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The Iron–Nitrogen System: The Crystal Structures of ε-Phase Iron Nitrides*

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At compositions near Fe_3N and Fe_2N the structures proposed for ε iron nitrides by previous workers from incomplete X-ray data are confirmed. At intermediate nitrogen concentrations and at concentrations less than that of Fe_3N, additional superlattice reflexions, unaccounted for by these previously proposed structures, are observed. Over the complete ε range, the true unit of structure (space group D_3^1–$C312$) has dimensions $a' = (2\sqrt{3})a$, $c' = c$; where a and c are the dimensions of the approximately close-packed hexagonal unit of the iron-atom arrangement. The nitrogen atoms tend towards maximum separation and achieve considerable ordering at all concentrations within the phase limits. The proposed structures are correlated with the observed unit cell dimensional changes.

In the ζ-Fe_2N structure the iron atoms retain the same relative positions as in ε-Fe_2N, but because of a rearrangement of the nitrogen atoms, which in ζ are packed more closely in one direction, the iron-atom lattice is anisotropically distorted. A mechanism for the ε-Fe_2N → ζ-Fe_2N transition is suggested.

A discussion of the structural features of the iron–nitrogen system indicates that the interstitial-atom ordering shown by all phases except one, and particularly by the α″ and ε phases, and the sharp change from one ordered arrangement (ε) to a different but equally ordered interstitial-atom arrangement (ζ) cannot be ascribed to ordinary close-packing or size factors.

Introduction

The work described in this paper is part of a chemical and structural investigation of binary and ternary interstitial alloys of iron, carbon and nitrogen (see also Jack, 1948*a*, *b*, *c*, 1951*a*, *b*, *c*; Goodeve & Jack, 1948).

The iron–nitrogen phase diagram shown in Fig. 1 has been discussed elsewhere (Jack, 1951*a*). Previous workers (Hendricks & Kosting, 1930) considered the structures of ε iron nitrides to be based on those assumed for alloys represented as Fe_3N and Fe_2N. The upper limit of nitrogen concentration for the ε phase (49·3 N atoms/100 Fe atoms) is slightly less than is required for Fe_2N, the composition of which lies within the ζ phase (see Fig. 1) and the structure of which has been reported (Jack, 1948*a*). The lower ε phase limit varies widely with temperature, and at 700° C. the nitrogen concentration is even less than that required for Fe_4N. Preliminary X-ray observations on a number of ε nitrides showed, in addition to the single superlattice reflexion upon which Hendricks & Kosting's interpretation was based, the presence of fainter superlattice lines, some of which were unaccounted for by the proposed structures. A detailed investigation over the whole range of compositions appeared to be desirable.

The results show that at compositions near Fe_3N and Fe_2N the X-ray data are in agreement with the two structures previously proposed. At other compositions the degree of ordering shown by the interstitial atoms is unexpectedly high, and throughout the ε range the equilibrium arrangement is one in which the nitrogen atoms tend towards maximum separation.

In the ζ-Fe_2N structure the iron atoms retain the same relative positions as in ε-Fe_2N, but because of a rearrangement of the nitrogen atoms, which in ζ are packed more closely in one direction, the iron-atom lattice is anisotropically distorted. It is suggested that the formation of ζ from ε can occur simply by the movement of particular nitrogen atoms to empty interstices adjacent to those occupied initially.

Experimental

Preparation of ε and ζ iron nitrides

Pure iron–nitrogen ε alloys near the lower nitrogen limit could not be retained on quenching from above 700° C. without some decomposition. It was anticipated that manganese would have a similar stabilising effect upon the close-packed hexagonal arrangement of iron atoms as it is known to have on the γ structures (see Jack, 1951*a*) which are cubic close-packed. ε nitrides containing 5·7 and 5·9 wt.% nitrogen were therefore prepared from 15% manganese–iron alloy powders by heating at 700° C. in the appropriate ammonia–hydrogen gas mixture and then quenching. Other ε iron nitrides were obtained by thermal decomposition of ζ-Fe_2N at temperatures from 300° C.

