

XXXV. The Crystal Structure of Fe_2P , Fe_2N , Fe_3N and FeB .

By

Sterling B. Hendricks and Peter R. Kesting in Washington.

(With 13 figures.)

The derived crystal structure of cementite suggests that many compounds of metals with non-metals such as B , C , N , Si etc., might have coordination type structures. There are, moreover, indications that such structures probably have characteristics different from those of ionic coordination compounds. It was necessary to investigate more compounds of this type before these differences could be formulated clearly.

Crystal structure determinations are given below for Fe_3N , Fe_2N , Fe_2P and FeB . In these structures it is possible to determine rigorously the positions of the iron atoms. The atoms of low atomic numbers are located by the symmetry requirements of the structures and by geometrical coordination considerations.

The Nitrides of Iron.

Experimental Data.

Recent commercial processes for the surface hardening of iron by the action of ammonia on the hot metal have led to enhanced interest in the iron nitrogen system. The results obtained from chemical analyses and from x-ray powder photographs suggest that the compounds Fe_4N , Fe_3N and Fe_2N and a series of solid solutions between Fe_3N and Fe_2N are the possible solid phases in the system. The crystal structure of Fe_4N was first determined by R. Brill¹⁾ and later by G. Hägg²⁾ and by A. Osawa and S. Iwaizumi³⁾. The results of these investigators indicate that Fe_4N is cubic and that the unit of structure containing 4 Fe_4N has $a_0 = 3.79 \text{ \AA}$. The iron atoms are at $0\ 0\ 0$; $\frac{1}{2}\ \frac{1}{2}\ 0$; $\frac{1}{2}\ 0\ \frac{1}{2}$; $0\ \frac{1}{2}\ \frac{1}{2}$ and the nitrogen atom is at $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$.

Investigations carried out by Hägg²⁾ and by Osawa and Iwaizumi³⁾ on Fe_3N and Fe_2N indicate that the iron atoms have approximately a

1) R. Brill, Z. Krist. **68**, 379. 1928. 2) G. Hägg, Nova Acta Soc. Sci. Upsaliensis **4**, 7. 1929. 3) A. Osawa and S. Iwaizumi, Z. Krist. **69**, 26. 1928.

hexagonal close-packed arrangement in these compounds. The dimensions of the units of structure containing $2Fe$ are (Hägg):

ca. Fe_3N	$a = 2.695 \text{ \AA}$	$c = 4.362 \text{ \AA}$	$c/a = 1.619 \text{ \AA}$
Fe_2N	$a = 2.767 \text{ \AA}$	$c = 4.417 \text{ \AA}$	$c/a = 1.596 \text{ \AA}$

The data obtained by Hägg from a powder photograph of a homogeneous nitride of iron containing ca. 8% nitrogen is reprinted here as Table I. He obtained similar data, with slightly different values of the interplanar spacings, from a sample containing ca. 11% nitrogen. The intensities of all lines, save the four indicated by question marks, can

Table 1.
Powder Photographic Data for Fe_3N , FeK Radiation. (Hägg.)

Plane	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	I	line
?	0.106		w.	
110	0.140	0.1440	w.	β
002	0.1605	0.1620	w.	β
?	0.1635		w.	
110	0.1705	0.1745	st.	α
111	0.180	0.1815	m.	β
002	0.1955	0.1965	st.	α
111	0.2195	0.2207	st.	α
?	0.293		w.	
112	0.303	0.3030	w.	β
112	0.368	0.3684	st.	α
300	0.423	0.4230	w.	β
103	0.5055	0.5055	w.	β
300	0.516	0.5146	st.	α
302	0.585	0.5850	w.	β
221	0.6055	0.6045	w.	β
113	0.6135	0.6129	st.	α_1
113	0.6155	0.6155	st.	α_2
?	0.6596		v. w.	
220	0.6855	0.6854	w.	α_1
220	0.687	0.6877	w.	α_2
302	0.710	0.7103	st.	α_1
302	0.714	0.7129	st.	α_2
221	0.7345	0.7345	st.	α_1
221	0.737	0.7370	st.	α_2
004	0.785	0.7850	w.	α_1
004	0.7885	0.7885	w.	α_2
222	0.881	0.8816	m.	α^1
222	0.8845	0.8848	m.	α_2
114	0.956	0.9563	w.	α_1
114	0.961	0.9604	w.	α_2

