one another forming infinite tubes in the c direction. The void in each ring is in the shape of a twelve-cornered Nb_{12} polyhedron, which can be regarded as composed of two very distorted Nb_8 cubes sharing one face. The Nb(4) atoms are situated at the centres of these distorted cubes. If all cubes were filled with Nb(4) atoms, these atoms would form pairs with an Nb–Nb distance of 2.54 Å, which is more than 0.1 Å shorter than the shortest Nb–Nb distance reported in any previous structure determination. The structure determination of Nb_8P_5 has shown that the Nb(4) position is occupied to only 50 %. It therefore seems most probable that any Nb–Nb contacts of 2.54 Å never occur, but each central void in the six-membered rings contains only one single Nb(4) atom. This atom can, however, occupy any one of the two possible cubic holes in a perfectly random manner.

A similar metal atom arrangement occurs in the Ta_2P -type structure (as represented by Ta_2P ,⁸ Ti_2S ,⁹ Hf_2P ,^{10,11} Ti_2Se , Zr_2S , Zr_2Se ,¹² Hf_2As ,¹³ and Ta_2As ¹⁴). In this case, the two adjoining cubic holes are much less distorted, and both holes are filled with metal atoms having a quite normal distance to one another.

Disregarding the disordered Nb(4) position, the atomic coordination and the interatomic distances in Nb_8P_5 are normal and very similar to those in Nb_7P_4 ² and Nb_5P_3 .⁴ Although the phosphide Mo_8P_5 ¹⁵ has the same stoichiometry as Nb_8P_5 , the two compounds are not isostructural. The space-filling in the Mo_8P_5 structure is greater than in Nb_8P_5 due to the large voids in the Nb_8P_5 structure at the empty Nb(4) positions.

It may finally be mentioned that there is an isostructural counterpart to Nb_8P_5 in the Zr–As system. A structure determination of Zr_8As_5 is currently being carried out by B. Carlsson at this institute, and the results will be reported in this journal.

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