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

By

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(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. Brill[1]) and later by G. Hägg[2]) and by A. Osawa and S. Iwaizumi[3]). The results of these investigators indicate that Fe_4N is cubic and that the unit of structure containing 1 Fe_4N has $a_0 = 3.79$ Å. 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 Hägg[2]) and by Osawa and Iwaizumi[3]) on Fe_3N and Fe_2N indicate that the iron atoms have approximately a

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[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 $a = 2.695$ Å $c = 4.362$ Å $c/a = 1.619$ Å
Fe_2N $a = 2.767$ Å $c = 4.417$ Å $c/a = 1.596$ Å

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	0.1410	w.	β
002	0.1605	0.1620	w.	β
?	0.1635		w.	
110	0.1705	0.1715	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	0.3681	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:

$a = 2.695$; $c = 3 \times 4.362$ $2\,Fe_3N$
$a = \sqrt{3} \times 2.695$; $c = 4.362$ $2\,Fe_3N$

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:

N at $0\,0\,0$; $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{2}$
Fe at $0\,\frac{1}{3}\,\frac{1}{4}$; $0\,\frac{2}{3}\,\frac{3}{4}$; $\frac{1}{3}\,0\,\frac{1}{4}$; $\frac{2}{3}\,0\,\frac{3}{4}$; $\frac{1}{3}\,\frac{1}{3}\,\frac{3}{4}$; $\frac{2}{3}\,\frac{2}{3}\,\frac{1}{4}$

The structure can be derived from space group D_6^6.

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	1	a
101	2.69	2.96	3	w
200		2.02	1	a
102		1.92	1	a
201		1.83	3	v. w. or a.

[1] S = structure factor σN = Relative scattering power of nitrogen

A representation of the unit of structure containing $2 Fe_3N$ is shown as Figure 1. The projection of the structure on (0 0 1) 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. 2.681 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 1.90 Å from six iron atoms at the corners. This distance is slightly greater than the $Fe—C$ distances, ca. 1.82, 1.86, and 1.89 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;

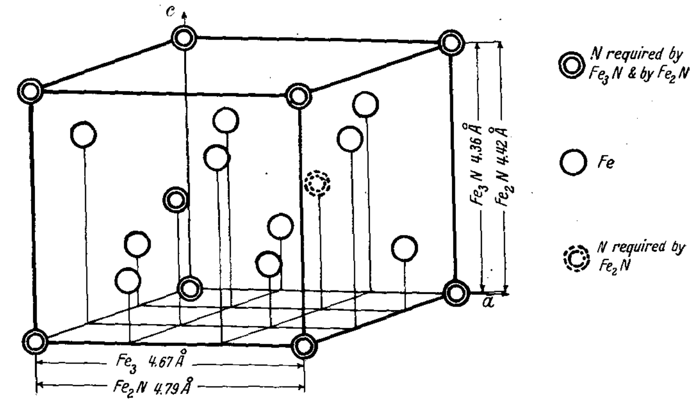

Fig. 1. The unit of structure for Fe_3N and for Fe_2N.

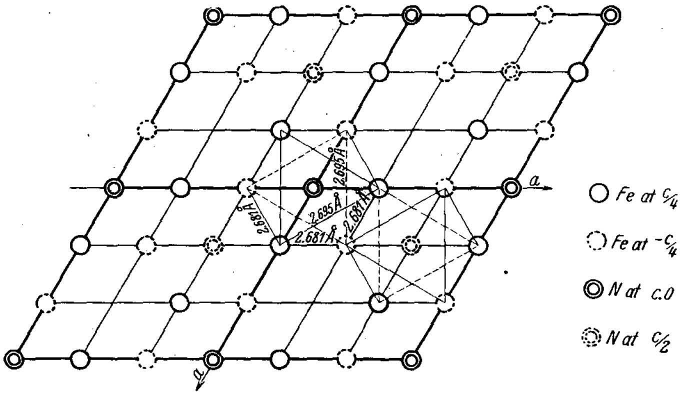

Fig. 2. A projection of the structure of Fe_3N on (001).