be explained by an approximately hexagonal close-packed arrangement of iron atoms ($\frac{1}{3} \frac{2}{3} 0$, $\frac{2}{3} \frac{1}{3} \frac{1}{2}$). Only the first of the extra lines of Table I was reproducible. Photographs from many preparations from the system $Fe-NH_3-H_2$, that is being investigated in this laboratory, show only this first line; it is easily discernible. A derived structure of Fe_3N and of Fe_2N should account for the presence of this line. The other extra lines reported might be due to impurities in the sample or in the target of the x-ray tube.

Structure Determination for Fe_3N .

The unit of structure must contain an integral number of Fe_3N and in it the iron atoms must approximate a hexagonal close-packed arrangement. If one assumes that Fe_3N is truly hexagonal then the two smallest possible units of structure have:

$$\begin{array}{ll} a = 2.695; & c = 3 \times 4.362 \quad 2Fe_3N \\ a = \sqrt{3} \times 2.695; & c = 4.362 \quad 2Fe_3N \end{array}$$

This hexagonal close-packed arrangement can be considered as an array of octahedra defined by iron atoms at the corners that are joined by the sharing of faces, corners, or edges, or combination of these elements. If it is assumed that all iron atoms are approximately equidistant from the same number of nitrogen atoms of closest approach and that each octahedron of iron atoms contains one nitrogen atom at the center, then each iron atom must be shared by two octahedra. If the octahedra share faces or edges the resulting array consists of isolated groups of octahedra. It would thus seem that each octahedron shares each of its corners with one other octahedron. This could not be true for a unit of structure having $a = 2.695$ and $c = 3 \times 4.362$. The other unit listed above gives a satisfactory structure. The atomic positions are:

$$\begin{array}{l} N \text{ at } 0\ 0\ 0; \frac{1}{3} \frac{2}{3} \frac{1}{2} \\ Fe \text{ at } 0\ \frac{1}{3} \frac{1}{4}; 0\ \frac{2}{3} \frac{3}{4}; \frac{1}{3} 0\ \frac{1}{4}; \frac{2}{3} 0\ \frac{3}{4}; \frac{1}{3} \frac{1}{3} \frac{3}{4}; \frac{2}{3} \frac{2}{3} \frac{1}{4} \end{array}$$

The structure can be derived from space group D_6^h .

The following types of absences of reflections are required by this structure:

Nitrogen atoms: (hkl) (Hexagonal indices are written in this manner, throughout) in odd orders when $h-k=3n$ and l is odd.

Iron atoms: (hkl) in all save the 3rd, 6th, etc., orders when $h-k \neq 3n$. $(h, 3n \cdot l)$ in all save the 6th, 12th etc. orders when l is odd.

The observed intensities, calculated structure factors, and observed and calculated interplanar spacings for all reflections due to nitrogen atoms alone are shown for planes having spacings greater than that of (112) in Table 2. The calculations are in very good agreement with the limited observations. This experimental data was not used in the derivation of the structure.

Table 2.
Data for some reflections from Fe_3N that are due to nitrogen atoms alone.

Plane	Interplaner Spacing		S/σ_N^2 ¹⁾	Intensity
	Observed	Calculated		
100		4.04	4	a
104	2.69	2.96	3	w
200		2.02	4	a
102		4.92	4	a
204		4.83	3	v. w. or a.

