

## The Crystal Structure of Ni<sub>5</sub>P<sub>4</sub>

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The crystal structure of Ni<sub>5</sub>P<sub>4</sub> has been determined and refined using single crystal methods. The space group is *P6<sub>3</sub>mc* with 18 nickel in 6(*c*) positions:  $x_1 = 0.5358$ ,  $z_1 = 0.0000$ ,  $x_2 = 0.2078$ ,  $z_2 = 0.1493$ ,  $x_3 = 0.5418$ ,  $z_3 = 0.2903$ , and two nickel in 2(*a*):  $z = 0.1117$ , and with 12 phosphorus in 6(*c*) positions:  $x_1 = 0.8181$ ,  $z_1 = 0.143$  and  $x_2 = 0.178$ ,  $z_2 = 0.353$ , two phosphorus in 2(*b*):  $z = 0.468$  and two phosphorus in 2(*a*):  $z = 0.413$ . The cell dimensions are  $a = 6.789$  Å and  $c = 10.986$  Å, with a content of four formula units. The number of near neighbours to the phosphorus atoms varies from four to nine. The structure is the most metal-rich transition metal phosphide that shows close phosphorus-phosphorus contacts.

The binary system nickel-phosphorus seems to be complex. The number of intermediate phases that have been characterized is about ten and there is still room for further discoveries. Recently Larsson<sup>1</sup> has discussed the system at some length and presented a tentative phase diagram which includes ten binary phases. Among these, Ni<sub>3</sub>P, Ni<sub>12</sub>P<sub>5</sub>, Ni<sub>2</sub>P, NiP, and NiP<sub>2</sub> have been the subject of single crystal structure determinations.<sup>1-3</sup> Furthermore, the cell dimensions and crystal symmetries are known for NiP<sub>3</sub> (which has the CoAs<sub>3</sub>-type structure<sup>4</sup>) and for Ni<sub>5</sub>P<sub>2</sub>.<sup>5</sup> The latter compound shows a complex behavior and further research about its formation and structure is needed. Among the remaining nickel phosphides, Larsson<sup>1</sup> has recorded Weissenberg photographs for Ni<sub>5</sub>P<sub>4</sub> and suggested its space group to be either *P6<sub>3</sub>mc*, *P6̄2c*, or *P6<sub>3</sub>mmc*. These photographs have now served as the basis for a complete structure determination.

### EXPERIMENTAL

Nickel powder and red phosphorus were mixed and heat treated at 900°C for one day and at 800°C for seven days in an evacuated silica tube. From this sample a small single crystal was selected. Weissenberg photographs were recorded using filtered MoK $\alpha$  radiation and multiple films for the zones 0-11. The intensities were estimated visually by comparison with a calibrated intensity scale. However, only the intensities from the first six zones were used in the calculations since the shape of the spots on the films gradually became less distinct for the higher zones. The material nevertheless included 489 independent reflexions (the eleven strongest not included).

Most of the calculations were carried out on the electronic computer BESK, although the final refinement of the atomic parameters was made on IBM 7090. The programs used have the numbers 6014, 6015, 6016, and 360 in *IUCr World List of Crystallographic Computer Programs*.<sup>6</sup> The atomic scattering factors given by Watson and Freeman<sup>7</sup> for Ni, and in *International Tables*<sup>8</sup> for P were used. The real part of the dispersion correction factor according to Dauben and Templeton<sup>9</sup> was included. No absorption correction seemed to be needed.

#### ANALYSIS OF THE PATTERSON FUNCTION

The condition for absences among the reflexions,  $(hh2\bar{h}l)$  for  $l = 2n + 1$ , leads to five possible space groups: the three aforementioned hexagonal, and two trigonal,  $P31c$  and  $P\bar{3}1c$ . As the difference between  $F(hkl)$  and  $F(h\bar{k}l)$  for all observed reflexions lay within the experimental errors, the structure was treated as having hexagonal symmetry. Preliminarily, no distinction could be made that could exclude any of the three hexagonal space groups. It was therefore found convenient to work as if the space group was  $P31c$ , as this space group contains only the symmetry elements common to the three possible space groups. In the computer programs, however, hexagonal codes for generation of equivalent reflexions were inserted.

