The Crystal Structure of $Ni_{12}P_5$

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The crystal structure of $Ni_{12}P_5$ has been determined with single-crystal methods. The unit cell, containing 2 formula units, is tetragonal, $a = 8.646$ Å; $c = 5.070$ Å. The space group is $I4/m-(C_{4h}^5)$ with 16 Ni in 16(i): $x = 0.116_6$; $y = 0.182_2$; $z = 0.248$; 8 Ni in 8(h): $x = 0.368$; $y = 0.060$; 8 P in 8(h): $x = 0.195$; $y = 0.415$; and 2 P in 2(a). A comparison of $Ni_{12}P_5$ with related structures is made. Some phase-analytical observations in the Ni-P system are reported. NiP_3 is cubic, $a = 7.819$ Å; and isostructural with CoP_3, $a = 7.706$ Å. Both NiP_3 and CoP_3 belong to the $D2$ ($CoAs_3$) structure type.

Although the nickel phosphides have been the object of several investigations, the knowledge of them is still very incomplete. Therefore, an X-ray investigation of the Ni-P system has been started at this institute in order to establish the existence and compositions of the intermediate phases and to determine the crystal structures. The present paper gives an account of the crystal structure determination of the phase $Ni_{12}P_5$, which has not earlier been properly characterized. In addition, some preliminary phase-analytical observations in the Ni-P system are reported.

EXPERIMENTAL

Alloys were prepared by heating mixtures of nickel powder (99.8 %, kindly donated by Mond Nickel Co., Ltd.) and red phosphorus (99 %) in evacuated and sealed silica tubes at temperatures between 700°C and 900°C. No appreciable attack on the silica tubes was detected. The reaction products were investigated with X-ray powder methods using Guinier-type cameras with $CrK\alpha$ and $CuK\alpha$ radiations. Unit cell dimensions were determined using CaF_2 as internal calibration standard on each powder film. The lattice parameter values have an accuracy better than 0.05 %. For the single-crystal work, a small, roughly spherical crystal fragment was selected from a crushed $Ni_{2.4}P$ alloy. The intensity material was recorded in an ordinary Weissenberg camera with MoK radiation using the multiple-film technique with thin iron foils between successive films. The intensities were visually estimated with the aid of a standard intensity scale. No absorption correction was applied. Fourier summations were made with the Hägg-Laurent machine and with Beevers-Lipson strips.

THE Ni-P SYSTEM

Previous work on the Ni-P system is summarized in Ref.[1] As the result of a thermal and microscopical investigation in the range 0—35 at.% P, Konstantinow [2] reported the existence of the phases Ni_3P, Ni_5P_2 and Ni_2P. Ni_5P_2 was stated to undergo a polymorphic transformation. Nowotny and Henglein [3], who made an X-ray investigation in the same range of composition, found four phases with compositions close to Ni_3P, Ni_5P_2, Ni_7P_3 and Ni_2P. Ni_3P was stated to be isostructural with Fe_3P and Ni_2P isostructural with Fe_2P. The Ni_3P structure was later determined by Aronsson [4]. Using mainly tensimetric methods, Heimbrecht and Biltz [5] studied the Ni-P system and reported the existence of the following phases: $Ni_{0.83}P$, NiP_2 and NiP_3.

Our phase-analytical work with the X-ray powder method is still in progress and only a few observations will be mentioned here. In the range $Ni-Ni_2P$ four phases have been found with compositions close to Ni_3P, $Ni_{2.5}P$, $Ni_{2.4}P$ and Ni_2P, respectively. No transformations in the solid state were observed in the range 700—900°C *. For Ni_3P we determined the tetragonal unit cell dimensions as $a = 8.954$ Å; $c = 4.387$ Å in very close agreement with the values given by Aronsson [4]. The powder pattern of $Ni_{2.5}P$ is complicated and has not yet been interpreted. The powder pattern of $Ni_{2.4}P$ (which is presumably the same phase as Nowotny and Henglein's "Ni_7P_3") could be indexed with the body-centered tetragonal unit cell $a = 8.646$ Å; $c = 5.070$ Å. Lattice parameter variations indicating an extended homogeneity range were not observed. Nowotny and Henglein indexed their "Ni_7P_3" powder pattern with a cubic unit cell ($a = 8.63$ Å), but additional weak lines indicated lower symmetry in their opinion. For Ni_2P we found the hexagonal unit cell dimensions $a = 5.864$ Å; $c = 3.385$ Å. Ni_2P belongs to the revised C 22 structure type [6].