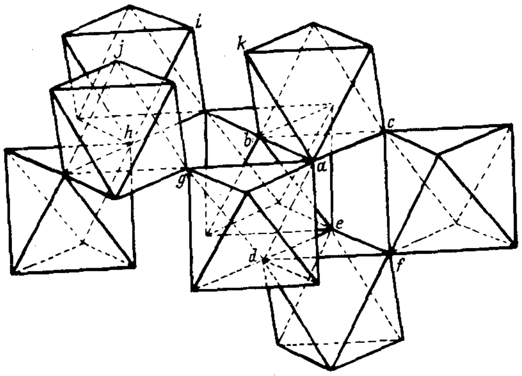

Fig. 3. Spatial relationships of the octahedra representing the crystal structure of Fe_3N.

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

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

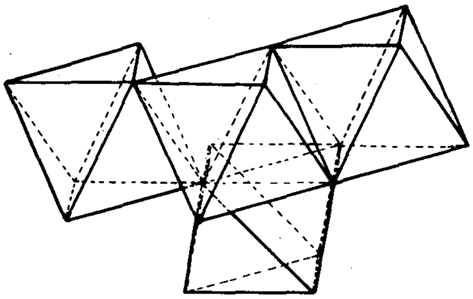

Fig. 4. Coordination structure of Fe_2N.

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		
100		4.15	0	a
101	3.03	3.03	4	v. w.
200		2.07	0	a
102		1.95	0	a
201		1.87	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 (101) and the absence of other reflections due to nitrogen atoms alone. The unit of structure containing $3\,Fe_2N$ is shown as Fig. 1. 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.

Hägg[1]) 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. Arnfelt[2]), 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		

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[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
110	0.088	0.0877			390		
020	0.124	0.1236	710				
101	0.1645	0.1643	1400				
120	0.1805	0.1804	730				
111	0.1955	0.1951	1400				
200		0.2272					14
021	0.231	0.2311	940				
210	0.259	0.2581	1100				
121	0.286	0.2879		680			
130	0.333	0.3349	410				
220		0.3508					6
211	0.3635	0.3656	330				
002	0.4295	0.4300		370			
131	0.441	0.4424				39	
221		0.4583					14
040		0.4944					12
230		0.5053					41
112		0.5177					98
310		0.5421					39
140	0.5505	0.5512		324			
022	0.5535	0.5536			250		
041	0.601	0.6019		568			
122 231	0.6115	0.6104 0.6128	390 1100				
301	0.619	0.6187			180		
320	0.634	0.6348			110		
311	0.649	0.6496		650			
202		0.6572					10
212	0.688	0.6881	960				
240		0.7216					1
321	0.7415	0.7423			120		
132	0.765	0.7649		560			
222		0.7808					10
330	0.7885	0.7893			170		
241	0.829	0.8291			26		
331		0.8968					91
400	0.909	0.9088			510		
232	0.937	0.9353		170			

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[1] $I = C \cdot \frac{I + \cos^2 2\theta}{\sin 2\theta} \cdot J \cdot F\overline{F}$.

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. $V = a \cdot b \cdot c = 65.6 \times 10^{-24}$ cm³, $d =$ ca. 6.3 (B.-A.)

Molecular volume $= 10.6$ cm³.

No. of FeB in unit of Structure $= 3.75$.

II. Space Group.

Observed types of absences $(h0l)$ with $(h+l)$ odd
$(0kl)$ with k odd

Space 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 coordinates[1]). The possible atomic positions for V_h^{16} are:

With two degrees of freedom, on the reflection planes;

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

without degrees of freedom, at the symmetry centers;

b) $0\,0\,0;\ 0\,0\,\frac{1}{2};\ \frac{1}{2}\,\frac{1}{2}\,0;\ \frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$

c) $\frac{1}{2}\,0\,0;\ \frac{1}{2}\,0\,\frac{1}{2};\ 0\,\frac{1}{2}\,0;\ 0\,\frac{1}{2}\,\frac{1}{2}$.

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):

$(400)\text{s} > (200)\text{a}$ limit u_{Fe} to 0.11—0.14
$(301)\text{s} \gg (101)\text{s}$

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1) P. Niggli, Geometrische Kristallographie des Diskontinuums, S. 201. Leipzig 1919.

The observed presence of (241) 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, (041)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 (141) requires $v > 0.175$.

The derived parameter values are

$$u = 0.125 \pm 0.015 \quad \text{but} \neq 0.125$$
$$v = 0.180 \pm 0.015$$

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 (201) and (011). Both of these reflections are required to be absent by space group V_h^{16}. Apparently (201), $\sin^2\theta = .3347$, was confused with (130), $\sin^2\theta = .3349$, that is a strong reflection; (011) 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 is should have appeared.

