

## The Crystal Structure of Ni<sub>3</sub>P.(Fe<sub>3</sub>P-Type)

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The structure of Ni<sub>3</sub>P (Fe<sub>3</sub>P-type) has been determined using single crystal data. The space-groups is  $S_4^2-I_4$  and all atoms occupy general positions 8(*g*). The structure is rather close-packed, resulting in high coordination numbers. The phosphorus atoms have 9 nickel neighbours at an average distance of 2.30 Å. The relation to some other types of transition metal phosphides is discussed and the similarity between the Mo<sub>3</sub>Si<sub>3</sub>-phase (usually described as "Mo<sub>3</sub>Si<sub>4</sub>") and the Fe<sub>3</sub>P-type is noted.

The first X-ray crystallographic investigation of Fe<sub>3</sub>P was made by Hägg<sup>1</sup>. The unit cell was found to be bodycentered tetragonal with the axial lengths  $a = 9.090$  kX and  $c = 4.446$  kX. The cell contained 8 formula units and the Laue symmetry was  $C_{4h}-4/m$ . The appearance of 0,0,2 excluded all space-groups except  $S_4^2-I_4$ ,  $C_4^5-I_4$  and  $C_4^5-I_4/m$ . The first of these groups was considered to be the most probable one, owing to the external form of the crystals.

In more recent investigations the following isomorphous phases have been found: Mn<sub>3</sub>P<sup>2</sup>, Cr<sub>3</sub>P<sup>3</sup>, Ni<sub>3</sub>P<sup>4</sup>, Mo<sub>3</sub>P<sup>5</sup>, V<sub>3</sub>P<sup>6</sup> \* and Ti<sub>3</sub>P<sup>7</sup>. A determination of the Fe<sub>3</sub>P-structure was, therefore, considered to be of some interest. Ni<sub>3</sub>P was chosen for this investigation, because it permitted the use of CuK-radiation without disturbance from fluorescent radiation.

### EXPERIMENTAL

The preparation of Ni<sub>3</sub>P was made according to the method, described by Haughton<sup>8</sup> and Hägg<sup>1</sup>: Pastilles of red phosphorus were dropped into molten nickel. The nickel was molten in a N<sub>2</sub>-atmosphere in a high frequency induction furnace. After cooling the melt was crushed in a steel mortar. Powder photographs were taken in a camera of the Guinier type using CuK $\alpha$  radiation. Some crystal fragments were selected and the one that gave the best reflexions was used in the single crystal work. For the Weissenberg photographs MoK radiation was used. The crystal was rotated around the *c*-axis and the layer lines 0-4 were recorded. With the aid of Lu's<sup>9</sup> curves, relative  $|F|^2$ -values were calculated

\* Schönberg<sup>12</sup> has not been able to verify the existence of this phase. It seems probable, however, that it does exist.

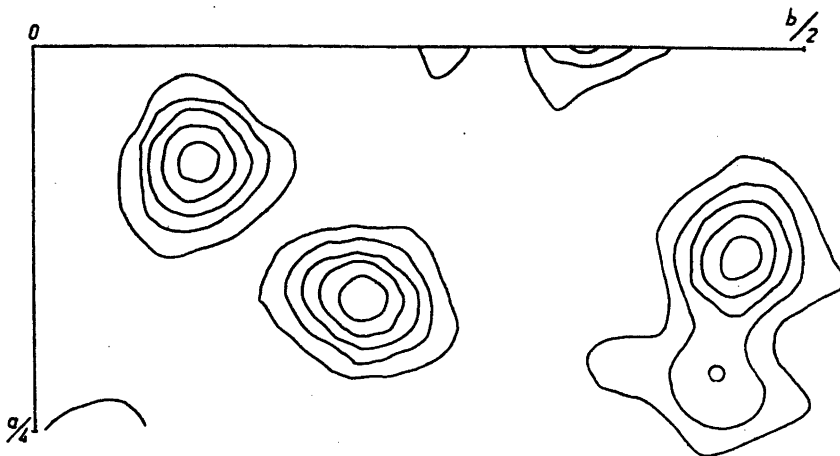


Fig. 1. Final Fourier projection  $\rho(x,y)$ . Contours drawn at intervals of approximately  $15e \text{ \AA}^{-2}$ .  $1/8$  of the unit cell is given.

from the visually estimated intensities. No corrections were made for adsorption and thermal movement. The computations of the Patterson sections  $P(x,y,z_n)$  ( $z_n = 0, 2/60, 5/60, 10/60, 15/60$ ) and the Fourier projection  $\rho(x,y)$  were made on the Hägg-Laurent machine<sup>10</sup>.