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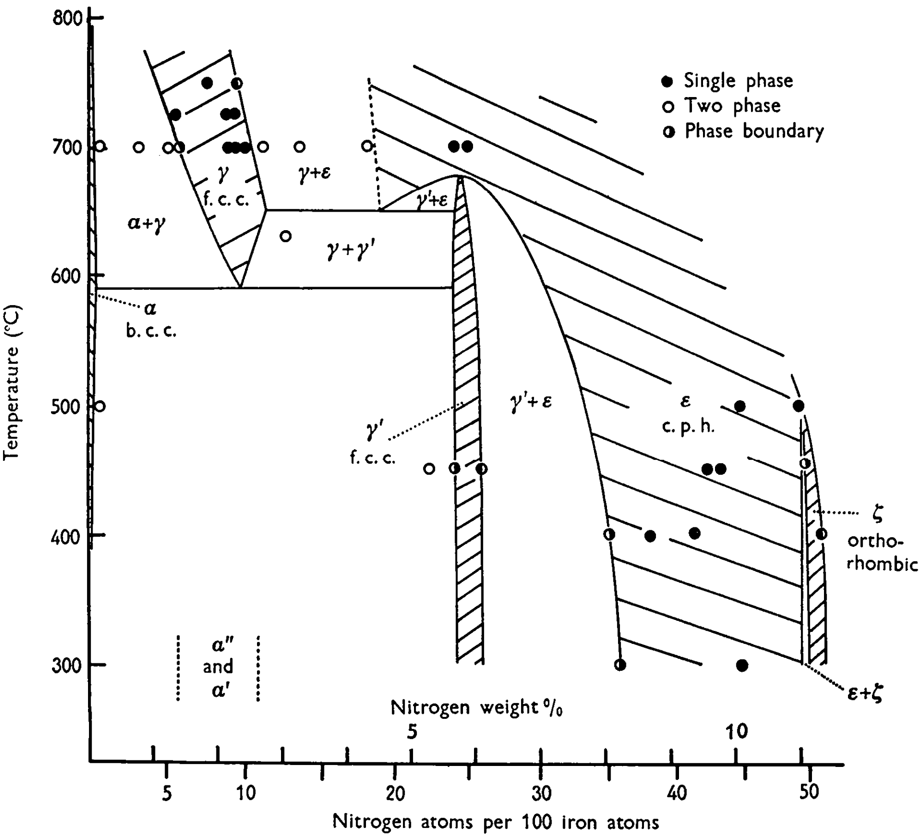

Fig. 1. The iron–nitrogen phase diagram (Jack, 1951 *a*).

to 450° C. for varying times. Details are given in Table 1. It has been shown (Goodeve & Jack, 1948) that the rate of diffusion of nitrogen atoms during decomposition of ε or ζ nitrides within this temperature range is at least 10^4 times as rapid as the rate-controlling process, the rate-controlling stage being the combination of pairs of nitrogen atoms at the solid surface. Nitrides obtained by interrupting the decomposition at any desired point are therefore homogeneous and their nitrogen-atom locations are characteristic of their compositions.

By passing pure ammonia over iron at such a high rate that the ammonia dissociation, and therefore the partial pressure of hydrogen, were negligible, nitrides of maximum nitrogen content were obtained. At 500° C. ε nitrides with not more than 11·0 wt.% nitrogen were formed, but at temperatures not exceeding 450° C. ζ nitrides with 11·1–11·3 wt.% nitrogen were observed (see Jack, 1948*a*).

X-ray investigation

Use was made of the absorption-edge effect (see James, 1948, pp. 160 and 608) which, in depressing the atomic scattering factors of the metal atoms, increases the relative influence of interstitial atoms on the intensities of the reflexions. Thus, Co $K\alpha$ radiation was used for the pure iron–nitrogen alloys and Fe$K\alpha$ radiation where manganese was also present. The depression of the atomic scattering factor of iron with Co $K\alpha$ radiation is 3·90 electronic units. In a favourable case, e.g. with the (220) reflexion of Fe_3N where for the proposed structure

$$F = -3f_{Fe} + 2f_N;\ \ \theta \approx 55°;\ \ f_{Fe} \approx 12{\cdot}8 \ \text{and}\ f_N \approx 2{\cdot}2\,,$$

the reduction of line intensity due to the presence of nitrogen atoms is increased from 22% with no absorption-edge effect to 30% using Co $K\alpha$ radiation. Thus, the determination from intensity data of the correct location of interstitial atoms is facilitated.

Relative intensities of reflexions were measured on films obtained with filtered radiation in a 19 cm. camera. Faint superlattice reflexions, due only to interstitial atoms, were obscured by the relatively high background intensity of photographs obtained with filtered radiation but were clearly observed with crystal-reflected monochromatic radiation used in a 9 cm. hydrogen-filled camera. Synthetic lithium fluoride was found to be superior to the monochromatizing crystals usually recommended (see Lipson, Nelson & Riley, 1945).