Geometrical Considerations. The Positions of the Boron Atoms.

The unit of structure containing $4\,FeB$ 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 $u_{Fe} = .115$, $v_{Fe} = .175$,

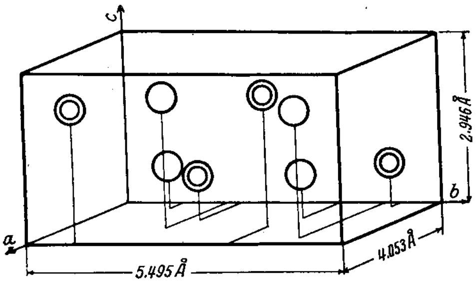

Fig. 5.

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

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

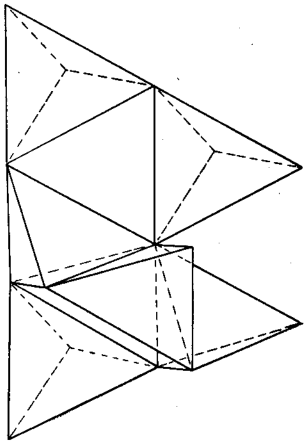

Fig. 6.

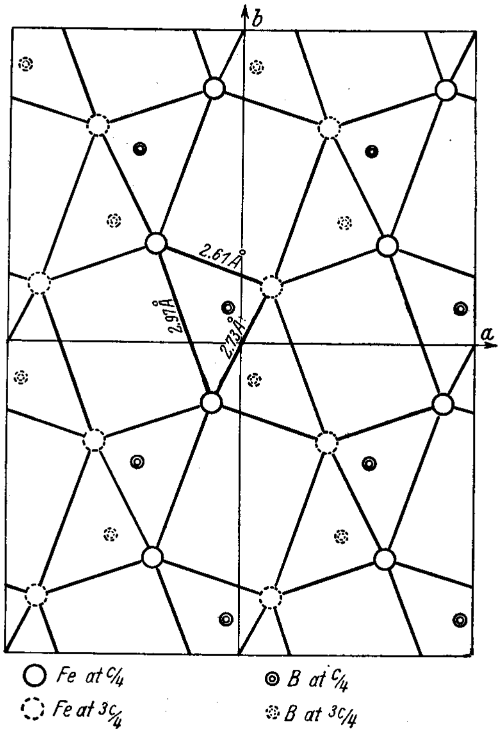

Fig. 7. A projection of the structure of *FeB* on (001).

then values $u_B =$ ca. .0.70 and $v_B =$ 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 Å in length, the other two edges ca. 2.95 Å. The Fe—B distance would be ca. 1,68 Å. 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 $u_B =$ ca. 0.68, $v_B =$ 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 Å and the Fe—B distances ca. 1.70 Å.

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 Å and two longer edges giving an Fe—Fe distance of ca. 2.95 Å. If the boron atoms are at the centers of the coordinated polyhedra the Fe—B distances are ca. 1.70 Å, 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. Hägg[1]) 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 $a = 5.852$ Å (Hägg)

$c = 3.453$ Å

$c : a = 1 : 0.5900.$

c) Volume $v = a^2 \cdot c \cdot .866 = 10.25 \times 10^{-24}$ cm³. $d = 6.83$.

Molecular volume $= 20.89$ cm³.

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

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

Table 6.

Rotating crystal photographic data from Fe_2P. Axis of Rotation parallel to (001) (Hägg). Iron-K-Radiation.

»Schichtlinie« 0		»Schichtlinie« 1	
Int.	*hkl*	Int.	*hkl*
v.w.	110	st.	111
w.	200	st.	201
w.	210 β	st.	211
st.	210	w.	221
w.	300 β	m.	311
st.	300	w.	401
v.w.	220 β	st.	321
w.	310 β	st.	411
w.	220		
st.	310		
v.w.	320 β		
m.	400		
w.	410 β		
st.	320		
v.w.	500 β		
st.	410		
w.	330 β		
w.	420 β		
st.	500		
w.	510 β		
st.	530		

Table 7.

Rotating crystal photographic data for Fe_2P. Axis of Rotation Perpendicular to (110) (Hägg). Iron-K-Radiation.