1) S = structure factor σN = Relative scattering power of nitrogen

A representation of the unit of structure containing $2Fe_3N$ is shown as Figure 4. The projection of the structure on (001) is shown in Figure 2. The spatial relationships of the octahedra are shown in Figure 3. Six of the edges of an octahedron are ca. 2.695 Å in length, the other six ca. 2.684 Å; it is not possible for these distances to be equal. Any marked variation in these values would give an appreciable calculated structure factor to planes that are observed to be absent. A nitrogen atom at the center of an octahedron is about 4.90 Å from six iron atoms at the corners. This distance is slightly greater than the $Fe-C$ distances, ca. 4.82, 4.86, and 4.89 Å in cementite.

The Structure Determination of Fe_2N .

In the case of Fe_2N , the iron atoms of which also approximate a hexagonal close-packed arrangement, the array of octahedra with iron atoms at the corners must share elements other than corners. Fe_2N forms a complete series of solid solutions with Fe_3N . This probably necessitates the addition of extra nitrogen atoms to the structure of Fe_3N in such a manner as to have each iron atom equidistant from three nitrogen atoms when the composition is that of Fe_2N . If the additional nitrogen atoms are in octahedral spaces such as (a, b, c, f, d, e) of Fig. 3, then there are two types of octahedra in the structure: one of these types shares two faces and six corners with other octahedra;

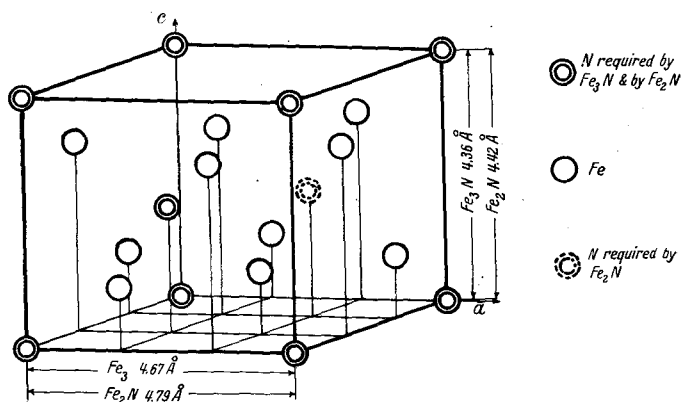


Fig. 1. The unit of structure for Fe_3N and for Fe_2N .

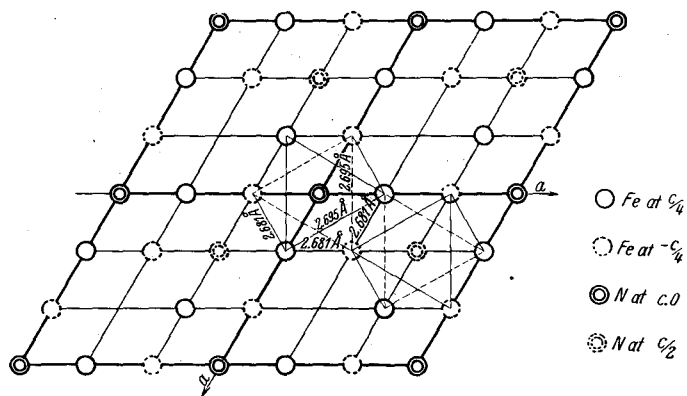


Fig. 2. A projection of the structure of Fe_3N on (001).

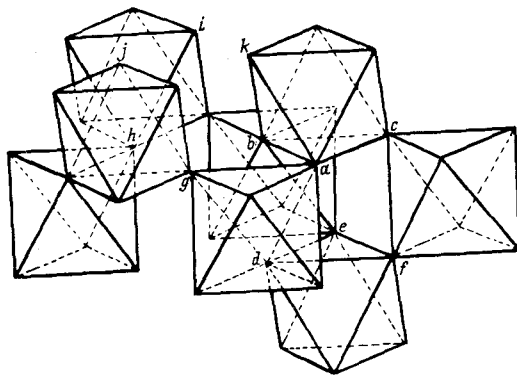


Fig. 3. Spatial relationships of the octahedra representing the crystal structure of Fe_3N .

