

The Structures of $\text{Ni}_6\text{Si}_2\text{B}$, Fe_2P and Some Related Phases

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It has been found that the Fe_2P (*C* 22) structure previously proposed must be revised. The true symmetry is hexagonal, rather than trigonal. The phases $\text{Ni}_6\text{Si}_2\text{B}$, Mn_2P , and Ni_2P are isotypic with Fe_2P , but Co_2P possesses a different — orthorhombic — structure. Some structurally related phases are also discussed.

In the course of a study of the system Ni-B¹ it was observed that Ni-B mixtures containing more than approximately 35 at % of B, attack silica tubes at elevated temperatures. A ternary phase of composition $\text{Ni}_6\text{Si}_2\text{B}$ is formed. The structure of the compound was determined and found to be very closely related to the Fe_2P structure (*C* 22-type) as proposed by Hendricks and Kosting², the only difference being that — while in $\text{Ni}_6\text{Si}_2\text{B}$ the Si atoms are surrounded by 9 Ni — the corresponding P I atoms in the *C* 22-type are shifted 0.43 Å in the *c* direction in order to obtain a distorted octahedral environment. This shift lowers the symmetry of the structure from hexagonal (space group $P\bar{6}2m$) to trigonal (space group $P321$). As experimental evidence confirming this lowering of the symmetry was lacking, and the structural arguments which led Hendricks and Kosting² to their structure proposal are not longer very convincing, it was considered worth while to reinvestigate the structure of Fe_2P . Indeed it was found that the *C* 22-type must be revised: Fe_2P actually is isotypic with $\text{Ni}_6\text{Si}_2\text{B}$. The same applies to Mn_2P and Ni_2P , but for Co_2P a different structure — already determined by Nowotny³ — was confirmed.

EXPERIMENTAL

† The $\text{Ni}_6\text{Si}_2\text{B}$ samples were prepared by heating mixtures of nickel powder (99.9 %), boron powder (99.7 %) and silicon powder (99.9 %) in evacuated and sealed silica tubes at 950°C. These mixtures did not attack the silica tubes appreciably, while mixtures of nickel and boron only, containing more than 35 at % boron attacked the tubes severely

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at temperatures above 900°C. The attack resulted in formation of $\text{Ni}_6\text{Si}_2\text{B}$, often in the form of needle-like crystals.

Fe_2P was prepared by dropping pellets of red phosphorus (99 %) into molten iron (97.5 %; main impurity oxygen). The iron was melted in an induction furnace under nitrogen atmosphere.

Weissenberg diagrams around the c axes of $\text{Ni}_6\text{Si}_2\text{B}$ (layer lines 0–3) and Fe_2P (layer lines 0, 3, 4) were taken with MoK radiation; in the case of Fe_2P an equatorial diagram about the a axis was also made. Intensities were estimated visually. Some very weak reflexions were estimated only in a qualitative way; these were not used in the structure refinements. As the crystals used were quite small, no absorption correction was considered necessary.

Powder photographs were taken in Guinier-type cameras, using $\text{CrK}\alpha$ (for Fe_2P , Mn_2P and Co_2P) and $\text{CuK}\alpha$ (for $\text{Ni}_6\text{Si}_2\text{B}$ and Ni_3P) radiations. The phosphides possess rather narrow homogeneity ranges, while in the case of $\text{Ni}_6\text{Si}_2\text{B}$ a limited Si-B substitution was found. The unit-cell dimensions given in this paper are believed to correspond closely to the ideal compositions indicated. The accuracy of the lattice-parameter measurements is better than 0.05 %.

DETERMINATION OF THE $\text{Ni}_6\text{Si}_2\text{B}$ STRUCTURE

The unit-cell dimensions of $\text{Ni}_6\text{Si}_2\text{B}$ were found as $a = 6.105 \text{ \AA}$; $c = 2.895 \text{ \AA}$; $c/a = 0.4742$; $U = 93.4 \text{ \AA}^3$; with one formula unit in the cell. The density is calculated to be 7.45 g.cm^{-3} .