#### DETERMINATION OF THE STRUCTURE

The dimensions of the bodycentered tetragonal cell were determined from the powder photographs. The lengths of the axes are  $a = 8.952 \text{ \AA}$  and  $c = 4.388 \text{ \AA}$  ( $\pm 1\%$ ). The Weissenberg photographs showed that  $F_{hkl} \neq F_{\bar{h}\bar{k}l}$  and as  $F_{0,0,2} \neq 0$  the only possible spacegroups were  $S_4^2-I\bar{4}$ ,  $C_4^2-I\bar{4}$  and  $C_{4h}^2-I\frac{4}{m}$ . An inspection of the Patterson section  $P(x,y,0)$  immediately showed that the fourfold axis could not be a rotation axis. Thus, the spacegroup was found to be  $S_4^2-I\bar{4}$ —in agreement with the supposition made by Hägg<sup>1</sup>. A further analysis of the Patterson function gave the approximate Ni-positions, which corresponded to general positions  $8(g)$ . Successive Fourier-projections  $\rho(x,y)$  refined the  $x$  and  $y$  parameters of the Ni-atoms and in addition gave those of the P atom, which was also found to occupy a general position  $8(g)$ . The conspicuous similarity between the layer lines 0 and 4 as well as the layer lines 1 and 3 indicated that all the atoms must lie very near the planes  $z = 0, \frac{1}{4}, \frac{1}{2}$  and  $\frac{3}{4}$ . This fact was confirmed by the Patterson function, where all the maxima were found in the sections  $P(x,y,0)$  and  $P(x,y,\frac{1}{4})$ .

Fig. 1 shows the final Fourier projection from which the final coordinates were obtained. The maximum corresponding to the P atom is very flat and does not permit an accurate determination of the parameters of this atom. In order to obtain these, different positions of the P atom were tried, until the best agreement between observed and calculated intensities was obtained.

The resulting parameters are

	<i>x</i>	<i>y</i>	<i>z</i>
Ni <sub>I</sub> in 8( <i>g</i> )	0.080	0.109	0.25
Ni <sub>II</sub> in 8( <i>g</i> )	0.363	0.030	0
Ni <sub>III</sub> n 8( <i>g</i> )	0.164	0.220	0.75
P n 8( <i>g</i> )	0.290	0.042	0.50

Assuming these parameters to be correct all the maxima of the Patterson function can be explained.

#### THE STRUCTURE

The structure may be considered as rather close-packed, resulting in high coordination numbers. The environment of each atom is given in Table 1.

One of the Ni-atoms has 12 nickel neighbours (as in pure nickel) but the other two have 10 neighbours. The intermetallic distances are on the average 8 % longer than in the pure metal. The weakening of the metal-metal bonds in comparison with pure nickel is compensated by the metal-phosphorus bonds created here.

The phosphorus atom has 9 nickel neighbours at an average distance of 2.30 Å. Half on the P atoms in Fe<sub>2</sub>P<sup>11</sup> and the isomorphous Ni<sub>2</sub>P<sup>4</sup> have a similar environment — even the spatial arrangement of the 9 metal neighbours around the P atom is almost the same.

By the determination of the Fe<sub>3</sub>P-structures another type of transition metal phosphide has been added to those recently discussed by Schönberg<sup>12</sup>. The way in which an increase of the non-metal concentration results in a decrease of the metallic properties is illustrated by the sequence Fe<sub>3</sub>P, Fe<sub>2</sub>P and FeP. The coordination numbers become lower. The P atom, for example, has 9 close metal neighbours in Fe<sub>3</sub>P. In Fe<sub>2</sub>P half of the P-atoms have also 9 neighbours, while the other half have 6, as have the P atoms in FeP. The structures become less densely packed. Assuming  $r_{\text{Fe}} = 1.26$  Å and  $r_{\text{P}} = 1.06$  Å, the volume occupied by each atom in Fe<sub>3</sub>P is  $6.35 r^3$ , in Fe<sub>2</sub>P  $6.8 r^3$  and in FeP  $7.25 r^3$ . (The corresponding values are  $6.16 r^3$  for  $\alpha$ -Fe and  $5.66 r^3$  for  $\gamma$ -Fe.) The shortest P—P distances, being 3.9 Å, 3.6 Å and 2.6 Å, become smaller.

As was mentioned in the introduction several phosphides of the Fe<sub>3</sub>P-type have been found among the transition metals (represented in the phosphide systems of Ti, V, Cr, Mn, Fe, Ni and Mo). As the experimental difficulties make

Table 1. (Only distances < 3 Å have been given.)