»Schichtlinie« 0		1		2		3		4	
Int.	*hkl*	Int.	*hkl*	Int.	*hkl*	Int.	*hkl*	Int.	*hkl*
v.w.	110	st.	210	w.	200	v.w.	110	st.	201
w.	111 β	w.	211	st.	201	st.	111	st.	210
st.	111	m.	212	m.	310	st.	300	st.	211
m.	002 β	w.	320	m.	311	st.	302	st.	212
st.	002	st.	321	m.	312	w.	410	st.	400
w.	220	st.	213 α_1	st.	203	st.	113	st.	401
w.	221	st.	213 α_2			st.	411		
v.w.	222 β								
w.	113 β								
w.	222								
st.	113								
st.	330								

Atomic Arrangement and Space Group.

The Laue photographs from Fe_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 (001) and (003) cannot be explained if all the iron atoms are in one plane parallel to (001). The determined value, $c = 3.453$ Å, 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}^1 $u\,v\,0;\ v-u, \bar{u}, 0;\ \bar{v}, u-v, 0;\ v\,u\,\frac{1}{2};\ \bar{u}, v-u, \frac{1}{2};$ $u-v, \bar{v}, \frac{1}{2}$.
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 $c\,0$, $c/3$, $2c/3$. (D_6^5, D_6^5, D_6^4, D_6^4) and 4 sets requiring iron atoms to be at $c\,0$, $c/6$, $c/3$, $c/2$, $2c/3$, $5c/6$ (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 Å. Arrangement 6. gives a structure in satisfactory agreement with the experimental data.

Parameter Determinations.

The intensities of reflections can be expressed by the formula:

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

in which the terms have their usual meaning. The factor F is a complex quantity giving the amplitude of the scattered wave and its phase defined with respect to the origin of the unit of structure.

The presence of phosphorus atoms in Fe_2P gives rise to two difficulties in determining the positions of the iron atoms. In the first place, it is rather difficult to fix positions that they might occupy, and in the second place the F curve for phosphorus is not known and that for iron in such a compound as Fe_2P is only known approximately from measurements on Fe[1]) and on Fe_3O_4[2]). It is probable, however, that the grosser features of the diffraction data must be accounted for by iron atoms alone. Rather exact parameter determinations can be made for the iron atom, bearing in mind at all times that the phosphorus atoms might have a maximum effect in either increasing or decreasing the calculated intensities of reflections.

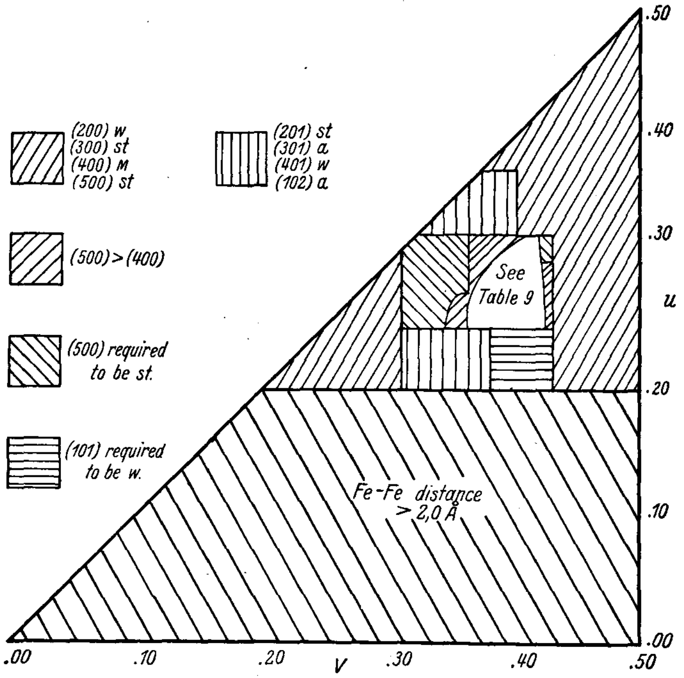

Fig. 8. Limitation of the parameter values for Fe_2P.

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[1]) A. H. Armstrong, Physic. Rev. **34**, 931. 1929.

[2]) A. Classen, Pr. physic. Soc. **38**, 482. 1926.