A three-dimensional Patterson function was calculated. The sections  $P(xy0)$  and  $P(xy\frac{1}{2})$  were used to reveal the arrangements of the atoms with the same  $z$ -coordinate. As can be seen from Fig. 1, the shortest Ni—Ni vectors are parallel to the  $a$ -axes or to the shortest diagonal of the section. The origin maximum with the height 465 leads to the value 18 or 19 for a single Ni—Ni vector, and to 4 or 5 for a single P—P vector. Maxima lying on mirror planes in the section must have at least double height compared with a peak from

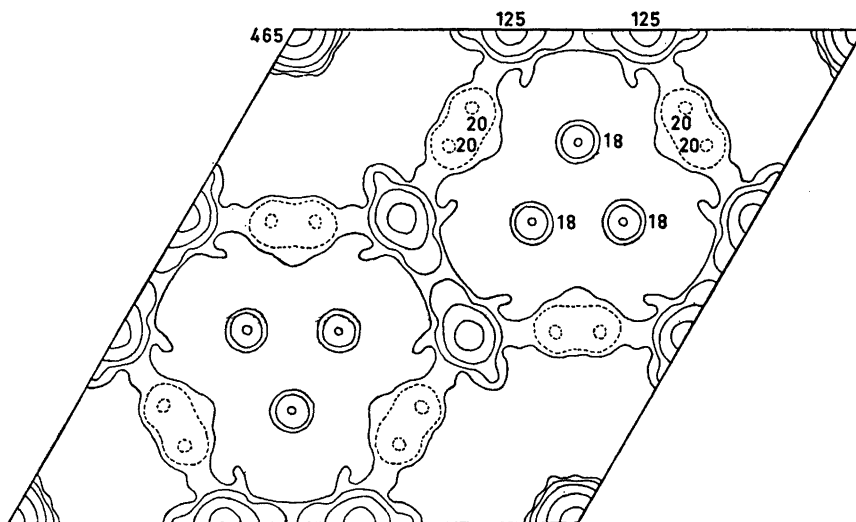


Fig. 1. The Patterson section  $P(xy0)$ .

a single vector. The maxima with the height 18 in Fig. 1 are therefore of no interest when discussing Ni—Ni vectors. The maxima with the height 20 are dotted as their true maxima lie in another section,  $P(xy0.04)$ . The remaining maxima give the following relations between the nickel atomic parameters:  $2x = y$ ,  $2y = x$ , and  $x = -y$ .

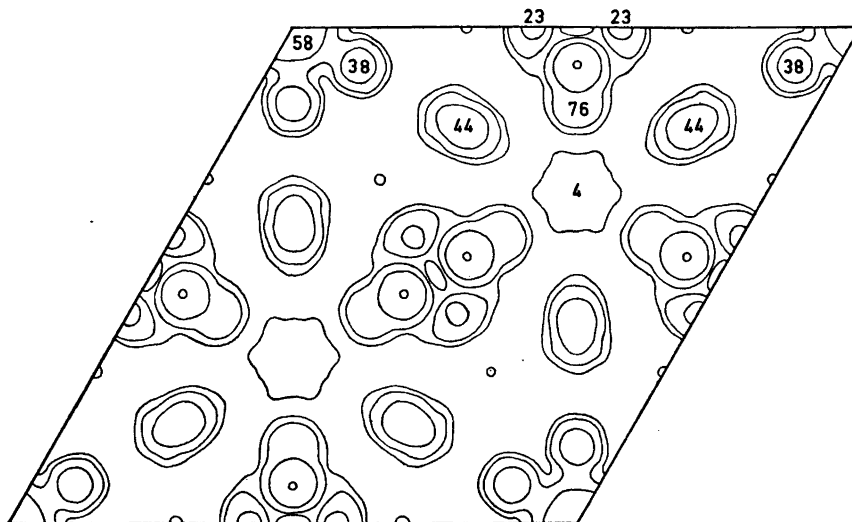


Fig. 2. The Patterson section  $P(xy\frac{1}{2})$ .