	Interatomic distances in Å
Ni <sub>I</sub> — 12 Ni	2.44; 2.52 (2); 2.56 (2); 2.72; 2.79 (5) 2.86
— 2 P	2.25 (2)
Ni <sub>II</sub> — 10 Ni	2.43; 2.50; 2.54; 2.71 (2); 2.83 (4); 2.86
— 4 P	2.29 (3) 2.32
Ni <sub>III</sub> — 10 Ni	2.43; 2.52 (3); 2.71; 2.75 (4) 2.78
3 P	2.25 (2) 2.44
P — 9 Ni	2.25 (4); 2.29 (3); 2.33 2.44

the preparation of these compounds rather difficult, it is too early to say definitely which factors determine the occurrence of the  $\text{Fe}_3\text{P}$ -type phosphide. Evidently, it is only formed by the transition metals, belonging to the groups IV—VIII of the periodic system, and most readily by the lightest of those — the only exception between Ti and Ni being Co. In  $\text{Co}_2\text{P}$ , the structure of which has been determined by Nowotny<sup>13</sup>, the P atoms have a very similar environment to that of the P atoms in  $\text{Fe}_3\text{P}$  — according to Nowotny the average of the 9 Co—P distances is 2.30 Å. There is no Cu-compound of this type.  $\text{Cu}_3\text{P}$  has a different structure which has been determined by Steenberg<sup>14</sup>. To what extent the  $\text{Fe}_3\text{P}$ -type phosphide is formed by the heavier transition elements cannot yet be stated with certainty.

Another question is whether any other non-metal forms a similar phase with the transition metals. The Mo—Si and W—Si systems have recently been investigated at this institute and the phases usually described as " $\text{Mo}_3\text{Si}_2$ " and " $\text{W}_3\text{Si}_2$ " have been found to possess a bodycentered tetragonal structure with  $a = 9.617$  Å,  $c = 4.899$  Å (" $\text{Mo}_3\text{Si}_2$ ") and  $a = 9.645$  Å,  $c = 4.969$  Å (" $\text{W}_3\text{Si}_2$ "). The correct formulae are  $\text{Mo}_5\text{Si}_3$  and  $\text{W}_5\text{Si}_3$  with 4 formula units in the elementary cell. Thus, the elementary cell of this structure resembles very strikingly that of  $\text{Fe}_3\text{P}$ . A structure determination of  $\text{W}_5\text{Si}_3$ , which has recently been completed at this institute, shows, however, that this similarity is not caused by any deeper analogies between the  $\text{Fe}_3\text{P}$  and  $\text{W}_5\text{Si}_3$  structures. (The space group of  $\text{W}_5\text{Si}_3$  is  $I-\bar{4}2m$ ; 16 W are situated in 16 ( $j$ ) with  $x = 0.277$ ,  $y = 0.074$ ,  $z = 0.25$ , 2 W in 2 ( $b$ ), and 2 W in 2 ( $a$ ), while the probable positions of Si are 8 Si in 8 ( $i$ ) with  $x = 0.17$ ,  $z = 0.75$  and 4 Si in 4 ( $c$ )).

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#### REFERENCES

1. Hägg, G. *Nova Acta Regiae Soc. Sci. Upsaliensis* [4] 7 (1929) No. 1.
2. Årstad, O. and Nowotny, H. *Z. physik. Chem.* [B] 38 (1937) 356.
3. Nowotny, H. and Henglein, E. *Z. anorg. Chem.* 239 (1938) 14.
4. Nowotny, H. and Henglein, E. *Z. physik. Chem.* [B] 40 (1938) 281.
5. Faller, J. F., Biltz, W., Meisel, K. and Zumbusch, M. *Z. physik. Chem.* 248 (1941) 216.
6. Zumbusch, M. and Biltz, W. *Ibid.* 249 (1942) 1.
7. Schönberg, N. *To be published.*
8. Haughton, J. L. *J. Iron Steel Inst. (London)* 115 (1927) 417.
9. Lu, Chia-Si *Rev. Sci. Instr.* 14 (1943) 331.
10. Hägg, G. and Laurent, T. *J. Sci. Instr.* 23 (1946) 155.
11. Hendricks, S. B. and Kosting, P. R. *Z. Krist.* 74 (1930) 511; See also *Strukturbericht II*: 15.
12. Schönberg, N. *Acta Chem. Scand.* 8 (1954) 226.
13. Nowotny, H. *Z. anorg. Chem.* 254 (1947) 31.
14. Steenberg, B. *Arkiv Kemi, Mineral. Geol.* A 12 (1938) No. 26.

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