An inspection of the Weissenberg diagrams showed that — apart from normal decline — the intensities of $(hk2)$ reflexions are the same as those of the corresponding $(hk0)$ reflexions, while the same holds for $(hk3)$ and $(hk1)$. This indicates that all atoms (except possibly B) are arranged in layers with $z = 0$ and $z = 1/2$, respectively. Therefore, a Patterson section $(xy0)$ was calculated. This section proved to be compatible with space group $P\bar{6}2m$, if 3 NiI are placed in $3(f)$, 3 NiII in $3(g)$ and 2 Si in $2(c)$. From structural arguments B was placed in $1(b)$ and, indeed, the Patterson synthesis gave support to this hypothesis.

Approximate Ni parameters were read from the Patterson map. Structure factors of the $(hk0)$ reflexions were calculated; the scattering factors of Ni were interpolated from tables given by Thomas and Umeda ⁴, those of Si from Tomiie and Stam ⁵, and B scattering factors from Ibers ⁶; the small correction for dispersion and anomalous scattering was neglected. Refinement of the Ni parameters by an algebraic method led to an R value of 5.5 % for the 23 measured $(hk0)$ reflexions, when a temperature factor with $B = 0.52 \text{ \AA}^2$ was applied. Using the same temperature and scale factors, R was calculated to be 5.1 % for the 25 observed $(hk1)$ reflexions. Therefore, no further refinement was considered worth while. Observed and calculated structure factors are compared in Table 1.

The final structure is the following:

Space group $P\bar{6}2m$ — (D_{3h}^3) ;

3 NiI in $3(f)$: $x00$; $0x0$; $\bar{x}\bar{x}0$ with $x = 0.247$

3 NiII in $3(g)$: $x0\frac{1}{2}$; $0x\frac{1}{2}$; $\bar{x}\bar{x}\frac{1}{2}$ with $x = 0.608$

2 Si in $2(c)$: $\frac{1}{2}\frac{2}{3}0$; $\frac{2}{3}\frac{1}{3}0$

1 B in $1(b)$: $00\frac{1}{2}$.

Table 1. Observed and calculated (*hk*0) and (*hkl*) structure factors for Ni₉Si₂B.

<i>hk</i>	<i>l</i> = 0			<i>l</i> = 1		
	<i>F</i> _o	<i>F</i> _c	<i>a</i> _c in°	<i>F</i> _o	<i>F</i> _c	<i>a</i> _c in°
00		201.0	0.0		16.9	0.0
10	w. *	4.3	0.0	21.6	21.4	0.0
20	w. *	2.3	0.0	61.5	56.0	180.0
30	66.4	67.6	0.0		3.0	180.0
40	31.1	26.6	0.0	43.3	44.0	0.0
50	44.1	45.9	0.0	26.1	27.1	180.0
60		1.0	180.0		0.5	0.0
70		11.1	0.0		6.3	180.0
80	35.7	35.1	0.0		0.7	0.0
90		7.8	0.0	17.1	17.0	0.0
100		7.4	0.0	16.2	19.7	180.0
11	29.2	29.1	192.1	84.6	84.5	74.3
21	63.9	68.4	114.6	31.3	28.8	152.0
31	31.7	31.3	250.8	38.0	37.6	51.4
41	21.3	20.8	340.2	31.0	33.7	8.3
51	31.7	31.3	125.7	19.4	18.9	126.4
61	23.5	26.5	186.4	35.9	39.8	93.7
71	16.3	15.7	34.7	15.3	15.1	331.8
22	29.3	28.5	104.7	23.5	21.4	283.3
32	32.9	29.5	277.8	45.4	47.1	209.3
42	37.9	39.0	142.6	23.1	25.9	262.6
52	23.9	23.1	60.1	20.2	20.8	126.7
62		12.3	132.0	15.9	15.3	198.7
72		14.1	183.8	23.7	24.9	259.2
82		11.8	36.2		13.1	211.4
92	19.2	22.3	121.0		1.8	191.0
33	37.2	36.6	275.2	14.3	14.0	244.0
43	14.0	15.6	268.5	14.0	14.9	63.3
53	21.8	23.4	5.3	14.5	13.3	178.6
63	30.7	27.7	254.8		6.8	0.0
73	16.9	15.3	265.9	18.3	20.1	210.9
44	30.5	29.0	27.8	41.4	42.8	342.3
55	24.4	21.9	31.3	19.2	20.4	148.2

* The reflexions designed by w. were discernible above the background, but it was not possible to estimate them with any accuracy.