In the region Ni_2P—NiP the system seems to be rather complicated, and transformations in the solid state probably occur. It was mentioned by Biltz, Heimbrecht and Meisel [7], that the X-ray powder pattern of NiP_3 was similar to that of CoP_3. This was indeed found to be the case, since our powder photographs of CoP_3 and NiP_3 could be indexed with cubic unit cells: for NiP_3 $a = 7.819$ Å and for CoP_3 $a = 7.706$ Å. These two phosphides are isostructural with $CoAs_3$ (D 2 type), the structure of which was determined by Oftedal [8].

DETERMINATION OF THE $Ni_{12}P_5$ CRYSTAL STRUCTURE

From powder and single-crystal data, the unit cell of the phase $Ni_{2.4}P$ was determined to be tetragonal: $a = 8.646$ Å; $c = 5.070$ Å; $c/a = 0.5864$; $U = 379.0$ Å^3. The measured density 7.44 g·cm^{-3} indicated a unit cell content of 24 Ni atoms and 10 P atoms, giving the calculated density value 7.53 g·cm^{-3}. The formula of the $Ni_{2.4}P$ phase should therefore be written $Ni_{12}P_5$.

* Professor T. Rosenqvist, Norges Tekniske Høgskole, Trondheim, Norway, has kindly informed us that X-ray powder investigations made at his institute in the range $Ni-Ni_3P$ confirm our results. Our interpretation of the $Ni_{12}P_5$ powder pattern is in agreement with his findings.

For the structure determination, the intensity material from the layer lines 0—4 around the c-axis was used. The intensities from the layer lines with $l > 4$ were very difficult to estimate and were not included in the refinements.

Only reflexions with $h + k + l = 2n$ were observed. Since $|F(hkl)|$ was different from $|F(\bar{h}kl)|$ the possible space groups were $I4$, $I\bar{4}$ and $I4/m$. Using the entire intensity material, the Patterson section $P(xy0)$ was calculated. The Patterson function had a large peak at $(\frac{1}{2}, \frac{1}{2}, 0)$ [equivalent to a peak in $(0,0,\frac{1}{2})$], whose height, being roughly 2/3 of the origin peak height, showed that about 2/3 of the Ni atoms must lie in pairs with the same x and y parameters and spaced about $c/2$ apart. This indicated strongly that the space group was $I4/m$ with 16 Ni in 16(i) having a z parameter close to 1/4. Further analysis showed that the heights and positions of all large peaks in $P(x\,y\,0)$ could be interpreted by assuming the space group to be $I4/m$ with 16 Ni$_I$ in a 16(i) position and 8 Ni$_{II}$ in an 8(h) position.

Starting with the rough parameter values read from the Patterson map, signs were calculated for the observed $F(hk0)$ values and the electron density projection $\varrho\,(xy)$ was computed. Ni maxima were found at the expected positions and, in addition, P maxima were found at the origin and in an 8(h) position. The different x and y parameters were refined by successive difference syntheses. The scattering factors for Ni were interpolated from tables given by Thomas and Umeda [9] and those of P from Tomiie and Stam [10]. After the final refinement cycle, the R-value 8.0 % for the observed independant $hk0$ reflexions was obtained, when an empirical temperature factor with $B=0.49$ Å² was applied. The following parameters were found: Ni$_I$ in 16(i): $x = 0.116_0$; $y = 0.182_2$; Ni$_{II}$ in 8(h): $x = 0.368$; $y = 0.060$; P$_I$ in 8(h): $x = 0.195$; $y = 0.415$; P$_{II}$ in 2(a) or 2(b) $(x = y = 0)$. Since the observed $|F(hk0)|$ and $|F(hk4)|$ values were almost equal (apart from the normal decline) and the same was true for the $|F(hk1)|$ and $|(F(hk3)|$ values, the z parameter of the Ni$_I$ atoms could not be very far from 1/4. With these parameters, a reasonable structure with normal interatomic distances could be visualized. Since there was apparently enough space for a P atom in both $(0,0,0)$ and $(0,0,\frac{1}{2})$, it could not be immediately decided whether P$_{II}$ was situated in 2(a) or in 2(b). However, a comparison of calculated and observed $|F(hk1)|$ values proved beyond doubt that P$_{II}$ was situated in 2(a). With P$_{II}$ in 2(a), the R-value for the recorded $|F(hk1)|$ values was 9.0 %, whereas with P$_{II}$ in 2(b), the R-value was larger than 40 %.