Unit cell dimensions are given in Ångströms in the tables but are expressed graphically in kX. units to facilitate comparison with previous work. Wavelengths used in their calculation are:

Table 1. *Preparation and unit-cell dimensions of ε and ζ phases of the iron–nitrogen system*

Phase	Composition		Unit-cell dimensions				Preparation		
							Nitriding		ζ-decomposition time (hr.)
	wt. % N	N/100 Fe	a (Å)	c (Å)	c/a	V/Fe (Å^3)	Temp. (°C.)	NH_3/H_2 ratio	
ε*	5·7	24·1	2·660	4·344	1·633	13·31	700	0·10	
ε*	5·9	24·9	2·667	4·349	1·630	13·40	700	0·10	
ε	8·7	37·4	2·723	4·394	1·613	14·12	400	—	9
ε	9·4	41·3	2·742	4·409	1·608	14·35	400	—	6
ε	9·6	42·3	2·748	4·409	1·605	14·41	450	—	1
ε	10·1	45·0	2·752	4·413	1·604	14·47	300	—	92
ε	11·0	49·3	2·764	4·420	1·599	14·62	500	∞	
ζ	11·1	49·8	2·764	4·425	$b/\sqrt{3}$ =2·788	14·76	450	∞	
ζ	11·3	50·8	2·765	4·425	$b/\sqrt{3}$ =2·789	14·77	400	∞	

* Corrected for presence of 15 % Mn.

Fe $K\alpha_1$, 1·93597; Fe $K\alpha_2$, 1·93991; Co $K\alpha_1$, 1·78890; Co $K\alpha_2$, 1·79279 Å.

References to the standard methods employed for structure analyses are given in the author's previous papers.

Unit-cell dimensions of ε iron nitrides

The observed unit cell dimensions of ε iron nitrides (see Table 1) show fair agreement with values given by Brunauer, Jefferson, Emmett & Hendricks (1931) except that these workers were unable to distinguish between the ε and ζ phases, and therefore their values at the supposed upper limit of ε are anomalous. Fig. 2 shows that *a* increases with increasing nitrogen concentration more rapidly than *c* so that the axial ratio *c*/*a* decreases steadily. Cell dimensions published by Paranjpe, Cohen, Bever & Floe (1950) after completion of the present work are also not in complete agreement with those now reported. No explanation can be offered for the differences between the results of these three investigations. The observation of Eisenhut & Kaupp (1930) that the unit cell dimensions are a linear function of the nitrogen concentration is unconfirmed.

The structures of ε iron nitrides

ε-Fe_3N *and* ε-Fe_2N

Throughout the ε-phase range, the iron-atom arrangement is close-packed hexagonal. Octahedral interstices in such an array of metal atoms are arranged in planes perpendicular to the *c* axis with an interplanar distance $\frac{1}{2}c$, and with a two-dimensional close-packing in each layer (see Fig. 3). The interstices of one layer are directly above those of the layer below, and together they may be imagined to occupy the points of a simple hexagonal lattice of dimensions

$$a' = a \quad \text{and} \quad c' = \tfrac{1}{2}c\,,$$

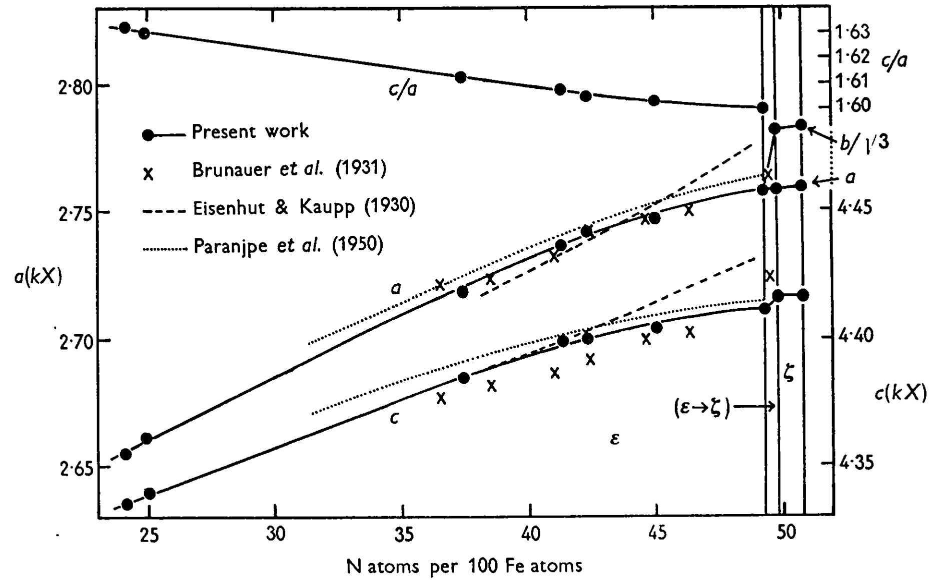

Fig. 2. Unit-cell dimensions for ε and ζ iron nitride phases.

where a and c are the dimensions of the close-packed hexagonal lattice of iron atoms and are those given in Table 1 and Fig. 2. On the evidence of one observed superlattice reflexion, Hendricks & Kosting proposed that the nitrogen atoms of ε nitrides occupy certain interstices in an ordered manner. For Fe_3N it was considered that one-third of the interstices in each layer is filled in such a way that the six interstices nearest to a nitrogen atom in its own layer plane and the interstices directly above and below it in adjacent planes remain unoccupied, giving a sequence of nitrogen-atom layers $ABAB\ldots$. ε-Fe_2N was assumed to be formed by additional nitrogen atoms going only into alternate layers, giving an $A\,B'\,A\,B'\ldots$ structure shown in Fig. 4.