the other, three non-adjacent edges and six corners. If the additional nitrogen atoms are in octahedral spaces such as (i, j, k, b, g, h) of Fig. 3, then one of the two resulting types of octahedra shares three non-adjacent edges and six corners with other octahedra; the other kind shares each corner with three octahedra. It is not possible to decide between these two structures on the basis of the present x-ray data. It would seem, from the sequel, that the structure in which the octahedra share corners and edges is the more probable one. The atomic positions required by this structure are:

$$N \text{ at } 0\ 0\ 0; \frac{1}{3}\ \frac{2}{3}\ 0; \frac{2}{3}\ \frac{1}{3}\ \frac{1}{2}$$

$$Fe \text{ at } 0\ \frac{1}{3}\ \frac{1}{4}; 0\ \frac{2}{3}\ \frac{3}{4}; \frac{1}{3}\ 0\ \frac{1}{4}; \frac{2}{3}\ 0\ \frac{3}{4}; \frac{1}{3}\ \frac{1}{3}\ \frac{3}{4}; \frac{2}{3}\ \frac{2}{3}\ \frac{1}{4} \text{ (as for } Fe_3N)$$

The structure can be derived from space group D_{3d}^1 .

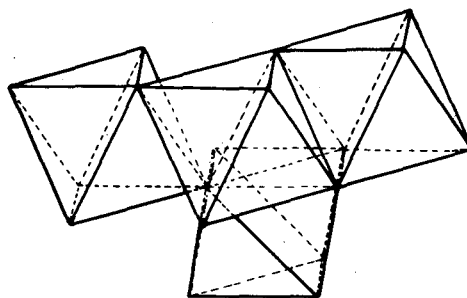


Fig. 4. Coordination structure of Fe_2N .

Table 3.

Data for Some Reflections of Fe_2N that are due to nitrogen atoms alone.

Plane	Interplaner Spacing		S/σ_N^2	Intensity
	Observed	Calculated		
400		4.45	0	a
404	3.03	3.03	4	v. w.
200		2.07	0	a
402		4.95	0	a
204		4.87	4	a

The agreement between observations and calculations for this structure is shown in Table 3. The derived structure accounts for the presence of reflection from (404) and the absence of other reflections due to nitrogen atoms alone. The unit of structure containing $3Fe_2N$ is shown as Fig. 4. The coordination characteristics of the structure can be seen by a study of Fig. 3 and 4. The dimensions of six of the edges of an

octahedron with iron atoms at the corners are ca. 2.77 Å; the other six edges are ca. 2.72 Å in length. Here, as for Fe_3N , marked changes in these distances would probably require the presence of reflections from planes that are observed to be absent.

Hägg¹⁾ has shown that a nitride containing as much as 11.23% nitrogen (calculated for $Fe_2N = 11.14\%$ nitrogen) can be formed by passing pure ammonia over iron. The additional .1% nitrogen causes a rather prominent change in the powder diffraction pattern. The reflections from planes to which iron atoms contribute are observed to be doubled. The faint reflection from (101) persists.

Addition of nitrogen to Fe_2N can take place only by the formation of coordinated octahedra that share faces with the array of octahedra representing the structure of Fe_2N . Hägg's results indicate that this sharing of faces leads to a distortion of the structure and that the extension of the series of solid solutions of Fe_3N-Fe_2N to some lower nitride of iron is limited by this distortion.

The Crystal Structure of FeB .

Experimental Data.

T. Bjurström and H. Arnfelt²⁾, referred to below by (B.-A.), have investigated the system $Fe-B$ by means of powder and single crystal photographs. They identified the compounds Fe_2B and FeB . Laue, rotating crystal and powder photographs were made from FeB . The rotating crystal data are republished here, as Table 4, for the sake of ready reference. The powder photographic data published by (B.-A.) are given in table 5.

Table 4.
Rotating crystal data for FeB (010) axis of rotation
(Bjurström and Arnfelt). Iron K -radiation.