Interatomic distances are listed in Table 2; the accuracy of the given values is better than 0.01 Å. Fig. 1 shows the environment of the B and Si atoms. Si is surrounded by 6 NiII forming a trigonal prism and by 3 NiI in a triangle, situated outside the centers of the rectangular prism faces; the 9 Ni atoms forming the described tetrakaidecahedron around Si are approximately equidistant from the central atom. The B environment is similar, but the 3 Ni in the triangle are much farther away than those forming the trigonal prism and cannot be regarded as true neighbours. Adopting r_{Ni} as 1.24 Å the plausible values of $r_{\text{Si}} = 1.12$ Å and $r_{\text{B}} = 0.84$ Å are derived.

Table 2. Interatomic distances in Ni₆Si₂B.

Si	— 3 NiI	2.34 Å	B	— 6 NiI	2.08 Å
	— 6 NiII	2.37		— 3 NiII	2.39
NiI	— 2 B	2.08	NiII	— 4 Si	2.37
	— 2 Si	2.34		— 1 B	2.39
	— 4 NiII	2.55		— 4 NiI	2.55
	— 2 NiI	2.60		— 2 NiI	2.64
	— 2 NiII	2.64		— 2 NiII	2.895
	— 2 NiI	2.895		— 4 NiII	3.26

REDETERMINATION OF THE Fe₂P STRUCTURE

For Fe₂P we found the unit-cell dimensions as $a = 5.865$ Å; $c = 3.456$ Å; $c/a = 0.5893$; $U = 103.0$ Å³; in close agreement with the values given by Hägg⁷ and Friauf⁸, less so with the values by Nowotny and Henglein⁹. With three formula units in the cell the calculated density is 6.90 g.cm⁻³, which compares favourably with the observed values of 6.83 ⁷, 6.89 ⁸ and 6.77 ¹⁰ g.cm⁻³.

In the structure Hendricks and Kosting² proposed for Fe₂P, using Hägg's⁷ experimental data, the Fe atoms occupy the same sites as the Ni atoms in Ni₆Si₂B, PII is situated in $00\frac{1}{2}$, but PI is shifted from the plane $z = 0$ to the position $\frac{1}{3} \frac{2}{3} \frac{1}{8}$, $\frac{2}{3} \frac{1}{3} \frac{7}{8}$. This shift lowers the symmetry from space group $P\bar{6}2m$ to $P321$.

A comparison of the intensities of $(hk0)$ and $(hk4)$ reflexions showed at once that Hendricks and Kosting's structure cannot be the correct one;

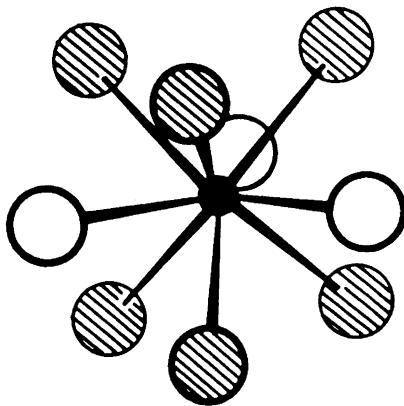


Fig. 1. The Si and B environments in Ni₆Si₂B. The nonmetal (black) is surrounded by six metal atoms (shaded) forming a trigonal prism, and by three metal atoms (white) in a triangle. The resulting coordination figure (a tetrakaidecahedron) is built up by fourteen triangles sharing all edges. The nine Ni atoms around Si are approximately equidistant from the central atom. The B environment is more distorted, as the three Ni in the triangle are much farther away from the central atom than the six Ni forming the trigonal prism.

adopting their proposed structure the intensity sequences in the zero and fourth layer lines about the *c* axis should be quite different, while actually they were identical. Furthermore, within experimental accuracy it was found that $|F(hkl)| = |F(\bar{h}kl)|$, indicating that the symmetry of Fe₂P is hexagonal and that PI lies in the plane (*xy*0).