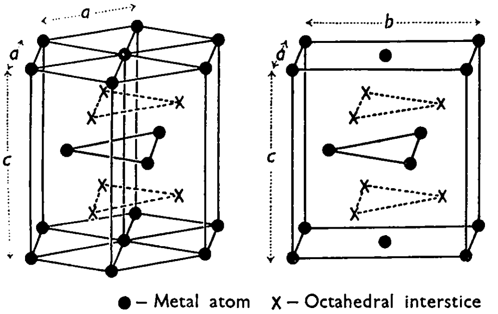

Fig. 3. Octahedral interstices in ε and ζ phases.

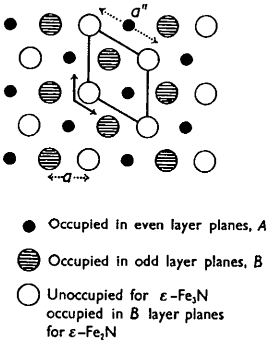

Fig. 4. Layer plane of octahedral interstices in ε iron nitrides, showing nitrogen-atom arrangements proposed by Hendricks & Kosting (1930) for Fe_3N and Fe_2N.

After examination of X-ray data from nitrides of various compositions within the ε phase, and also of photographs of the isomorphous ε iron carbonitrides (Jack, 1948*b*), it was found that near compositions of 33·3 interstitial atoms/100 metal atoms and 50·0 interstitial atoms/100 metal atoms no reflexions were observed which could not be accounted for by the structures proposed by Hendricks & Kosting. Of the faint superlattice reflexions, all those which might be expected to be seen were quite clearly observed. As shown in Table 2, the relative intensities measured for an ε iron carbonitride of composition 36·8 (C+N) atoms/100 Fe atoms are in excellent agreement with those calculated for Hendricks & Kosting's 'Fe_3N'. The true unit cell is hexagonal with dimensions

$$a'' = \sqrt{3}\,a \quad \text{and} \quad c'' = c\,.$$

Table 2. *X-ray reflexions from ε iron carbonitride*

(36·8 interstitial atoms/100 Fe atoms.) $a''=\sqrt{3}\,a$; $c''=c$.

Indices		I_c		I_o	Error (%)
001		0		0*	—
100	*s*	22		0*	—
101	*s*	64		95±30	—
110		724		709	−2
002		962		953	−1
111		4394	4398	4480	+2
200	*s*	4			
102	*s*	6		*vvw*	—
201	*s*	16		*vw*	—
112		976		1012	+4
210	*s*	3		0	—
202	*s*	3		0	—
003		0		0	—
211	*s*	16		*vw*	—
103	*s*	7		0	—
300		1203		1209	0
301		0		0	—
212	*s*	4		0	—
113		1474		1515	+3
203	*s*	7		0	—
220		189		216±30	—
302		1797		1805	0
221		1596		1549	−3
310	*s*	2		0	—
004		438	453	483±30	—
311	*s*	15			
213	*s*	18	21	*vw*	—
104	*s*	3			
222		1000		950	−5
400	*s*	2		*vvw*	—
312	*s*	10		*vw*	—
303		0	998	1016	+2
114		979			
401	*s*	19			

s Superlattice reflexion.

* Not visible in the background caused by scatter of the incident beam.

Although it may be assigned to space group D_6^6–$C6_32$ (Hendricks & Kosting, 1930), it is more satisfactorily associated with the derived lower-symmetry group D_3^1–$C312$ when its relationships with ε-Fe_2N and intermediate nitrides are considered. According to the latter space group, six iron atoms are placed at sites (l) (see *International Tables*, 1935, vol. 1, p. 245), i.e. at

$$x, y, z;\quad \bar{y}, x-y, z;\quad y-x, \bar{x}, z;$$
$$\bar{y}, \bar{x}, \bar{z};\quad x, x-y, \bar{z};\quad y-x, y, \bar{z};$$

which, with $x = 0$, $y = \frac{2}{3}$, $z = \frac{1}{4}$, reduce to

$$0, \tfrac{2}{3}, \tfrac{1}{4};\quad \tfrac{1}{3}, \tfrac{1}{3}, \tfrac{1}{4};\quad \tfrac{2}{3}, 0, \tfrac{1}{4};$$
$$\tfrac{1}{3}, 0, \tfrac{3}{4};\quad 0, \tfrac{1}{3}, \tfrac{3}{4};\quad \tfrac{2}{3}, \tfrac{2}{3}, \tfrac{3}{4}\,.$$