It still remained to be settled whether the z_I parameter of Ni$_I$ was appreciably different from 1/4 or not. The $F(hkl)$ values with $l = 2n$ should hardly be affected by a small shift, but the $F(hkl)$ values with $l = 2n + 1$ should be more sensitive. Starting with the z_I parameter exactly 1/4, the $F(hk3)$ values were calculated, and the R-value obtained, was 10.9 %. It was then found that the agreement was somewhat improved with a z_I-value slightly less than 1/4. The best agreement was obtained with $z_I = 0.248$, giving the R-value 10.1 %. The $F(hk1)$ values were recalculated using this z_I value and the R-value for these reflexions dropped from 9.0 % to 8.8 %. Finally the remaining $F(hk2)$ and $F(hk4)$ values were calculated, and the R-value 8.7 % for all measured reflexions was obtained after applying an overall temperature factor with

Table 1.

h k l	F_o	F_c	h k l	F_o	F_c
0 0 0	—	822	1 7 0	142.0	−142.7
2 0 0	37.8	− 34.2	3 7 0	181.1	−173.3
4 0 0	238.1	−241.0	5 7 0	163.3	−147.4
6 0 0	57.5	39.2	7 7 0	58.4	41.0
8 0 0	28.6	− 32.0	9 7 0	—	20.2
10 0 0	64.1	71.7	11 7 0	—	− 11.4
12 0 0	—	− 44.0	13 7 0	—	− 14.4
14 0 0	37.1	− 48.0	15 7 0	79.3	96.5
16 0 0	98.1	103.2	2 8 0	107.5	− 90.1
1 1 0	—	− 6.2	4 8 0	201.3	189.5
3 1 0	148.8	−147.1	6 8 0	39.9	44.3
5 1 0	171.3	183.3	8 8 0	148.3	−162.9
7 1 0	191.7	200.4	10 8 0	—	− 4.5
9 1 0	80.5	− 84.5	12 8 0	—	39.1
11 1 0	—	− 16.1	14 8 0	—	22.2
13 1 0	—	− 5.3	1 9 0	142.0	118.6
15 1 0	—	− 26.6	3 9 0	—	− 18.8
2 2 0	62.9	− 49.7	5 9 0	69.9	74.9
4 2 0	218.2	−230.4	7 9 0	37.1	30.3
6 2 0	190.0	188.5	9 9 0	—	− 44.8
8 2 0	54.9	47.4	11 9 0	—	76.0
10 2 0	95.3	− 92.2	13 9 0	—	− 26.8
12 2 0	—	66.0	2 10 0	38.5	45.3
14 2 0	—	31.0	4 10 0	46.9	− 62.6
16 2 0	—	47.5	6 10 0	—	− 24.0
1 3 0	—	− 0.3	8 10 0	—	− 43.6
3 3 0	234.6	236.5	10 10 0	65.0	63.0
5 3 0	49.7	46.6	12 10 0	95.3	100.1
7 3 0	—	− 10.0	1 11 0	193.6	191.9
9 3 0	119.4	−128.6	3 11 0	—	9.9
11 3 0	—	− 22.2	5 11 0	135.1	−123.8
13 3 0	120.1	137.7	7 11 0	77.9	85.0
15 3 0	—	− 42.5	9 11 0	—	4.9
2 4 0	332.2	381.0	11 11 0	—	− 43.5
4 4 0	44.6	33.9	2 12 0	53.0	− 50.9
6 4 0	163.8	−164.3	4 12 0	—	− 39.5
8 4 0	100.4	97.8	6 12 0	104.2	98.8
10 4 0	57.0	50.0	8 12 0	102.1	98.3
12 4 0	—	45.0	10 12 0	—	− 55.1
14 4 0	—	− 14.2	1 13 0	61.7	− 66.6
16 4 0	57.0	− 65.5	3 13 0	68.0	58.1
1 5 0	—	− 14.5	5 13 0	60.8	− 53.9
3 5 0	—	26.9	7 13 0	—	− 5.9
5 5 0	120.1	−119.8	9 13 0	—	25.8
7 5 0	45.8	− 44.7	11 13 0	—	− 34.4
9 5 0	117.3	126.2	13 13 0	56.6	57.8
11 5 0	—	− 40.0	2 14 0	—	30.6
13 5 0	—	− 0.4	4 14 0	106.1	106.1
15 5 0	—	44.3	6 14 0	—	− 0.2
2 6 0	—	7.6	8 14 0	—	− 35.8
4 6 0	78.1	67.8	1 15 0	67.6	− 55.9
6 6 0	85.2	− 80.3	3 15 0	73.4	70.9
8 6 0	102.5	111.3	5 15 0	—	22.5
10 6 0	55.1	62.7	7 15 0	63.8	− 73.5
12 6 0	116.6	−116.6	1 0 1	—	26.9
14 6 0	—	− 19.7	3 0 1	93.7	85.0