Fig. 2 illustrates the section  $P(xy\frac{1}{2})$ . The space group  $P31c$  has the following vectors in this section:

$$\pm (2x, x, \frac{1}{2}; 2y, y, \frac{1}{2}; y, 2y, \frac{1}{2}; \bar{x}, 2\bar{x}, \frac{1}{2}; x - y, 2x - 2y, \frac{1}{2}; 2y - 2x, y - x, \frac{1}{2}; x - y, y - x, \frac{1}{2}; \bar{x}, x, \frac{1}{2}; y, y, \frac{1}{2})$$

The relations between  $x$  and  $y$  cause the vectors to lie on the lines  $2x, x, \frac{1}{2}$ ,  $x, 2x, \frac{1}{2}$ , and  $x, x, \frac{1}{2}$ . Fig. 2 shows that these three alternatives are equivalent and the first line is therefore selected and the coordinates of its maxima are tabulated in Table 1.

Table 1. Coordinates of the peaks in  $P(xy\frac{1}{2})$ .

No.	$x$	$y$	peak height	labelled
1	0.1542	0.0770	38	—
2	0.4051	0.2026	44	III
3	0.9214	0.4607	76	I
4	1.0786	0.5393	76	II
5	1.5949	0.7974	44	IV
6	1.8458	0.9230	38	—
7	2.0000	1.0000	58	VII

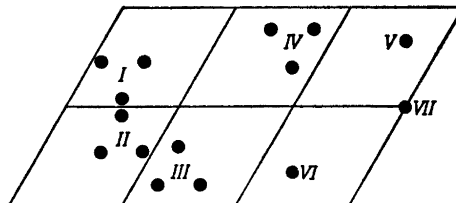


Fig. 3. Possible nickel positions.

The maxima Nos. 1 and 6 in Table 1 lead to too short interatomic distances and can therefore be excluded, but the others are represented in Fig. 3 together with two two-fold positions that do not seem to be occupied by nickel atoms. The glide planes of the space group relate positions I and II to each other, as well as III and IV, and V and VI.

Position VII has a peak in this section lying at the origin where the maximum is 58. If position VII was exclusive for phosphorus the maximum could be explained by about 12 P—P vectors. This corresponds to six two-fold positions of phosphorus. Such an arrangement would lead to unreasonably short P—P distances (about 1 Å). The maximum must therefore be explained with the help of one (or several) nickel atoms in position VII.

The vectors between any two of the seven positions were plotted and a set of these vectors was selected. As the symmetry of the structure is high, overlapping cannot be avoided with any choice of vectors. The selected vectors were:

- .54/.08/ $z$  containing the vectors I—II, I—VII, II—VII, (III—VI and IV—V)
- .21/.42/ $z$  containing the vectors III—IV, III—VII, IV—VII, (I—VI and II—V).
- .05/.34/ $z$  containing the vectors I—IV and II—III
- .00/.62/ $z$  containing the vectors I—I, II—II, III—III and IV—IV
- .25/.50/ $z$  containing the vectors I—III and II—IV

These five lines in the Patterson space are plotted in Figs. 4 and 5.

The third line of Fig. 4 is very simple, and contains only a maximum for  $|z| = 0.14_5$ . If position I is arbitrarily given the  $z$ -coordinate 0.0000, then position IV must have the  $z$ -coordinate  $0.14_5$ . The glide planes create a position II with  $z = 0.5000$  and a position III with  $z = 0.64_5$ . There are no further possibilities but for the uninteresting change of direction of the  $z$ -axis.