One nitrogen atom occupies site (d) at $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$, with two unoccupied interstices at $0, 0, \frac{1}{2}$ and $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ (sites (b) and (f)) in the same even layer-plane, A. The second nitrogen atom is at $\frac{2}{3}, \frac{1}{3}, 0$ (site (e)) in an odd layer plane, B, together with unoccupied holes at $0, 0, 0$ (site (a)) and $\frac{1}{3}, \frac{2}{3}, 0$ (site (c)).

The structure of ε at its upper homogeneity limit is similar to that of Fe_3N except that in addition to the nitrogen atoms at $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ and $\frac{2}{3}, \frac{1}{3}, 0$ the interstices at 0, 0, 0 are almost completely filled. Just before the nitrogen concentration is sufficient to give the ideal ε-Fe_2N structure, a phase change occurs, but the composition of the limiting ε nitride (49·3 N atoms/100 Fe atoms) is near enough to Fe_2N for descriptive purposes. The observed and calculated intensities, given in Table 3, show good agreement. It will be noted that some of the superlattice reflexions which are observed for Fe_3N have zero intensities (calculated and observed) for Fe_2N, but no reflexions additional to those for Fe_3N are observed. This is of significance when nitrides of intermediate compositions are examined. The nitrogen-atom arrangement of ε-Fe_2N is indicated in Fig. 4.

Table 3. *X-ray reflexions from ε iron nitride*

(49·3 N atoms/100 Fe atoms.) $a'' = \sqrt{3}\,a$; $c'' = c$.

Indices		I_c		I_o	Error (%)
001	*s*	12		0	—
100		0		0	—
101	*s*	120		109±30	—
110		494		506	+2
002		767		759	−1
111		4480		4350	−3
200		0		0	—
102		0		0	—
201	*s*	30		*vw*	—
112		989		994	−5
210		0		0	—
202		0		0	—
211	*s*	26	28	*vw*	—
003	*s*	2			
103	*s*	10	978	931	−5
300		968			
301	*s*	2		0	—
212		0		0	—
113		811		845	+4
203	*s*	7	84	82	−2
220		77			
302		801		806	+1
221		694		736	+6
310		0		0	—
311	*s*	13	219	210	−4
004		206			
213	*s*	13		*vvw*	—
104		0		0	—
222		383		387	+1
204		0		0	—
400		0		0	—
312		0		0	—
401	*s*	7		0	—
303	*s*	7		0	—
114		152		153	+1
320		0		0	—
402		0		0	—
321	*s*	23	1391	1287	−7
223		1368			

s Superlattice reflexion.

The sequence of nitrogen atom layers ($AB'AB'\ldots$) remains unchanged, but whereas the even layers are identical with those of Fe_3N, the odd layer-planes of interstices are two-thirds filled. The interstices which are filled with nitrogen atoms in odd layers are empty in even layers, and vice versa, so that each nitrogen atom still has an unoccupied hole above and below it in adjacent planes.

'Intermediate' ε-structures

The ε phases with compositions near Fe_4N and between Fe_3N and Fe_2N give photographs which show very faint superlattice reflexions additional to those accounted for by the two structures described above, although reflexions due to these still persist. The additional reflexions and, of course, all the 'Fe_3N' and 'Fe_2N' reflexions were indexed on a unit cell of dimensions

$$a''' = 2\sqrt{3}\,a; \quad c''' = c\,.$$

Alternatively, if the unit cell for Fe_3N and Fe_2N is retained (a'' and c'') the additional reflexions have indices which include halves as well as integers. This is shown in Table 4. It would not be expected to observe all such superlattice reflexions, and therefore those noted are probably the strongest. For a nitride intermediate between Fe_3N and Fe_2N, i.e. with the contents of the true unit cell near $Fe_{24}N_{10}$, three of the four 'extra' reflexions have indices (again referred to the cell of dimensions a''' and c''') in which $(2h+k)$ or $(h+2k)$ equals $3n$. The only simple arrangement of nitrogen atoms which requires such reflexions to be the strongest of all possible 'extra' reflexions, and which requires a unit cell of the size observed, is that shown in Fig. 5. Again there is a sequence of nitrogen layer-planes $A\ B\ A\ B\ldots$ in which the even layers (A) are identical with those of ε-Fe_3N and ε-Fe_2N. In the odd layers (B) the interstices directly above and below the nitrogen atoms of adjacent (A) layers remain empty. Two holes at 0, 0, 0, and $\frac{2}{3}, \frac{1}{3}, 0$ (see Fig. 5) are also unoccupied. The structure may be described by reference to space group D_3^1–$C312$ (*International Tables*, 1935, vol. 1, p. 245). Twenty-four iron atoms are at the six-fold sites (l) with parameters