$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c
5 0 1	89.6	96.1	1 12 1	50.0	38.8
7 0 1	80.2	− 79.8	3 12 1	—	21.3
9 0 1	42.2	− 51.5	2 13 1	—	− 36.8
11 0 1	—	19.2	1 14 1	32.2	43.0
13 0 1	—	− 7.5			
2 1 1	37.3	32.6	0 0 2	—	− 34.4
4 1 1	27.7	− 27.5	2 0 2	136.6	148.9
6 1 1	47.4	38.2	4 0 2	102.3	94.0
8 1 1	125.7	127.7	6 0 2	86.9	− 63.2
10 1 1	—	18.2	8 0 2	—	− 16.9
12 1 1	—	− 36.9	10 0 2	74.6	− 80.0
1 2 1	32.2	− 22.1	12 0 2	—	6.0
3 2 1	56.4	− 69.3	14 0 2	116.1	119.6
5 2 1	—	15.7	16 0 2	—	− 19.5
7 2 1	43.3	− 45.0	1 1 2	—	−207.0
9 2 1	43.5	− 45.3	3 1 2	391.2	428.0
11 2 1	89.2	84.8	5 1 2	77.0	76.0
13 2 1	62.5	62.1	7 1 2	138.9	−131.8
2 3 1	151.1	145.9	9 1 2	65.2	61.7
4 3 1	81.6	83.8	11 1 2	—	12.6
6 3 1	38.5	− 34.9	13 1 2	—	37.7
8 3 1	—	20.8	15 1 2	—	− 38.2
10 3 1	—	− 16.5	2 2 2	—	3.9
12 3 1	65.6	− 68.0	4 2 2	68.2	− 63.6
1 4 1	110.3	−107.0	6 2 2	158.5	−173.7
3 4 1	65.8	− 68.1	8 2 2	65.9	65.5
5 4 1	70.5	65.6	10 2 2	178.3	186.4
7 4 1	107.2	122.2	12 2 2	62.7	− 58.5
9 4 1	—	12.3	14 2 2	—	− 26.9
11 4 1	—	22.1	16 2 2	—	27.8
2 5 1	56.2	53.9	1 3 2	—	4.4
4 5 1	26.4	− 19.9	3 3 2	107.1	− 83.3
6 5 1	99.6	−114.1	5 3 2	94.7	93.5
8 5 1	39.4	− 41.2	7 3 2	64.1	− 60.7
10 5 1	73.8	73.2	9 3 2	61.5	63.3
1 6 1	48.2	32.5	11 3 2	—	− 6.3
3 6 1	66.8	63.3	13 3 2	75.6	− 76.4
5 6 1	67.0	70.0	15 3 2	—	44.2
7 6 1	60.3	72.4	2 4 2	125.0	−132.4
9 6 1	43.3	− 28.2	4 4 2	38.7	− 29.8
11 6 1	63.6	− 66.7	6 4 2	167.3	169.5
2 7 1	43.3	− 42.3	8 4 2	—	15.5
4 7 1	—	8.7	10 4 2	—	25.8
6 7 1	36.5	27.7	12 4 2	—	− 21.1
8 7 1	—	14.9	14 4 2	—	− 37.3
10 7 1	72.8	78.4	16 4 2	71.2	74.5
1 8 1	65.4	66.8	1 5 2	68.4	− 59.0
3 8 1	—	− 13.1	3 5 2	205.1	−189.3
5 8 1	55.6	− 66.2	5 5 2	193.3	196.0
7 8 1	—	− 10.0	7 5 2	56.0	47.7
2 9 1	62.9	59.4	9 5 2	158.3	−159.9
4 9 1	83.0	83.6	11 5 2	—	23.5
6 9 1	45.9	55.3	13 5 2	66.1	63.2
8 9 1	—	− 26.0	15 5 2	—	52.3
1 10 1	—	− 11.7	2 6 2	216.1	216.5
3 10 1	49.6	− 46.2	4 6 2	50.7	53.5
5 10 1	—	− 22.6	6 6 2	—	24.2
7 10 1	—	21.2	8 6 2	53.9	− 56.8
9 10 1	59.9	61.2	10 6 2	—	− 28.4