The second line of Fig. 4 contains the vectors between the positions I—VI and II—V, but as positions V and VI contain no nickel, there can be no such Ni—Ni vectors. The line has two maxima, one for  $|z| = 0.04$ , and a broad one around  $|z| = \frac{1}{2}$ . The latter obviously consists of at least three maxima, one at  $z = \frac{1}{2}$  (from III—IV), one at  $z = 0.46$  and one at  $z = 0.54$  (these two being generated by the glide planes from the vector  $|z| = 0.04$ ). The broad maximum thus contains no more interesting information than is contained in the other maximum. Thus at a  $z$ -coordinate of either  $0.10_5$  or  $0.18_5$  (or both) there will be nickel atoms having either or both of the positions III and VII.

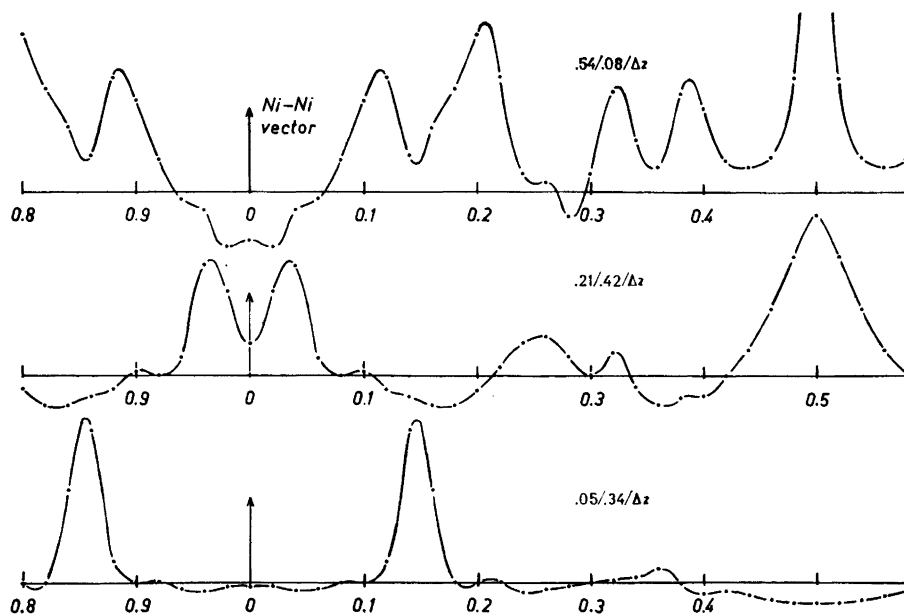


Fig. 4. Lines in Patterson space.

These possibilities can be tested. The second line of Fig. 5 contains the vectors I–III. It has however no maxima at the two  $z$ -coordinates,  $0.10_5$  and  $0.18_5$ . The first line contains the vectors I–VII. It has maxima at both these  $z$ -coordinates. Thus there remains an ambiguity regarding the coordinate of position VII. Both cannot be occupied by it as this would imply two nickel atoms within a distance of 1 Å.

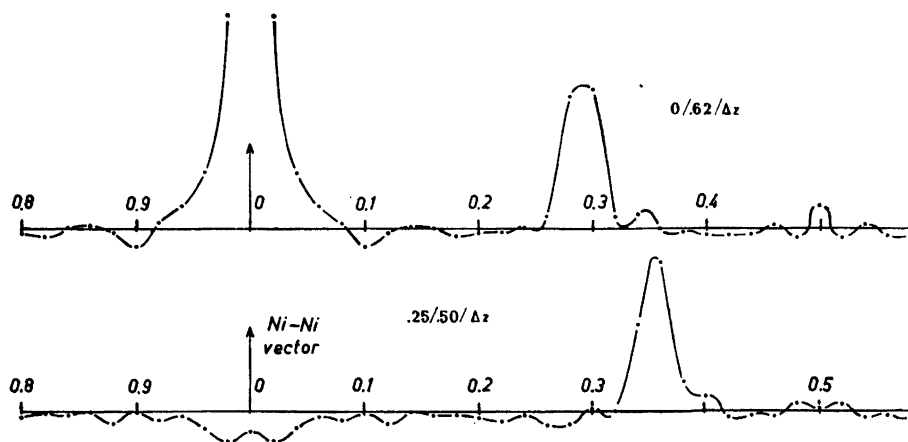


Fig. 5. Lines in Patterson space.