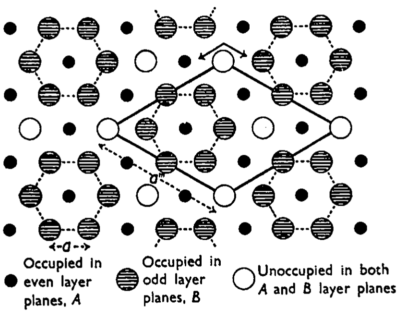

Fig. 5. The nitrogen-atom arrangement for an 'intermediate' ε nitride, $Fe_{24}N_{10}$.

$$x_1 = 0,\ y_1 = \tfrac{1}{3},\ z_1 = \tfrac{1}{4};$$
$$x_2 = \tfrac{1}{2},\ y_2 = \tfrac{1}{3},\ z_2 = \tfrac{1}{4};$$
$$x_3 = 0,\ y_3 = \tfrac{5}{6},\ z_3 = \tfrac{1}{4};$$
$$x_4 = \tfrac{1}{2},\ y_4 = \tfrac{5}{6},\ z_4 = \tfrac{1}{4}\,.$$

Table 4. *Superlattice reflexions directly observed in ε phases*

$a'' = \sqrt{3}\,a;\quad c'' = c.$

Indices	Composition and concentration (interstitial atoms per 100 metal atoms)				
	Fe–Mn–N 24·9	Fe–C–N 36·8	Fe–N 37·4	Fe–N 41·3	Fe–N 49·3
$1\frac{1}{2}0$	*vvf*	—	—	—	—
101	*vw*	*w*	*w*	*w*	*w*
$1\frac{1}{2}1$	—	—	*vvw*	*vvw*	—
102	—	*vvw*	*vvw*	—	—
201	*vvw*	*vw*	*vw*	*vw*	*vw*
210	—	—	—	—	—
$\frac{3}{2}\frac{3}{2}1$	—	—	*vvw*	*vvw*	—
211	*vvw*	*vw*	*vw*	*vw*	*vw*
$2\frac{1}{2}2$	—	—	*vvw*	—	—
213	—	*vw*	*vvw*	*vw*	*vvw*
$\frac{7}{2}\frac{1}{2}1$	—	—	*vvw*	*vvw*	—
400	—	*vvw*	—	—	—
312	—	*vw*	—	—	—
X-radiation	Fe *Kα*	Fe *Kα* & Co *Kα*	Fe *Kα*	Fe *Kα*	Fe *Kα* & Co *Kα*

Of the four nitrogen atoms in the (*A*) layer, one occupies site (*d*) and three are at sites (*k*) with $x_1=\frac{5}{6}$. The six nitrogens in the (*B*) layer are in three-fold sites (*i*) with $x_1 = \frac{1}{2}$ and $x_2 = \frac{1}{6}$. Fourteen unoccupied interstices are at sites (*a*), (*b*), (*c*), (*e*) and (*f*), and at the three-fold positions (*i*) $(x_3=\frac{5}{6})$ and (*k*) $(x_2=\frac{1}{2}; x_3=\frac{1}{6})$. The structure is that of ε-Fe_2N in which two nitrogen atoms out of every eight in odd layers have been removed in a strictly ordered manner. The remaining odd-layer nitrogen atoms are arranged in six-membered rings each surrounded in its own plane by empty interstices and each with an empty interstice at its centre. On removing a further two nitrogen atoms from the unit cell the ε-Fe_3N structure is obtained, but only by diffusion of some of the remaining interstitial atoms to neighbouring interstices (cf. Figs. 4 and 5).

Only one superlattice reflexion additional to those required for ε-Fe_3N was observed on photographs of ε-$Fe_{24}N_6$ (actually an iron–manganese nitride quenched from 700° C.; see Table 4). Although the ordering must be almost complete, it is impossible to deduce the exact nitrogen-atom arrangement from such limited data. It is possible, however, that the structure is similar to that of $Fe_{24}N_{10}$ except that in the (*B*) layers the nitrogen-atom arrangement of $Fe_{24}N_6$ is the same as the interstice pattern of $Fe_{24}N_{10}$ (see Fig. 5).

Although it is considered unnecessary to reproduce the quantitative X-ray data here, the observed intensitites of all non-superlattice reflexions on photographs of 'intermediate' ε iron nitrides were within ±5% of the intensities calculated for the proposed structures. This agreement, which is as good as that found for the ε-Fe_3N and ε-Fe_2N structures (see Tables 2 and 3) indicates only that the proposed structures are possible, and in the case of ε-$Fe_{24}N_6$ there must remain some doubt about the correct nitrogen-atom locations.