Planes of the type $(h0l)$ have structure factors simple enough to allow ready determination of the two parameters, u_{Fe}, v_{Fe}, defining the positions of the iron atoms;

$$\text{a)}\ u\,u\,0;\ \bar{u}\,0\,0;\ 0\,\bar{u}\,0$$
$$v\,v\,\tfrac{1}{2};\ \bar{v}\,0\,\tfrac{1}{2};\ 0\,\bar{v}\,\tfrac{1}{2}.$$

It is necessary to consider values of u from .0 to .50 and v from .0 to 1.0, except in so far as u and v are interchangeable. It is assumed that the iron atoms must be at least 2.0 Å apart, although the parameters can be determined without making this assumption. The comparisons afforded by the data listed in Tables 6, 7 and 8, led to the restrictions of the parameter values shown in Fig. 8. Closer determinations of u_{Fe} and v_{Fe} are given in Table 9. From this table it can be seen that the values are probably $u = .26$, $v = \pm .40$, to within quite small limits. The observed intensity of reflection, (111) s, requires:

$$u_{Fe} = .26 \qquad v_{Fe} = -.40$$

These values used in calculations of the intensities of reflections from (hkl) do not give results in accord with observations, especially for planes having a large interplaner spacing. This effect is probably due to the phosphorus atoms. It will later be considered in detail.

Geometrical Considerations. The Positions of the Phosphorus Atoms.

A representation of the unit of structure containing 6 *Fe* is shown as Fig. 9. Examination of this structure shows many striking characteristics that can partially be seen in the projection on (001) shown as Fig. 10. The iron atoms at a) $u\,u\,0$; $0\,\bar{u}\,0$; $\bar{u}\,0\,0$ (4, 5, 6 of Fig. 10) are equidistant from six other iron atoms at b) $v\,v\,\tfrac{1}{2}$; $0\,v\,\tfrac{1}{2}$; $v\,0\,\tfrac{1}{2}$ (1, 2, 8, 1′, 2′, 8′) and from two iron atoms (5, 6) in the same plane. The iron atoms at b) (1 of Fig. 10) are equidistant from six iron atoms at a) (5, 4, 9, 5′, 4′, 9′). In each case the *Fe—Fe* distance is ca. 2.65 Å, a value in close agreement with that found for Fe_3N, Fe_2N, Fe_3C, $FeAs$[1]), FeS[2]) and FeB.

The structure can be considered as an array of octahedra with iron atoms at the corners of each octahedron. The octahedra are markedly distorted from regular figures. If one inquires into possible positions for the phosphorus atoms several interesting factors appear. The intensities of reflection of (110), (001), (002), and (220) suggest that the phosphorus atoms are at $0\,0\,x$; $\tfrac{1}{3}\,\tfrac{2}{3}\,y$; $\tfrac{2}{3}\,\tfrac{1}{3}\,z$. If a phosphorus atom at $0\,0\,x$ is assumed to be equidistant from the corners of the coordinated polyhedron, then it must be displaced to the center of a face of the octahedron

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[1]) G. Hägg, l. c.

[2]) N. Olsen, Geol. Fören. Förh. Stockholm **47**, 19—72. 1925.

(note Fig. 10-11) the face itself being shared with another octahedron. The resulting figure is a tetrakaidecahedron (1, 2, 3, 4, 5, 6, 4′, 5′, 6′ of Fig. 10), with a phosphorus atom at 0 0 $\frac{1}{2}$ in the center. This center phosphorus atom (a of Fig. 10) is equidistant from nine iron atoms; three in the plane, perpendicular to the c axis that contains the phosphorus

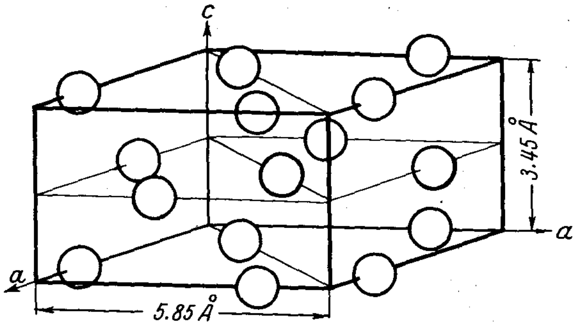

Fig. 9. The unit of structure of Fe_2P showing the positions of the iron atoms.