The first line of Fig. 5 contains the vectors between the four first positions and themselves. It has one interesting maximum at  $z = 0.29$ . This gives one single choice compatible with the discussion above, namely a position I with  $z = 0.29$ . It can now be seen that the two choices for position VII in fact are equivalent. The stacking sequence 0, 0.11, 0.14, 0.29 is the same as 0.29, 0.18, 0.14, 0. The first sequence has been chosen in this paper.

Thus there is one single choice of nickel positions that is compatible with the Patterson space. Despite the high symmetry and the overlappings a discussion like the above is possible because the  $a$ -axis is so short that the number of different atomic arrangements that can appear in this high symmetry is strictly limited.

The phase angles calculated on the basis of this nickel skeleton were used together with the observed  $F$  values to calculate the electron density function. Besides the maxima that belonged to nickel, there were twelve other maxima well resolved from the background. Their positions were satisfied by phosphorus positions. New phase angles on the basis of the nickel and the twelve phosphorus atoms were calculated and used in the same manner. The electron density function now showed four new maxima of heights nearly equal to the other phosphorus maxima. Phase angles on the basis of the nickel and all sixteen phosphorus atoms gave no new maxima in the electron density function. The proposed structure was then refined with the program OR FLS on IBM 7090. The program uses the least squares method. The parameters that were refined were atomic coordinates, individual isotropic temperature factors and one scale factor. A weighting scheme according to Cruickshank *et al.*<sup>10</sup>,  $w = 1/(a + |F_o| + c|F_o|^2)$ , was used with the values  $a = 39.0$  and  $c = 0.00948$ . After three cycles of refinement the shifts were less than one-tenth of their estimated standard values, derived from the inverse least-squares matrix. The structure thus obtained is consistent with all the maxima in Patterson space, and all interatomic distances have reasonable values. The discrepancy factor  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  was 0.10. The eleven strongest reflexions all showed too small observed values and were therefore excluded. Interatomic distances and angles between any three atoms were calculated with the program OR FFE (obtainable from the same source as OR FLS<sup>6</sup>). The program also calculates the corresponding standard deviations.

Table 2. Final structure data. Space group  $P6_3mc$ .

Atom	Pos.	$x$	$\sigma$	$z$	$\sigma$	$B$	$\sigma$
Ni 1	6(c)	0.5357	0.0005	0.0000	—	0.23	0.05
Ni 2	6(c)	0.2078	0.0003	0.1493	0.0006	0.27	0.03
Ni 3	6(c)	0.5418	0.0005	0.2903	0.0004	0.27	0.06
Ni 4	2(a)	—	—	0.1117	0.0008	0.22	0.07
P 1	6(c)	0.8181	0.0006	0.1434	0.0010	0.18	0.08
P 2	6(c)	0.1777	0.0008	0.3534	0.0009	0.27	0.10
P 3	2(a)	—	—	0.4128	0.0013	0.30	0.18
P 4	2(b)	—	—	0.4684	0.0015	0.29	0.16

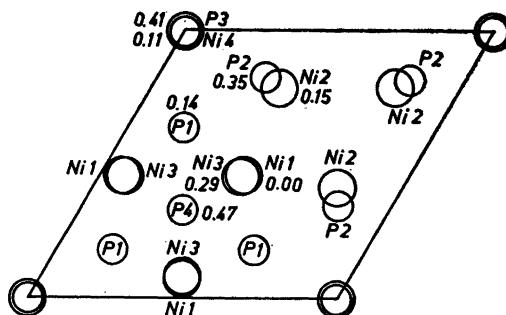
## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Table 2 contains the final atomic parameters and the temperature factors with the standard deviations. Table 3 contains all interatomic distances shorter than 3.5 Å with standard deviations in most cases. In these standard deviations

Table 3. Interatomic distances shorter than 3.5 Å (in Å).