Discussion of ε iron–nitrogen structures

The structures proposed above not only provide an explanation for the observed intensities of superlattice reflexions and of those reflexions predominantly due to iron atoms, but can also be correlated with the observed unit cell dimensional changes. The closest approach of all nitrogen atoms in the *c* direction throughout the complete ε range is equal to $c''' = c$. In even nitrogen-atom layer-planes the closest distance of approach in the *a* direction is always equal to $a'' = \sqrt{3}\,a$. In odd layers, however, the nitrogen atoms become increasingly closely packed in the *a* direction as the nitrogen concentration increases. Thus, in ε-$Fe_{24}N_6$ each nitrogen atom in an odd layer has three nitrogen-atom neighbours at a distance of 2*a*. For ε-Fe_3N ($Fe_{24}N_8$) the corresponding nitrogen atom has six neighbours in its own plane at distances of $\sqrt{3}\,a$, while in $Fe_{24}N_{10}$ the same atom, has two nitrogen atoms each at a distance *a*. Finally for ε-Fe_2N ($Fe_{24}N_{12}$) each odd-layer nitrogen atom has three neighbouring atoms at distances *a*. Quite clearly then, the closest approach of nitrogen atoms increases more rapidly in the *a* directions than in the *c* direction because of the interstitial-atom arrangements adopted at various concentrations. The increasing close-packing of nitrogen atoms in *a* directions will expand the iron-atom lattice preferentially and so the observation that the axial ratio *c*/*a* decreases with increasing nitrogen concentration is in accordance with the proposed interstitial-atom locations.

The closest possible approach of nitrogen atoms would occur if holes directly above and below each other in adjacent layer-planes were occupied. The observation, therefore, that each nitrogen atom always has unoccupied interstices above and below it adds weight to the suggestion that the interstitial atoms tend towards maximum separation. Similar considerations apply in the ζ phase (Jack, 1948*a*).

The $\varepsilon \rightarrow \zeta$ phase change

When the interstitial-atom concentration of the ε phase is increased from 49·3 to 49·8 N atoms/100 Fe atoms there appears to be a marked structural discontinuity. The iron atoms retain their same relative positions but there is a small anisotropic distortion of the ε lattice which reduces the symmetry of the new structure, ζ, to orthorhombic. As discussed elsewhere (Jack, 1948*a*), the lattice distortion consists of a disproportionately large expansion parallel to the *b* axis and is caused by a rearrangement of the nitrogen atoms which in ζ are packed most closely in the *b* direction (see Fig. 6).

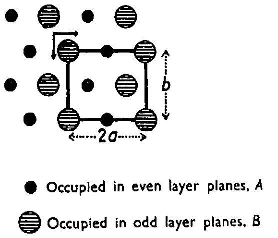

Fig. 6. Layer plane of interstices in ζ-Fe_2N showing locations of nitrogen atoms.

The only other known example of a structural change which, in the opinion of the present author, is caused primarily by the transition from one ordered interstitial-atom arrangement to another is in the cobalt–nitrogen system (Juza & Sachsze, 1945) where γ cobalt nitride (*c*.Co_3N) transforms to δ-Co_2N. However, the nitrogen concentration at the upper γ phase limit is much smaller than that at the lower limit of the δ phase so that the increased interstitial-atom concentration may be a decisive factor. In the iron–nitrogen system the $\varepsilon \rightarrow \zeta$ change is accompanied by an interstitial-atom concentration change not greater than 0·5 N atoms/100 Fe atoms which appears insufficient to influence the effective atomic sizes or the close-packing of the atoms—the factors which usually account for structural changes in interstitial alloys. γ cobalt nitrides are probably isomorphous with ε iron nitrides, but although δ-Co_2N has a distorted close-packed hexagonal arrangement of cobalt atoms the anisotropy of the distortion differs from that in ζ-Fe_2N because the nitrogen-atom locations in the two cases are quite different (Clarke & Jack, 1951). Thus, there are certain features of these two similar transitions which are peculiar to the atoms concerned.

The X-ray photographs of iron nitride specimens at progressive stages of the $\varepsilon \rightarrow \zeta$ transition showed that the 'splitting' into pairs of all the non-superlattice powder reflexions (except those with indices (00*l*)), due to the departure from hexagonal symmetry, was to some extent gradual. As the apparent anisotropy of the iron-atom arrangement increased, the intensities of the ε-superlattice reflexions decreased and those of the ζ-superlattice reflexions increased. However, no further change in the ζ phase unit cell dimensions was observed after the ε-superlattice reflexions were completely absent. It must be remembered that X-ray data give only the average unit cell. The observations suggest that both ε and ζ nitrogen-atom arrangements co-exist within the same crystal and that the extent to which each exists determines the average degree of anisotropic distortion of the iron-atom lattice. The change from one ordered arrangement of nitrogen atoms to the other probably occurs most readily by the movement of particular nitrogen atoms to interstices directly above or below those occupied initially. These interstices are always vacant and are at the shortest distances from nitrogen atoms. A suggested transition mechanism is indicated in Fig. 7.