h k l	F_o	F_c	h k l	F_o	F_c
12 6 2	91.2	100.9	5 0 3	84.3	70.9
14 6 2	—	— 54.5	7 0 3	63.6	— 68.4
1 7 2	174.9	170.2	9 0 3	36.4	— 37.7
3 7 2	—	— 2.3	11 0 3	—	11.3
5 7 2	103.9	—113.0	13 0 3	—	— 6.3
7 7 2	64.7	56.5	2 1 3	25.6	28.8
9 7 2	—	12.6	4 1 3	—	— 19.5
11 7 2	55.5	54.0	6 1 3	—	23.2
13 7 2	57.1	53.5	8 1 3	115.8	117.7
15 7 2	—	— 48.1	10 1 3	—	16.2
2 8 2	138.2	151.0	12 1 3	—	— 38.5
4 8 2	—	— 26.0	1 2 3	—	— 14.7
6 8 2	130.9	—121.2	3 2 3	40.2	— 44.4
8 8 2	74.2	75.5	5 2 3	—	16.8
10 8 2	—	— 9.7	7 2 3	32.8	— 38.4
12 8 2	—	— 13.6	9 2 3	35.0	— 40.6
14 8 2	—	9.0	11 2 3	78.7	76.1
1 9 2	—	— 4.0	13 2 3	58.0	56.2
3 9 2	—	— 16.9	2 3 3	96.2	102.9
5 9 2	56.7	— 56.1	4 3 3	78.0	67.8
7 9 2	132.0	138.7	6 3 3	—	— 19.3
9 9 2	88.2	97.5	8 3 3	—	10.5
11 9 2	91.7	—105.7	10 3 3	—	— 14.0
13 9 2	—	— 37.6	12 3 3	61.8	— 56.9
2 10 2	143.5	—140.5	1 4 3	79.3	— 82.8
4 10 2	104.8	100.6	3 4 3	58.4	— 53.0
6 10 2	—	— 12.2	5 4 3	60.0	59.8
8 10 2	—	— 7.7	7 4 3	97.6	106.2
10 10 2	—	14.2	9 4 3	—	6.0
12 10 2	—	— 4.9	11 4 3	—	24.4
1 11 2	40.3	— 30.8	2 5 3	47.9	50.0
3 11 2	105.8	105.1	4 5 3	—	— 15.5
5 11 2	68.7	68.7	6 5 3	81.6	— 94.6
7 11 2	76.5	— 74.0	8 5 3	—	— 33.6
9 11 2	—	— 24.2	10 5 3	65.4	64.7
11 11 2	—	— 14.2	1 6 3	35.3	25.4
2 12 2	67.0	— 62.0	3 6 3	77.3	65.3
4 12 2	89.2	86.5	5 6 3	51.5	51.6
6 12 2	53.7	48.1	7 6 3	47.0	64.5
8 12 2	67.5	— 64.3	9 6 3	—	— 19.7
10 12 2	55.1	70.0	11 6 3	52.6	— 66.0
1 13 2	91.2	97.3	2 7 3	32.8	— 33.8
3 13 2	—	— 26.8	4 7 3	—	7.5
5 13 2	63.4	— 64.5	6 7 3	27.2	21.3
7 13 2	46.3	— 52.7	8 7 3	—	17.4
9 13 2	47.7	39.2	10 7 3	63.8	68.3
11 13 2	79.0	82.6	1 8 3	49.2	58.5
13 13 2	—	— 27.8	3 8 3	—	— 16.7
2 14 2	—	14.9	5 8 3	50.3	— 50.1
4 14 2	68.0	— 66.7	7 8 3	—	— 9.7
6 14 2	74.6	83.8	2 9 3	53.5	45.0
8 14 2	—	4.4	4 9 3	77.8	75.0
1 15 2	—	22.2	6 9 3	60.2	54.7
3 15 2	47.2	— 38.3	8 9 3	—	— 29.6
5 15 2	—	13.4	1 10 3	—	— 10.5
7 15 2	68.2	74.7	3 10 3	41.4	— 42.7
1 0 3	—	11.4	5 10 3	—	— 19.2
3 0 3	76.9	78.7	7 10 3	—	17.4