Ni 1—Ni 1:	2.666 ± 0.009 (2)	
—Ni 2:	2.650 ± 0.005 (2)	
—Ni 3:	2.478 ± 0.005 (1),	3.190 ± 0.004 (1)
—P 1:	2.298 ± 0.009 (2)	
—P 2:	2.344 ± 0.008 (2)	
—P 4:	2.405 ± 0.006 (1)	
Ni 2—Ni 1:	2.650 ± 0.005 (2)	
—Ni 2:	2.557 ± 0.007 (2)	
—Ni 3:	2.640 ± 0.006 (2)	
—Ni 4:	2.478 ± 0.005 (1)	
—P 1:	2.307 ± 0.004 (2)	
—P 2:	2.270 ± 0.010 (1)	
—P 4:	2.476 ± 0.015 (1)	
Ni 3—Ni 1:	2.478 ± 0.005 (1),	3.190 ± 0.004 (1)
—Ni 2:	2.640 ± 0.006 (2)	
—Ni 3:	2.543 ± 0.010 (2)	
—P 1:	2.306 ± 0.009 (2)	
—P 2:	2.314 ± 0.005 (2)	
—P 4:	2.446 ± 0.014 (1)	
Ni 4—Ni 2:	2.478 ± 0.005 (3)	
—P 1:	2.167 ± 0.008 (3)	
—P 2:	3.379 (3)	
—P 3:	2.186 ± 0.017 (1),	3.307 (1)
P 1—Ni 1:	2.298 ± 0.009 (2)	
—Ni 2:	2.307 ± 0.004 (2)	
—Ni 3:	2.306 ± 0.009 (2)	
—Ni 4:	2.167 ± 0.008 (1)	
—P 1:	3.084 ± 0.013 (2)	
—P 2:	3.129 ± 0.011 (2),	3.187 ± 0.014 (1)
—P 3:	3.316 (1)	
P 2—Ni 1:	2.344 ± 0.008 (2)	
—Ni 2:	2.270 ± 0.010 (1)	
—Ni 3:	2.314 ± 0.005 (2)	
—Ni 4:	3.379 (1)	
—P 1:	3.129 ± 0.011 (2),	3.187 ± 0.014 (1)
—P 2:	3.170 ± 0.017 (2)	
—P 3:	2.189 ± 0.011 (1)	
P 3—Ni 4:	2.186 ± 0.017 (1),	3.307 (1)
—P 1:	3.316 (3)	
—P 2:	2.189 ± 0.011 (3)	
P 4—Ni 1:	2.405 ± 0.006 (3)	
—Ni 2:	2.476 ± 0.015 (3)	
—Ni 3:	2.446 ± 0.014 (3)	

Fig. 6. A half-cell projected along the *c*-axis.



the uncertainty in the cell dimensions, as given by Larsson,<sup>1</sup> are included. This, however, means an adjustment in the second or the third significant figure of the standard deviations and has no practical influence in this case.

A half-cell of the Ni<sub>5</sub>P<sub>4</sub> structure is shown in Fig. 6 projected along the *c*-axis. The atoms P 3, P 4 and Ni 4 lie on a three-fold axis or a 6<sub>3</sub> axis, while every atom lies on a mirror plane. The same half-cell of the structure is shown in Fig. 7 as a three-dimensional view. The other half of the cell is to be placed

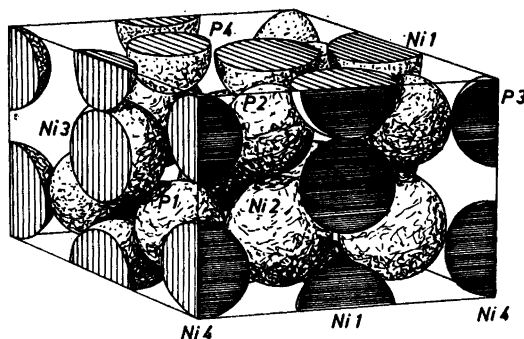


Fig. 7. A half-cell.

on top of the one shown. This second half is related to the first by the glide planes. One of these lies on the shorter diagonal of the surface shown in Fig. 6 and has its translational component along the *c*-axis. The rest of the figures show the near surroundings of all crystallographically different atoms. They are all viewed from the same direction as the half-cell of Fig. 7.