»Schichtlinie« 0		»Schichtlinie« 1		»Schichtlinie« 2	
Int.	hkl	Int.	hkl	Int.	hkl
st	101	w	110	st	120
m	002	st	111	st	021
st	301	st	210	st	121
st	400	st	211	w	022
		v. w.	112	m	122
		w	310	st	320
		st	311	st	321
		st	212		

1) G. Hägg, Nova Acta Soc. Upsaliensis 4, 7. 1929. 2) T. Bjurström and H. Arnfelt, Z. physikal. Ch. (B) 4, 469. 1929.

Table 5.
Observed and Calculated Intensities of Reflection for FeB .
The Powder Photographic Data is that of Bjurström and Arnfeldt.
 $Fe K\alpha_1$ -Radiation.

Plane	$\sin^2\theta$ obs.	$\sin^2\theta$ calc.	Observed and Calculated Intensities ¹⁾				
			st	m	w	v. w.	a
440	0.088	0.0877			390		
020	0.124	0.1236	710				
404	0.1645	0.1643	4400				
420	0.1805	0.1804	730				
444	0.1955	0.1954	4400				
200		0.2272					44
024	0.234	0.2314	940				
240	0.259	0.2581	4100				
424	0.286	0.2879		680			
430	0.333	0.3349	440				
220		0.3508					6
244	0.3635	0.3656	330				
002	0.4295	0.4300		370			
434	0.444	0.4424				39	
224		0.4583					44
040		0.4944					42
230		0.5053					44
442		0.5177					98
340		0.5424					39
440	0.5505	0.5512		324			
022	0.5535	0.5536			250		
044	0.604	0.6049		568			
422 } 234 }	0.6115	{ 0.6104 } { 0.6128 }	{ 390 } { 4400 }				
304	0.649	0.6487			180		
320	0.634	0.6348			440		
344	0.649	0.6496		630			
202		0.6572					40
242	0.688	0.6881	960				
240		0.7216					4
324	0.7445	0.7423			420		
432	0.765	0.7649		560			
222		0.7808					40
330	0.7885	0.7893			470		
244	0.829	0.8294			26		
334		0.8968					94
400	0.909	0.9088			540		
232	0.937	0.9353		470			

$$1) I = C \cdot \frac{I + \cos^2 2\theta}{\sin 2\theta} \cdot J \cdot F \cdot \bar{F}$$

I. Unit of Structure.

a) Symmetry, orthorhombic. Laue and rotating crystal photographs.

(B.-A.)

b) Dimensions $a = 4.053$ $b = 5.495$ $c = 2.946$ $a:b:c = 0.738:1:0.536$

The axes of (B.-A.) are changed to correspond to the space group axes of Niggli.

c) Volume. $V = a \cdot b \cdot c = 65.6 \times 10^{-24} \text{ cm}^3$, $d = \text{ca. } 6.3$ (B.-A.)Molecular volume = 10.6 cm^3 .No. of FeB in unit of Structure = 3.75 .

II. Space Group.

Observed types of absences $(h0l)$ with $(h+l)$ odd $(0kl)$ with k oddSpace group V_h^{16} , C_{2V}^9 (C_{2V}^9 is not further considered).

III. Atomic Arrangement.

A center of symmetry is selected as the origin of coordinates¹⁾. The possible atomic positions for V_h^{16} are:

With two degrees of freedom, on the reflection planes;

a) $uv\frac{1}{4}, \bar{u}\bar{v}\frac{3}{4}, \bar{u} + \frac{1}{2}, v + \frac{1}{2}, \frac{1}{4}; u + \frac{1}{2}, \bar{v} + \frac{1}{2}, \frac{3}{4}$

without degrees of freedom, at the symmetry centers;

b) $000; 00\frac{1}{2}; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}\frac{1}{2}\frac{1}{2}$ c) $\frac{1}{2}00; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}0; 0\frac{1}{2}\frac{1}{2}$.