Nevertheless, we tried to interpret the small differences between $F(\bar{h}kl)$ and $F(hkl)$ as due to a minor deviation from hexagonal symmetry (and not to experimental inaccuracy), but no selfconsistent result was possible. Therefore, space group $P\bar{6}2m$ was adopted. Structure factors for (*h*0*l*) reflexions were computed, using Fe scattering factors from Thomas and Umeda ⁴ and P scattering factors from Tomiie and Stam ⁵. The Fe parameters derived by Hendricks and Kosting were provisionally adopted, and they proved to be surprisingly accurate. Refinement by an algebraic method indicated only minor shifts, the final structure being:

Space group $P\bar{6}2m - (D_{3h}^3)$;

3 FeI in 3(*f*): $x00$; $0x0$; $\bar{x}\bar{x}0$ with $x = 0.256$

3 FeII in 3(*g*): $x0\frac{1}{2}$; $0x\frac{1}{2}$; $\bar{x}\bar{x}\frac{1}{2}$ with $x = 0.594$

2 PI in 2(*c*): $\frac{1}{3}\frac{2}{3}0$; $\frac{2}{3}\frac{1}{3}0$

1 PII in 1(*b*): $00\frac{1}{2}$

A temperature factor with $B = 0.67 \text{ \AA}^2$ was employed, giving $R = 6.1 \%$ for the 34 measured (*h*0*l*) reflexions. A comparison of observed and calculated structure factors is given in Table 3. In Table 4 interatomic distances are listed; the standard deviations are calculated to be less than 0.01 Å. The structure of Fe₂P is isotypic with that of Ni₆Si₂B and both PI and PII possess a distorted tetrakaidecahedral environment. However, the distortions are quite different in the two cases: while the three Fe atoms surrounding PI in a triangle are much closer to the central atom than the six Fe atoms forming the trigonal prism, just the opposite is true for the PII environment.

THE STRUCTURES OF SOME RELATED PHASES

Several binary phases have been described as isotypic with Fe₂P; as the isotypism generally was derived from a comparison of powder photographs, it is highly probable that the revised Fe₂P structure also applies to β-Co₂As ¹¹, Pd₂Si ^{12,13}, Pd₂Ge ¹², and Pt₂Ge ¹². This was actually proved to be the case for Mn₂P and Ni₂P. The unit-cell dimensions were found to be: for Mn₂P: $a = 6.074 \text{ \AA}$; $c = 3.454 \text{ \AA}$; $c/a = 0.5687$;

$$U = 110.4 \text{ \AA}^3; D_x = 6.36 \text{ g.cm}^{-3};$$

in agreement with values by Fylking ¹⁴, Wiechmann ¹⁵, and Årstad and Nowotny ¹⁶;

for Ni₂P: $a = 5.864 \text{ \AA}$; $c = 3.385 \text{ \AA}$; $c/a = 0.5772$;

$$U = 100.8 \text{ \AA}^3; D_x = 7.33 \text{ g.cm}^{-3};$$

Table 3. Observed and calculated ($h0l$) structure factors for Fe_2P .