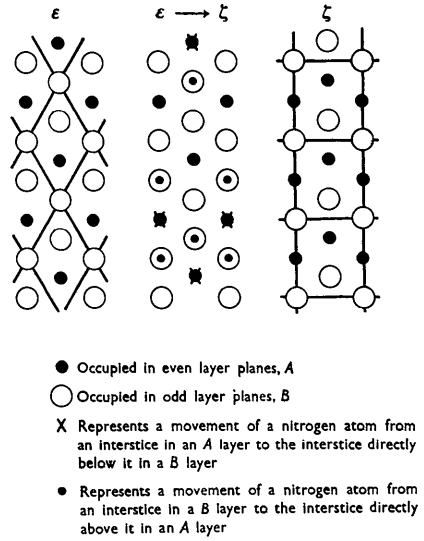

Fig. 7. A suggested mechanism for the $\varepsilon \rightarrow \zeta$ transition.

Out of every six nitrogen atoms, three remain stationary, two move from odd layer planes to adjacent even layer planes and one moves from an even layer to an odd layer. In any crystal the state of completion of the transition will not be the same at all points. Possibly because of small and localized concentration gradients, there may exist a region in which the ε nitrogen-atom arrangement is still maintained and another region in which the movement of nitrogen atoms has already resulted in the ζ arrangement. Between the two there is probably a region in which the 'mobile' nitrogen atoms are at various stages of transition. Since one-half of the number of nitrogen atoms do not move at all, a crystalline continuity will be maintained.

General structural features of the iron–nitrogen system

The outstanding common feature of all iron–nitrogen phases is the ordering of the interstitial atoms (for γ′ and ζ see Jack, 1948*a*; for γ, α′ and α″ see Jack, 1951*a*, *b*). Only in the γ phase do the nitrogen atoms occupy available interstices in a completely random manner. Two possible reasons for the random arrangement in this phase are:

(i) the concentration of nitrogen atoms in γ is so small (see Fig. 1) that they never approach close enough to influence one another;

(ii) γ is stable only at relatively high temperatures so that thermal movement of the interstial atoms prevents ordering, the disorder being retained on quenching.

The concentration range of nitrogen in the fully ordered α'' phase is the same as in the γ phase so that the concentration effect appears to be less important than the temperature effect. At equally high temperatures, however, thermal motion does not prevent ordering in the ε phase. It seems that there may be factors responsible for interstitial-atom ordering which have not previously been considered. In the α' phase the interstices occupied are those which result in minimum strain energy, but there is no simple explanation for the complete ordering which occurs on tempering α' to give α''. Again, it is not obvious why there is an extensive miscibility gap between the γ and γ' phases. These two phases have the same face-centred cubic arrangement of iron atoms and exist in equilibrium with each other at 590° C. to 650° C., yet γ'-'Fe_4N' has only a very limited range of composition. While γ nitrides are not ferromagnetic, the γ' phase has a Curie point of about 490° C. The difference may not be entirely due to the larger interatomic spacing in the latter structure. It is suggested that a valency factor might account for the structural discontinuity and the change in interstitial-atom ordering, and for the differences in magnetic properties.

The remarkable interstitial-atom ordering shown throughout the whole range of the ε phase must also involve valency factors, and the sudden change from one ordered arrangement (ε) to a different but equally ordered arrangement (ζ) within a nitrogen concentration range of not more than 0·1 wt.% cannot be ascribed to ordinary close-packing or size factors.

As a result of the anomalous effective atomic sizes observed in the iron–carbon–nitrogen system (Jack, 1948*b*), it was suggested by the present author that although the interstitial atoms are probably not fully ionized they do contribute some free electrons to the metallic structure. This idea was later used in the interpretation of interstitial boride structures (Kiessling, 1950). It has also received some support from evidence of the existence of a positive charge on the carbon atoms of austenite (Dayal & Darken, 1950), and is not inconsistent with the observed unit-cell dimensions of carbon and nitrogen austenites and martensites (Jack, 1951*a*). The unexplained features of the iron–nitrogen system, and particularly the change from the ε to ζ interstitial-atom arrangement at a composition of almost exactly Fe_2N, suggest changes in the directional-valency forces between the iron and nitrogen atoms which in turn suggest changes in their electronic configurations.

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