The observed intensities of reflection (200) a, (400) st. cannot be explained if the iron atoms are at (b) or (c). The derived structure is based on arrangement (a).

Evaluation of the Parameters.

The structure factors for (hkl) (indices corresponding to the space group axes will be used throughout) are similar to the ones previously listed for cementite. The limits of variation of u_{Fe} and v_{Fe} are 0.0 and 0.25; possible effects of the boron atoms are neglected.

a) The observed intensities of reflections (See Tables 4 and 5):

 $(400)s > (200)a$ limit u_{Fe} to 0.14—0.14 $(304)s \geq (404)s$

1) P. Niggli, Geometrische Kristallographie des Diskontinuums, S. 204. Leipzig 1919.

The observed presence of (244) prevents u_{Fe} from being equal to 0.125. u_{Fe} is probably near 0.115 or 0.135. A selection is not made between these two possibilities.

b) The observed intensities, (044)m, (040)a, (022)a, (111)st, (110)w and (130)s, limit v_{Fe} to the region 0.16—0.20. The presence of (131) prevents v being 0.167 and the absence of (144) requires $v > 0.175$.

The derived parameter values are

$$\begin{aligned} u &= 0.125 \pm 0.015 \quad \text{but} \neq 0.125 \\ v &= 0.180 \pm 0.015 \end{aligned}$$

The calculated relative values of the intensities listed in Table 5 are concomitant with the observed powder photographic data of (B.-A.). It is difficult to place a closer restriction on the parameter values; however, it might be remarked that calculations for $u = 0.125$ and $v = 0.165$ are quite discordant with the observed intensities.

Reflections were listed by (B.-A.) from (204) and (044). Both of these reflections are required to be absent by space group V_h^{16} . Apparently (204), $\sin^2\theta = .3347$, was confused with (130), $\sin^2\theta = .3349$, that is a strong reflection; (044) that is very weak, is not explained by the derived structure, it might arise from an impurity, especially so since it is not reported as present on a rotating crystal photograph on which it should have appeared.

Geometrical Considerations. The Positions of the Boron Atoms.

The unit of structure containing $4FeB$ is shown as Fig. 5. Inspection of this structure indicates that each iron atom is approximately equidistant from six iron atoms that approach it most closely, and is separated by a slightly greater distance from four other iron atoms. This structure can be considered as an array of tetrahedra with iron atoms at the corners that are joined by the sharing of corners and edges. Such an array is shown as Fig. 6, and as a projection on (001) in Fig. 7. It is to be noted that each iron atom is shared by four tetrahedra and that each tetrahedron shares two edges and four corners with other tetrahedra.

It is improbable that the boron atoms affect the intensities of reflections by a detectable amount. If it is assumed that they too conform to the symmetry requirements of V_h^{16} then they must either be at centers of symmetry or on the reflection planes. If the boron atoms are at the symmetry centers they would be separated by a distance equal to $C/2$; the resulting atomic arrangement would be a most unusual one. However, if they are in the reflection planes it is possible for them to be at or near the centers of the tetrahedra of iron atoms. If $u_{Fe} = .115$, $v_{Fe} = .175$,

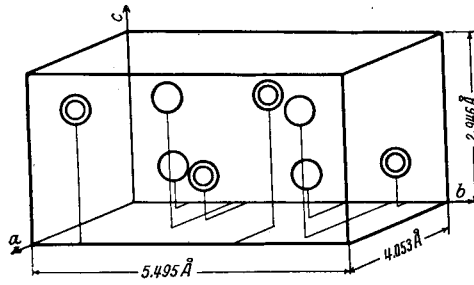


Fig. 5.

Fig. 5. The unit of structure of FeB . The annular circles represent Boron atoms the open ones Iron atoms.

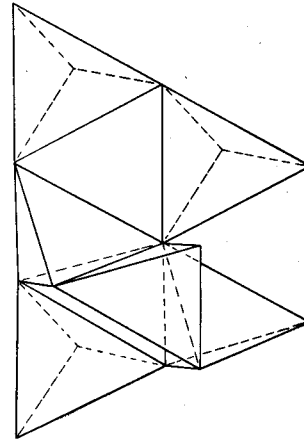


Fig. 6.