$h0l$	F_o	F_c	$h0l$	F_o	F_c	$h0l$	F_o	F_c
000		+201.0	300	66.9	+65.9	800	22.6	+21.7
001	11.1	+11.6	301	v.w.	+5.1	801		+4.2
002	107.2	+119.6	302	49.9	+52.7	802	22.6	+19.4
003	w. *	+6.6	303		+3.8	12 00	14.3	+14.3
004	61.8	+67.2	304	33.7	+32.4	12 01		+1.8
005		+3.6	305		+2.1	12 02	12.2	+13.1
006	34.0	+35.0	306	18.8	+17.1	12 03		+1.5
007		+1.6	400	35.3	+32.7	12 04	11.7	+10.0
008	21.0	+17.1	401	26.7	+27.8			
100	6.4	+6.3	402	27.5	+26.8			
101	11.0	+10.9	403	20.8	+19.2			
102	v.w.	+4.0	404	19.0	+17.1			
103	v.w.	+5.3	405	w.	+11.8			
200	16.2	+14.8	406	v.w.	+9.7			
201	66.3	-66.3	500	35.8	+37.4			
202	13.0	+10.7	501	35.4	-34.6			
203	40.7	-41.9	502	30.0	+31.7			
204	v.w.	+6.2	503	27.3	-25.6			
205	22.8	-23.4	504	22.0	+21.1			
206		+3.3	505	17.0	-15.4			
207	v.w.	-11.7	700	25.2	+24.7			
208		+1.7	701		-11.3			
209	v.w.	-5.6	702	24.3	+21.8			

* The reflexions designed by w. (weak) or v.w. (very weak) were observable on the diagrams, but it was not possible to estimate them with any accuracy.

which differs somewhat from Nowotny and Henglein's¹⁷ values. There are reasons to believe that the phase " Pd_3B_2 ", which Buddery and Welch¹³ prepared by heating Pd and B in silica tubes and to which a Fe_2P structure is ascribed, actually is the Pd analogue of $\text{Ni}_6\text{Si}_2\text{B}$. Indeed, in view of the structural non-equivalence of PI and PII in Fe_2P , it may be expected that several ternary phases containing two kinds of non-metals, crystallize in isotypic structures. FeI and FeII are also non-equivalent in Fe_2P , but — as far as we are aware of — no isostructural ternary phase containing two different transition metals, has yet been described. However, a superstructure of the Fe_2P type results, if in the structure proposed by Perlitz and Westgren¹⁸ for $\text{Al}_8\text{FeMg}_3\text{Si}_6$ the Si positions and part of the (Al,Fe) positions are interchanged; such a change would be compatible with the published experimental data.

Table 4. Interatomic distances in Fe_2P .

PI	— 3 FeI	2.22 Å	PII	— 6 FeI	2.29 Å
	— 6 FeII	2.48		— 3 FeII	2.38
FeI	— 2 PI	2.22	FeII	— 1 PII	2.38
	— 2 PII	2.29		— 4 PI	2.48
	— 2 FeI	2.60		— 2 FeI	2.63
	— 2 FeII	2.63		— 4 FeI	2.71
	— 4 FeII	2.71		— 4 FeII	3.08

In agreement with Nowotny³ we found for Co₂P an orthorhombic unit-cell, but the lattice dimensions observed by us are much smaller than those given by him. For the composition Co₂P we determined: $a = 6.608 \text{ \AA}$; $b = 5.644 \text{ \AA}$; $c = 3.512 \text{ \AA}$; $U = 131.0 \text{ \AA}^3$; $D_x = 7.55 \text{ g.cm}^{-3}$. With increasing P content the unit-cell contracts in all directions, contrary to Nowotny's³ observations.* Co₂P is isotypic with Co₂Si¹⁹ — a limited mutual solubility exists — with δ -Ni₂Si²⁰, Rh₂Ge²¹, Ru₂Si²³, Rh₂Si²³ (the alleged phase Rh₂B²² probably actually was Rh₂Si too) and several Pd compounds²⁶. The P environment is similar to that in Fe₂P, but the packing is different. This structure type is a distortion of the Ni₂In type, but — as was already pointed out by Nowotny³ — the Co₂P structure can also be regarded as an anti-PbCl₂-type.

It is noteworthy that both the revised and the old — incorrect — Fe₂P structures also have their counterparts in inorganic-salt structures: β_1 -K₂ThF₆ and β_1 -K₂UF₆²⁴ are formally isotypic with Ni₆Si₂B and Fe₂P, while SrCl₂·6H₂O²⁵, β_2 -Na₂ThF₆²⁴ and isotypes possess structures which are the anti-types to Hendricks and Kosting's² proposal for the C 22 structure.

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* *Note added in proof:* Professor H. Nowotny kindly informs us that a rechecking of his earlier investigations confirms our results.

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