Figs. 8–11 show the varying number of near neighbours that the different phosphorus atoms have. The number is lowest around the P 3 atoms, with three, whilst the P 2 atoms have six, the P 1 atoms seven and the P 4 atoms nine near neighbours.

The most striking feature is the environment of the P 3 atoms. They are surrounded by one nickel and three phosphorus atoms at very short distances, and grouped in a slightly distorted tetrahedron. As already mentioned, the



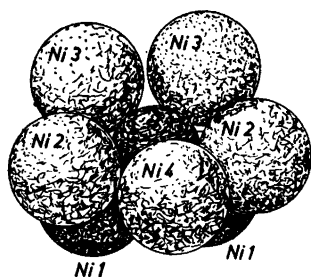


Fig. 8. The environments around the P 1 atoms.

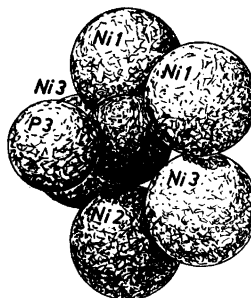


Fig. 9. The environments around the P 2 atoms.

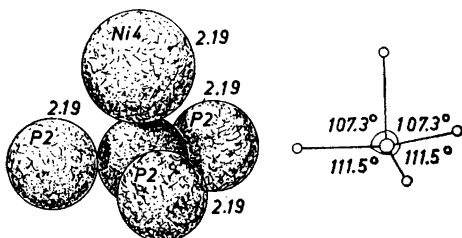


Fig. 10. The environments around the P 3 atoms.

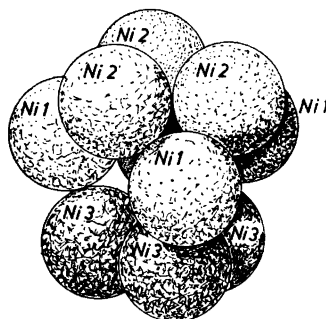


Fig. 11. The environments around the P 4 atoms.

P 3 and Ni 4 atoms lie on a three-fold axis, but the three P 2 atoms lie too near the Ni 4 atom to make the tetrahedron truly perfect. The deviation is best expressed by the central angles as shown in Fig. 10. The three Ni—P—P angles are  $107.3^\circ \pm 0.4$  and the three P—P—P angles  $111.5^\circ \pm 0.4$ . This arrangement can be compared with that found in the more phosphorus-rich phase NiP where the phosphorus atoms appear in pairs with a P—P distance of 2.43 Å, that is, about 10 % longer than in Ni<sub>5</sub>P<sub>4</sub>. The still more phosphorus-rich phosphides of nickel do not show this dense packing of phosphorus atoms. However, one can find a tetrahedral environment around a phosphorus atom both in NiP<sub>2</sub> and NiP<sub>3</sub>, but there are only two phosphorus atoms among the four neighbours. These tetrahedra are also more irregular. In NiP<sub>2</sub> the bond angles (vertex at the central P atom) differ by 12° from those in a regular tetrahedron, and the nickel distances to the center are shorter than the phosphorus ones. In NiP<sub>3</sub> the angles differ still more from regularity. As this structure is not known regarding the two free atomic parameters of phosphorus, the exact angles are unknown excepting the P—P—P angle that must be 90° according to symmetry.

Tetrahedra with three phosphorus and one metal atom around a central phosphorus atom occur however in CuP<sub>2</sub>.<sup>11</sup> CuP<sub>2</sub> thus has one of its two

structurally different phosphorus atoms coordinated in this way, and so probably also has  $\text{AgP}_2$ .<sup>11</sup> Further examples occur among the phosphides of zinc and cadmium. However, the P—P linkage in these compounds extends infinitely in two dimensions, while the four atoms P 3 and P 4 form an isolated phosphorus aggregate in the  $\text{Ni}_5\text{P}_4$  structure.