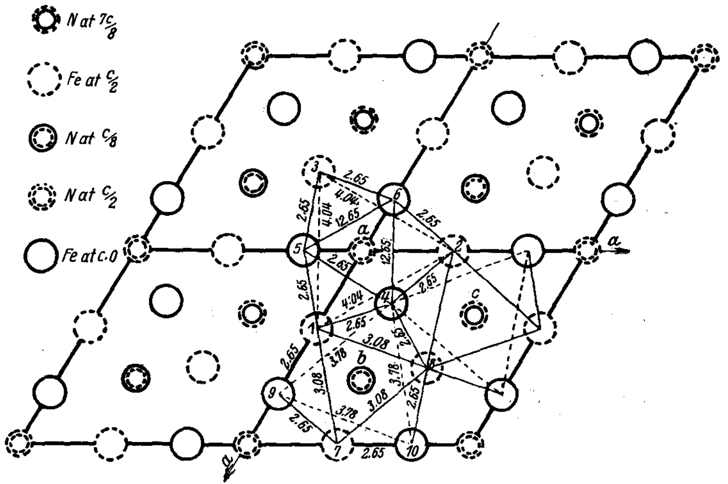

Fig. 10. A projection of the structure of Fe_2P on (001).

atom and two other sets of three in parallel planes separated by $c/2$ and $-c/2$ from this plane. The Fe—P distance is ca. 2.34 Å, a value to be expected.

If the phosphorus atoms at $\frac{1}{3}\ \frac{2}{3}\ y$ and $\frac{2}{3}\ \frac{1}{3}\ z$ are to be equidistant from the surrounding iron atoms they cannot be in the center of tetrakaidecahedra but must be in the centers of octahedra that are greatly distorted from regular figures (1, 7, 8, 4, 9, 10 of Fig. 10). The Fe—P distance

Table 8.

Partial Powder Data and Intensity Calculations for Fe_2P. Iron K Radiation (Lines due to $FeK\alpha_2$ and $FeK\beta$ omitted).

Plane	$\sin^2\theta$ Obs.	$\sin^2\theta$ Calc.	Observed and Calculated Intensities[1]				
			st.	m.	w.	v.w.	a.
100		0.0363					13
001		0.0783					8
110	0.108	0.1090			40		
101	0.1145	0.1146			19		
200	0.1445	0.1454			16		
111	0.1865	0.1873	1900				
201	0.223	0.2237	660				
120	0.255	0.2544	480				
002	0.3145	0.3132	320				
300	0.327	0.3271	320				
121	0.3335	0.3327	200				
102		0.3495					2
301		0.4054					2
112		0.4222					12
220	0.437	0.4361				9	
202		0.4586					8
310	0.474	0.4724		120			
221	0.515	0.5144			62		
311	0.551	0.5507		180			
122	0.5675	0.5676	420				
400	0.581	0.5814			48		
302	0.6405	0.6403	380				
401	0.6595	0.6597			120		
320	0.6915	0.6905			86		
003		0.7047					1
103		0.7410					4
222	0.7495	0.7493				16	
410	0.7635	0.7631			56		
321	0.7685	0.7688	770				
312	0.7865	0.7856			240		
113	0.815	0.8137			430		
411	0.8415	0.8414			150		
203	0.851	0.8500		350			
402	0.8945	0.8946			160		
500	0.9085	0.9085			190		
123	0.960	0.9591			48		

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[1] Intensities calculated for $u_{Fe} = .26$ $v_{Fe} = -.40$ and for phosphorus atoms at $0\,0\,\frac{1}{2}$, $\frac{1}{3}\,\frac{2}{3}\,0$; $\frac{2}{3}\,\frac{1}{3}\,0$.

Table 9.

A Determination of the values of u_{Fe} and v_{Fe} for Fe_2P.

$1/2\sqrt{S/\sigma^2 Fe}$ Calculated for Iron Atoms Alone ($I\alpha S$).