h k l	F_o	F_c	h k l	F_o	F_c
9 10 3	—	54.0	8 6 4	98.1	88.0
1 12 3	56.4	34.9	10 6 4	52.4	50.9
3 12 3	—	23.5	12 6 4	89.6	— 98.0
2 13 3	—	— 33.3	14 6 4	—	— 16.7
1 14 3	—	37.6	1 7 4	89.6	—103.4
			3 7 4	108.7	—130.0
0 0 4	—	—244.3	5 7 4	120.2	114.3
2 0 4	—	— 19.3	7 7 4	—	32.7
4 0 4	153.9	—155.0	9 7 4	—	17.0
6 0 4	43.4	27.9	11 7 4	—	— 9.9
8 0 4	—	— 24.2	13 7 4	—	— 12.5
10 0 4	74.7	56.5	15 7 4	75.6	82.5
12 0 4	—	— 36.4	2 8 4	85.5	— 69.0
14 0 4	52.2	— 40.9	4 8 4	150.5	147.5
16 0 4	75.8	87.7	6 8 4	58.1	35.3
1 1 4	—	— 3.3	8 8 4	118.3	—133.6
3 1 4	98.8	— 86.5	10 8 4	—	— 3.6
5 1 4	101.3	126.5	12 8 4	—	33.8
7 1 4	138.3	148.7	14 8 4	—	18.6
9 1 4	71.0	— 66.0	1 9 4	101.3	92.6
11 1 4	—	— 12.2	3 9 4	—	— 14.5
13 1 4	—	— 5.0	5 9 4	54.2	61.0
15 1 4	—	— 23.2	7 9 4	—	23.2
2 2 4	—	— 30.0	9 9 4	—	— 37.2
4 2 4	133.0	—154.0	11 9 4	58.6	63.5
6 2 4	159.4	139.0	13 9 4	—	— 22.7
8 2 4	35.8	36.5	2 10 4	58.1	36.3
10 2 4	91.9	— 74.3	4 10 4	52.2	— 51.7
12 2 4	58.8	54.1	6 10 4	—	— 19.0
14 2 4	—	27.0	8 10 4	43.2	— 36.0
16 2 4	—	40.1	10 10 4	49.2	52.0
1 3 4	—	— 0.1	12 10 4	63.6	85.3
3 3 4	156.5	157.0	1 11 4	146.6	159.3
5 3 4	—	32.3	3 11 4	—	6.5
7 3 4	—	— 7.9	5 11 4	108.2	—101.5
9 3 4	80.0	—101.6	7 11 4	73.1	70.0
11 3 4	—	— 19.1	9 11 4	—	4.6
13 3 4	110.1	114.2	11 11 4	—	— 36.8
15 3 4	—	— 36.4	2 12 4	45.0	— 41.2
2 4 4	259.2	268.1	4 12 4	42.7	— 32.8
4 4 4	36.8	24.3	6 12 4	74.4	81.8
6 4 4	117.9	—121.2	8 12 4	83.2	83.2
8 4 4	74.4	76.1	10 12 4	—	— 47.8
10 4 4	—	41.1	1 13 4	68.7	— 55.2
12 4 4	—	36.4	3 13 4	51.0	47.8
14 4 4	—	— 12.6	5 13 4	50.0	— 44.7
16 4 4	46.6	— 49.5	7 13 4	—	— 5.0
1 5 4	—	— 11.0	9 13 4	—	21.3
3 5 4	—	18.7	11 13 4	—	— 29.1
5 5 4	79.3	— 87.1	13 13 4	44.1	49.5
7 5 4	43.2	— 34.4	2 14 4	—	24.7
9 5 4	115.8	100.9	4 14 4	87.5	87.9
11 5 4	—	— 32.8	6 14 4	—	— 0.8
13 5 4	—	— 0.3	8 14 4	—	— 30.3
15 5 4	—	37.0	1 15 4	46.2	— 56.0
2 6 4	—	6.4	3 15 4	56.5	60.2
4 6 4	34.5	50.0	5 15 4	—	18.2
6 6 4	70.3	— 61.6	7 15 4	56.8	— 63.2