Fig. 6. An array of tetrahedra representing the structure of FeB .

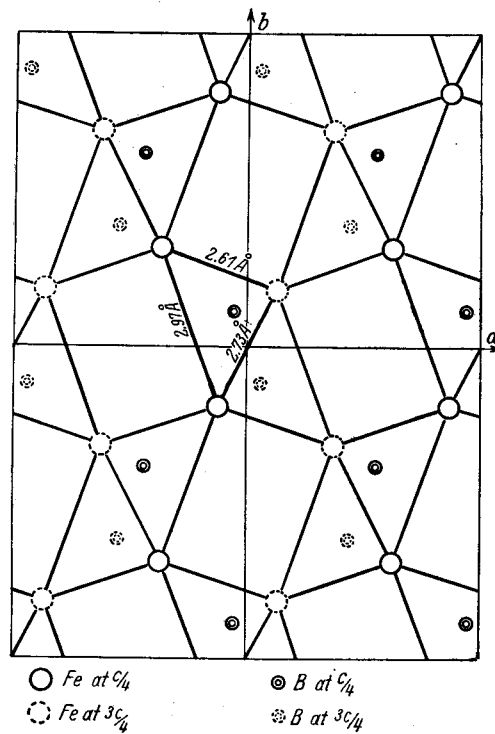


Fig. 7. A projection of the structure of FeB on (001).

then values $u_B = \text{ca. } .0.70$ and $v_B = \text{ca. } -.13$ would correspond to boron atoms at the centers of coordinated tetrahedra. In this case four of the edges ($Fe-Fe$ distance) of a tetrahedron would be ca. 2.64 \AA in length, the other two edges ca. 2.95 \AA . The $Fe-B$ distance would be ca. 1.68 \AA . If $u_{Fe} = .135$, $v_{Fe} = .180$, the corresponding values of the boron parameters, requiring the boron atoms to be in the centers of the tetrahedra would be $u_B = \text{ca. } 0.68$, $v_B = \text{ca. } -.12$. The dimensions of the edges of a tetrahedron of iron atoms in this case would be $2.61, 2.61, 2.73, 2.73, 2.97, 2.95 \text{ \AA}$ and the $Fe-B$ distances ca. 1.70 \AA .

It thus seems that to within the determined limits of the parameter values a tetrahedron of iron atoms can have four edges approximately equal in length corresponding to an $Fe-Fe$ distance of ca. 2.64 \AA and two longer edges giving an $Fe-Fe$ distance of ca. 2.95 \AA . If the boron atoms are at the centers of the coordinated polyhedra the $Fe-B$ distances are ca. 1.70 \AA , a value somewhat smaller than the $Fe-N$ distances in the nitrides of iron and the $Fe-C$ distances in cementite.

The Crystal Structure of Fe_2P .

G. Hägg¹) has investigated the system $Fe-P$ by means of single crystal and powder photographs. He identified the compounds Fe_3P , Fe_2P and a third phase that might have been the compound FeP . The determination of the crystal structure of Fe_2P is given below. It was made on the basis of Hägg's data that is replubished here as Tables 6, 7 and 8.

I. Unit of Structure.

a) Symmetry, hexagonal. Laue and rotating crystal photographs (Hägg). A Laue photograph made with the x-ray beam normal to (001) shows a six-fold axis and six planes of symmetry (Hägg). Departure from apparent holohedral symmetry might be due to phosphorus atoms alone.

b) Dimensions $a = 5.852 \text{ \AA}$ (Hägg)
 $c = 3.453 \text{ \AA}$
 $c : a = 1 : 0.5900$.

c) Volume $v = a^2 \cdot c \cdot .866 = 10.25 \times 10^{-24} \text{ cm}^3$. $d = 6.83$.

Molecular volume = 20.89 cm^3 .