Plane	Int. from Powder Photographs	J	u 32 v 38	32 40	32 42	30 36	30 38	30 40	30 42	28 36	28 38	28 40	28 42	26 36	26 38	26 40	26 42	Int. from Rotating Crystal Photographs
101	w.	12	.31	.38	.45	.32	.42	.49	.54	.44	.54	.61	.68	.56	.66	.74	.80	
200	w.	6	.45	.70	.90	.04	.30	.54	.74	.08	.18	.42	.62	.18	.02	.34	.54	w.
201	st.	12	.70	.94	1.14	.60	.86	1.08	1.30	.72	.98	1.22	1.42	.80	1.05	1.28	1.50	st.
300	st.	6	2.52	2.20	1.86	2.62	2.36	2.04	1.70	2.34	2.08	1.76	1.42	1.98	1.72	1.40	1.06	st.
102	a.	12	.13	.20	.27	.08	.02	.09	.16	.20	.10	.03	.04	.32	.22	.15	.08	
301	a.	12	.36	.68	1.02	.06	.20	.52	.86	.34	.10	.24	.58	.70	.42	.10	.22	a.
400	w.	6	.15	.07	.45	.40	.32	.54	.90	.82	.74	.96	1.32	1.06	1.00	1.22	1.59	m.
500	w.	6	1.05	1.25	1.05	.30	.80	1.00	.80	.47	1.05	1.25	1.05	1.10	1.60	1.80	1.60	st.

in this case is ca. 2.22 Å. The positions of the phosphorus atoms are approximately $\frac{1}{3}\frac{2}{3}\frac{1}{8}$, $\frac{2}{3}\frac{1}{3}\frac{7}{8}$ (b and c of Fig. 10). It cannot definitely be said that these phosphorus atoms too might not be displaced into faces of the octahedra. However, in such a case the determination of the parameters defining the positions of the iron atoms is sufficiently accurate

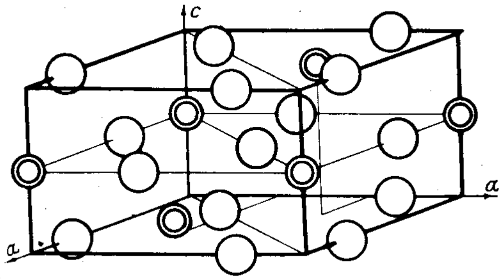

Fig. 11. The unit of structure of Fe_2P showing the positions of the iron atoms (open circles) and of the phosphorus atoms (annular circles).

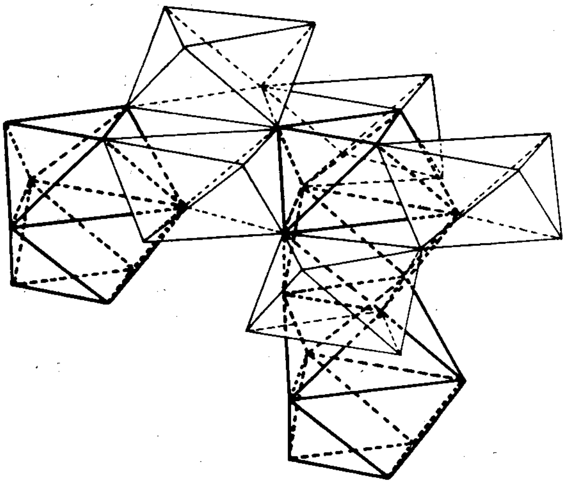

Fig. 12. Fe_2P represented as a coordination structure.

to indicate that these phosphorus atoms could not be equidistant from all the corners of the surrounding polyhedra. The phosphorus atoms would be ca. 2.18 Å from the iron atoms in the same plane perpendicular to the c axis and ca. 2.50 Å from the other six iron atoms. The resulting figures of the coordination structure would all share elements in an identical manner that would be improbable with such variations in the

$Fe—P$ distances. It is more probable that the coordinated polyhedra for these second kinds of phosphorus atoms are octahedra. The difference in the two sets of $Fe—P$ distances is probably to be accounted for by the difference in coordination number.

The derived structure is shown in Fig. 11 and as a coordination structure in Fig. 12. Each octahedron shares three non-adjacent edges with tetrakaidecahedra and each corner with one other octahedron. Each iron atom at $v\,v\,\frac{1}{2}$, $0\,\bar{v}\,\frac{1}{2}$, $\bar{v}\,0\,\frac{1}{2}$ is approximately equidistant from three phosphorus atoms while each iron atom at $u\,u\,0$, $0\,\bar{u}\,0$, $\bar{u}\,0\,0$ is approximately equidistant from four phosphorus atoms.