Table 2. Interatomic distances in $Ni_{12}P_5$ in Å. (Distances shorter than 3.25 Å are listed.)

Ni_I — 5 Ni_I : 2.45, 2.51, 2.56, 2.64 (2).
     — 3 Ni_{II} : 2.54, 2.58, 2.73.
     — 3 P_I : 2.24, 2.41, 2.47.
     — 1 P_{II} : 2.25.

Ni_{II} — 6 Ni_I : 2.54 (2), 2.58 (2), 2.73 (2).
      — 5 Ni_{II} : 2.51, 3.09 (4).
      — 4 P_I : 2.22 (2), 2.60 (2).
      — 1 P_{II} : 3.22.

P_I — 6 Ni_I : 2.24 (2), 2.41 (2), 2.47 (2).
    — 4 Ni_{II} : 2.22 (2), 2.60 (2).

P_{II} — 8 Ni_I : 2.25 (8).
     — 4 Ni_{II} : 3.22 (4).

$B = 0.49$ Å^2. No further refinement was considered worthwhile. Observed and calculated structure factors are given in Table 1. The final structure of $Ni_{12}P_5$ is the following:

Space group $I4/m$ — (C_{4h}^5); $Z = 2$

16 Ni_I in 16(i) with $x = 0.116_0$; $y = 0.182_2$; $z = 0.248$;
 8 Ni_{II} in   8(h) with $x = 0.368$; $y = 0.060$;
 8 P_I in   8(h) with $x = 0.195$; $y = 0.415$;
 2 P_{II} in   2(a).

Interatomic distances are listed in Table 2.

DESCRIPTION OF THE STRUCTURE

A projection of the $Ni_{12}P_5$ structure on the basal plane is shown in Fig. 1. As a comparison, an analogous projection of the Ni_3P structure (according to Aronsson [4]) is shown in Fig. 2. The structure of Ni_3P is based on space group $I\bar{4}$ and the unit cell contains 24 Ni atoms (as in $Ni_{12}P_5$) and 8 P atoms. All atoms are situated in 8(g) positions with z parameters close to 0, 1/4, 1/2 and 3/4. From Figs. 1 and 2, the similarities between the two structures are easily seen. If, for instance, the Ni_I and Ni_{III} atoms in Ni_3P are moved together (indicated by arrows in Fig. 2) so as to lie directly above each other at $z = 1/4$ and $z = 3/4$, a metal atom lattice of the $Ni_{12}P_5$ type is created. In fact, the mean value of the x parameters for Ni_I and Ni_{III} in Ni_3P corresponds closely to the x parameter for Ni_I in $Ni_{12}P_5$, and the same is true for the y-parameters. The positions of the Ni_{II} and P atoms in Ni_3P correspond rather closely to the positions of Ni_{II} and P_I in $Ni_{12}P_5$.