No. of Fe_2P in the unit of structure = 2.97.

1) G. Hägg, Nova Acta Soc. Sci. Upsaliensis 7, 1929.

Atomic Arrangement and Space Group.

The Laue photographs from Fc_2P that have been obtained and published by Hägg indicate that at least the iron atoms must have an arrangement isomorphous with point group D_3^h , C_6^v , D_6 , or D_6^h . The observed absence of reflections from (004) and (003) cannot be explained if all the iron atoms are in one plane parallel to (004). The determined value, $c = 3.453 \text{ \AA}$, makes it improbable that two iron atoms are on the same axis parallel to the c axis.

In the first treatment we shall assume that the arrangement of the six iron atoms in the unit of structure might be derived from a space group that does not necessarily give possible positions for the phosphorus atoms. There are twelve sets of equivalent positions that satisfy the conditions given in the preceding paragraph. They are:

1. D_{6h}^4 , D_6^6 , C_{6v}^4 $u \bar{u} 0$; $2\bar{u}$, \bar{u} , 0 ; u , $2u$, 0 ; $\bar{u} u \frac{1}{2}$; $2u$, u , $\frac{1}{2}$; \bar{u} , $2\bar{u}$, $\frac{1}{2}$.
2. D_6^6 , C_{6v}^3 $u u 0$; $0 \bar{u} 0$; $\bar{u} 0 0$; $\bar{u} \bar{u} \frac{1}{2}$; $0 u \frac{1}{2}$; $u 0 \frac{1}{2}$.
3. D_{3h}^4 $u v 0$; $v - u$, \bar{u} , 0 ; \bar{v} , $u - v$, 0 ; $v u \frac{1}{2}$; \bar{u} , $v - u$, $\frac{1}{2}$;
 $u - v$, \bar{v} , $\frac{1}{2}$.
4. D_{3h}^2 $u v 0$; $v - u$, \bar{u} , 0 ; \bar{v} , $u - v$, 0 ; u , $u - v$, $\frac{1}{2}$, $\bar{v} \bar{u} \frac{1}{2}$;
 $v - u$, v , $\frac{1}{2}$.
5. 4 sets of positions requiring iron atoms to be at $c0$, $c/3$, $2c/3$.
(D_6^5 , D_6^5 , D_6^4 , D_6^4) and 4 sets requiring iron atoms to be at $c0$,
 $c/6$, $c/3$, $c/2$, $2c/3$, $5c/6$ (D_6^3 , D_6^3 , D_6^2 , D_6^2).

The possible combinations of non-equivalent positions for the iron atoms are:

6. D_{3h}^3 a) $u u 0$; $0 \bar{u} 0$; $\bar{u} 0 0$,
b) $v v \frac{1}{2}$; $0 \bar{v} \frac{1}{2}$; $\bar{v} 0 \frac{1}{2}$.
7. D_{3h}^1 a) $u \bar{u} 0$; $2\bar{u}$, \bar{u} , 0 ; u , $2u$, 0 ,
b) $u \bar{u} \frac{1}{2}$; $2\bar{u}$, \bar{u} , $\frac{1}{2}$; u , $2u$, $\frac{1}{2}$.

The observed intensities of reflections, (002) s., (003) a cannot be explained by 5.; (111) s. by 1.; (201) s. by 2.; (111) s. by 3.; (201) s. by 4. The iron atoms are therefore probably not equivalent.

Arrangement 7. cannot explain the observed intensities of reflection (110) v.w.; (220) w.; (330) st. if the iron atoms are assumed to be separated by a distance greater than 2.0 \AA . Arrangement 6. gives a structure in satisfactory agreement with the experimental data.

Parameter Determinations.

The intensities of reflections can be expressed by the formula:

$$\rho = \frac{N^2 e^4 \lambda^3}{4 \mu m^2 c^4} \cdot J \cdot \frac{1 + \cos^2 2\theta}{\sin 2\theta} \cdot F \bar{F} \quad (1)$$