The P 4 atom is surrounded by nine nickel atoms in a rather regular manner. The distances Ni—P differ by only 0.07 Å at the most. Rundqvist<sup>12</sup> has pointed out the common occurrence of a coordination polyhedron, the tetrakaidecahedron, in metal-rich transition phosphides. In structures containing a three-fold axis, such arrangements and related ones are likely to occur if the packing around the axis should be dense. The tetrakaidecahedron is based upon a right triangular prism having three additional atoms outside the rectangular faces. The coordination polyhedron around P 4 differs from this in that the six atoms Ni 2 and Ni 3 together form a triangular antiprism.

Fig. 12 shows the environments of the atoms Ni 1 and Ni 3. The coordination figures around the two atoms look surprisingly alike. The atoms in the

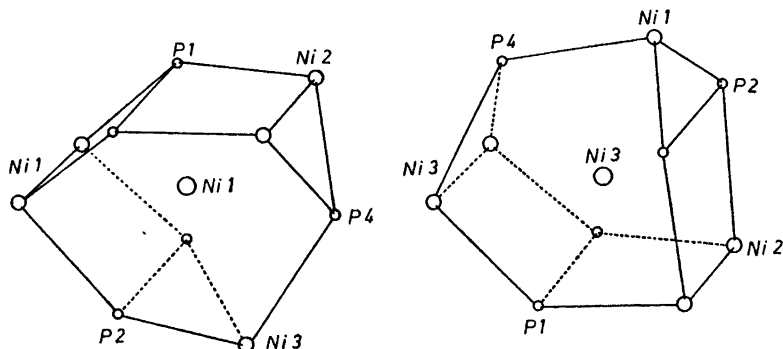


Fig. 12. The environments around the Ni 1 and Ni 3 atoms.

drawings are viewed from the same direction. The polyhedra are thus rotated slightly in relation to each other. The one around Ni 3 is more spherical in shape than the other.

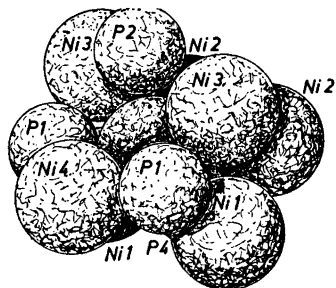


Fig. 13. The environments around the Ni 2 atoms.

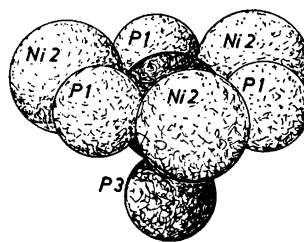


Fig. 14. The environments around the Ni 4 atoms.

The distribution of nearest neighbours about several of the atoms is considerably non-uniform. This can be exemplified by the environment of the Ni 4 atoms (Fig. 14). Six of the seven neighbours lie in a puckered ring and the seventh lies on beneath the ring in the figure. The next-nearest neighbours do not lie above the six membered ring as could be expected, but instead beneath.

The  $\text{Ni}_5\text{P}_4$  structure thus has some noteworthy features, especially regarding phosphorus and its neighbours. The knowledge available for the other nickel phosphides shows them to be strongly related to other transition metal phosphides, silicides and arsenides, but all the nickel phosphides retain a character of their own. The singularity of the nickel-phosphorus system is probably related to the position of nickel in the periodic table. In phosphides of transition metals on the left side of the periodic table, the phosphorus atoms are well separated from each other by long P—P distances. With transition metals to the right in the periodic table short P—P distances become more common, and  $\text{Ni}_5\text{P}_4$  is the most metal-rich phosphide that shows close phosphorus-phosphorus contacts. In this structure half of the phosphorus atoms are grouped in clusters of four with contact distances and bond angles consistent with  $sp^3$  bonds.

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