In many transition metal phosphides, the P atoms are surrounded by nine metal atoms in a more or less regular tetrakaidecahedral arrangement. This coordination is, *e.g.*, found in the Fe_2P [6], the Co_2P [11] and in the Fe_3P [4] type structures. In $Ni_{12}P_5$, the P_I atoms have 10 near Ni neighbours, whereas the P_{II} atoms have only 8 near Ni neighbours in an almost cubic arrangement.
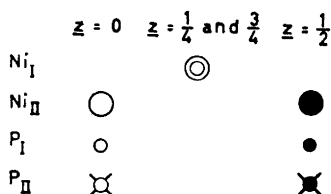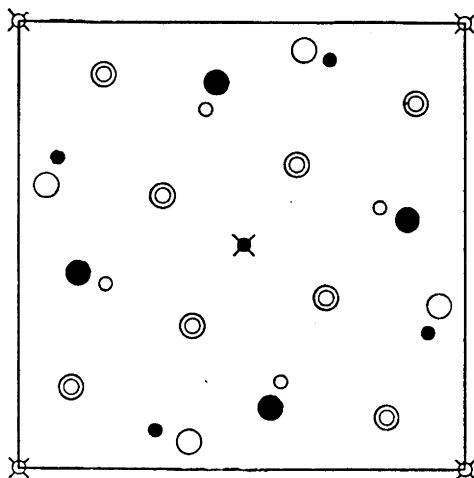
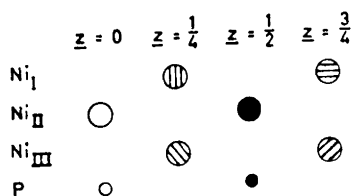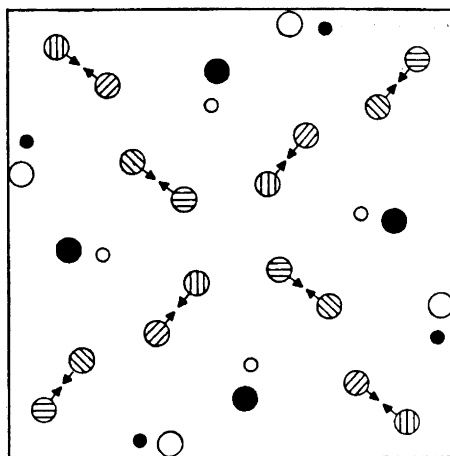*Fig. 1.* The unit cell of Ni$_{12}$P$_5$ projected on the basal plane.

Fig. 2. The unit cell of Ni$_3$P projected on the basal plane. Arrows on the Ni$_I$ and Ni$_{III}$ atoms indicate imagined displacements towards the Ni atom arrangement in Ni$_{12}$P$_5$.

The tendency for higher metal atom coordination than 8 around the P$_{II}$ atoms is perhaps indicated by the fact that P$_{II}$ is situated in 2(a) and not in 2(b). The cubic Ni$_I$ environment is the same for both 2(a) and 2(b) positions, but a P atom in 2(a) has 4 additional Ni$_{II}$ neighbours in the same plane at a distance of 3.22 Å, whereas a hypothetical P atom in 2(b) has 4 neighbouring P$_I$ atoms in the same plane at a distance of 2.73 Å.

REFERENCES

1. Hansen, M. *Constitution of Binary Alloys,* 2nd ed., (1958) 1027.
2. Konstantinow, N. *Z. anorg. Chem.* **60** (1908) 405.
3. Nowotny, H. and Henglein, E. *Z. physik. Chem.* **B 40** (1938) 281.

4. Aronsson, B. *Acta Chem. Scand.* **9** (1955) 137.
5. Biltz, W. and Heimbrecht, M. *Z. anorg. Chem.* **237** (1938) 132.
6. Rundqvist, S. and Jellinek, F. *Acta Chem. Scand.* **13** (1959) 425.
7. Biltz, W., Heimbrecht, M. and Meisel, K. *Z. anorg. Chem.* **241** (1939) 349.
8. Oftedal, I. *Z. Krist.* **66** (1928) 517.
9. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
10. Tomiie, Y. and Stam, C. H. *Acta Cryst.* **11** (1958) 126.
11. Nowotny, H. *Z. anorg. Chem.* **254** (1947) 31.