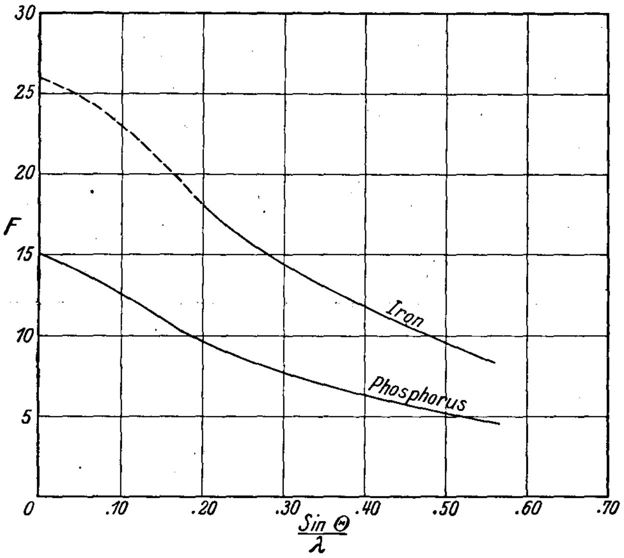

Fig. 13. F curves that were used in the structure determinations.

The phosphorus atoms, as was previously pointed out, have a rather decided influence on the intensities of reflections. Intensities of reflections were calculated using formula (1) and the F curves shown in Fig. 13. The F curve used for phosphorus is purely hypothetical as is the dotted portion of the F curve for iron. The concomitance of observed and calculated intensities can be seen by inspection of Table 8, that gives the powder photographic data obtained by Hägg. The calculations were made with $u_{Fe} = .26$, $v_{Fe} = -.40$ and phosphorus atoms at $0\,0\,\frac{1}{2}$, $\frac{1}{3}\,\frac{2}{3}\,0$; $\frac{2}{3}\,\frac{1}{3}\,0$. The phosphorus atoms do not have sufficient influence on the intensities of reflection to allow differentiation between the positions $0\,0\,\frac{1}{2}$; $\frac{1}{3}\,\frac{2}{3}\,\frac{1}{8}$; $\frac{2}{3}\,\frac{1}{3}\,\frac{7}{8}$ and those used in the calculations. Geometrical considerations given above, however, suggest that the latter positions are probably the correct ones.

This structure can be derived from space group C_{3h}^1, D_3^2, or C_3^1. If the phosphorus atoms were at $0\ 0\ 0$; $\frac{1}{3}\ \frac{2}{3}\ 0$, $\frac{2}{3}\ \frac{1}{3}\ 0$, the space group could be D_{3h}^3. The small departure of the phosphorus atoms from these positions does not have a detectable influence on the apparent symmetry determined by Laue photographs.

General Discussion.

The preceding structure determinations, together with that of cementite, give great support to the concept of non-ionic coordination structures. An examination of the literature[1]) indicates that many other compounds, probably have structures of this type. The structures of a number of compounds are summarized from the coordination viewpoint in Table 10. This problem is treated in greater detail in a paper to appear soon in the Journal of the American Chemical Society.

Table 10.

Coordination Structures of Some Non-Ionic Compounds.

(O) Octahedra (T) Tetrahedra (T.P.) Trigonal Prisms.

Compound	Type of Structure	Polyhedra	Shared Elements	No. of Polyhedra that share elements
Fe_3C		(O)	6 corners	2
Fe_3N		(O)	6 corners	2
Fe_2N		(O)	6 corners	3
W_2C			3 edges	2
			2 corners	3
FeB		(T)	4 corners	4
			2 edges	2
ZrC, ScN	$NaCl$	(O)	6 corners	6
			12 edges	2
$FeAs$		(T.P.)	6 corners	6
			9 edges	2
$NiAs$, FeS	Nickel Arsenide	(T.P.)	6 corners	6
			9 edges	2
$CoFeS_2$	Chalcopyrite	(T)	4 corners	4

The following general principles seem to be determining factors in the structures of non-ionic coordination compounds.

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[1]) P. P. Ewald and C. Hermann, Z. Krist. Strukturbericht. 1913—26.

I. A polyhedron of metal atoms is formed around each non-metallic atom, the metallic atoms being equidistant from the non-metallic atoms. These polyhedra are regular or are distorted so that the metal atoms have, along some elements, approximately the separation characteristic of the metal.

II. If a compound R_aX_b consists of coordinated polyhedra having N corners, then each corner is shared by Nb/a polyhedra. The sharing is usually of corners only, sometimes of edges, and less often of faces.

Finally we might remark that these structures supply concepts that should be of great value in elucidating the structures of other compounds of similar types.

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