Short Communications

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Results of further X-ray structural investigations of the iron–carbon and iron–nitrogen systems and of related interstitial alloys.*

By K. H. Jack,† *Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England.*

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The iron–carbon system: the tempering of carbon-martensite

Starting with a hardened structure consisting of tetragonal martensite and retained austenite, high-carbon steels undergo three structural changes during low-temperature tempering (see Antia, Fletcher & Cohen, 1944), each stage being accompanied by characteristic changes in hardness and other physical properties. It is generally agreed that the second stage is the transformation of retained austenite, but although the first and third stages are associated with the decomposition of martensite into the ultimate aggregate of ferrite and cementite, their exact natures have been in dispute (Honda & Nishiyama, 1932; Hägg, 1934). Honda & Nishiyama considered the first stage to be the transformation of tetragonal to cubic martensite. Hägg's view is supported by more recent workers (Antia *et al.* 1944; Arbusov & Kurdjumov, 1941; Kurdjumov & Lyssak, 1947) who conclude that the first stage of tempering involves the formation of ferrite and a precipitated phase which is not cementite but which is too finely dispersed to yield an X-ray diffraction pattern. From a martensite specimen tempered at 200° C., Heidenreich, Sturkey & Woods (1946*a*, *b*) obtained an electron-diffraction pattern corresponding to ϵ-iron nitride (Fe_3N) or some phase isomorphous with it. Because of the very small nitrogen concentration of the steel used, it was suggested (Jack, 1946, 1948*b*) that the hexagonal 'Fe_3N' was possibly an ϵ-iron carbonitride. New X-ray observations now give direct evidence that the loss of tetragonality of martensite during the first tempering stage is due to the precipitation of a close-packed hexagonal iron carbide which it is proposed should be named ϵ-iron carbide, or ϵ-Fe_2C, because of its structural similarity with ϵ-Fe_3N. ϵ-Iron carbide is formed as a coherent transitional phase in which the Laue condition for X-ray reflexion is obeyed preferentially in a direction normal to the (101) lattice planes. The unit-cell dimensions

$$a=2{\cdot}73,\quad c=4{\cdot}33\,\text{A.},\quad c/a=1{\cdot}58,$$

are similar to those given by Heidenreich *et al.* for their 'Fe_3N'. The spacing of the (101) planes is almost identical with that of the (101) planes of martensite, so that a simple orientation relationship between the two phases is probable. The hexagonal carbide forms the carbon-rich extreme of the series of close-packed hexagonal ϵ-iron carbonitrides (Jack, 1948*b*) at their lower interstitial-atom concentration limit, $Fe_3(C,N)$. A similar iron carbide, Fe_2C, has been described by Hofer, Cohn & Peebles (1949) as the carbon-rich extreme of the same carbonitride series at its upper interstitial-atom concentration limit, $Fe_2(C,N)$.

During the third stage of steel tempering, ϵ-iron carbide transforms to give a fine dispersion of very thin platelets of strained and slightly distorted cementite, still coherent with the matrix and with the plane of the platelet parallel with the (001) lattice plane of the cementite structure. The observed diffraction pattern is markedly different from that of crystalline cementite since the Laue condition is fulfilled completely only in directions parallel with the (001) planes and is relaxed in the [001] direction. Included among the strongest reflexions are the previously unidentified reflexions observed on X-ray photographs of tempered martensite by Arbusov & Kurdjumov (1941) and ascribed by them to a new iron carbide.

With increasing tempering times, or at higher temperatures, the gradual growth and recrystallization of the distorted cementite platelets are accompanied by loss of coherency and reduction in lattice strain. The proposed structural changes are correlated with observed changes in hardness and specific volume of steels during the three tempering stages, and are also supported by electron-microscope studies, the results of which were published (Trotter & McLean, 1949) after the completion of the present investigation.

The iron–nitrogen system: nitrogen austenite, nitrogen martensite and the tempering of nitrogen martensite

The γ-phase of the iron–nitrogen system (nitrogen austenite) is shown by quantitative X-ray examination to be structurally isomorphous with carbon austenite. When quenched, nitrogen austenite transforms to nitrogen martensite, the structure of which is similar to that of carbon martensite. The behaviour of nitrogen martensites on tempering is, however, quite different from that of the corresponding carbon alloys. At temperatures below 250° C. a new phase, α'', is formed as an intermediate in the decomposition

$$\text{nitrogen martensite } (\alpha') \rightarrow Fe_4N\ (\gamma').$$

Although it is a transition phase, α'' is relatively stable and has a structural unit which contains eight $(2\times2\times2)$ distorted and expanded body-centred tetragonal units of the original martensite structure. The contents of the unit cell, which has dimensions

$$a=5{\cdot}72,\quad c=6{\cdot}29\,\text{A.},\quad c/a=1{\cdot}10,$$

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† Formerly Senior Scientific Officer, B.I.S.R.A. Now at the Chemistry Department, King's College, Newcastle-upon-Tyne 1, England.

are ideally $Fe_{16}N_2$, with iron atoms at

$$0,0,\bar{z};\quad \tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}-z;\quad \tfrac{1}{2},\tfrac{1}{2},z;\quad 0,0,\tfrac{1}{2}+z;$$
$$\tfrac{1}{2},0,0;\quad 0,\tfrac{1}{2},0;\quad \tfrac{1}{2},0,\tfrac{1}{2};\quad 0,\tfrac{1}{2},\tfrac{1}{2};$$
$$\pm(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4});\quad \pm(\tfrac{1}{4},\tfrac{1}{4},\tfrac{3}{4});\quad \pm(\tfrac{1}{4},\tfrac{3}{4},\tfrac{1}{4});\quad \pm(\tfrac{3}{4},\tfrac{1}{4},\tfrac{1}{4}),$$

and with nitrogen atoms at $0,0,\frac{1}{4}$ and $\frac{1}{2},\frac{1}{2},\frac{3}{4}$; $z \fallingdotseq 0{\cdot}06$. The nitrogen atoms therefore occupy one twenty-fourth of the number of octahedral interstices in a completely ordered manner, but up to one-half of the number of nitrogen atom sites may be vacant. For such small concentrations of solute atoms separated by such large distances this type of ordering appears to be unique. The α'' phase is identified as the iron nitride which is reported by Dijkstra (1949) to be precipitated at low temperatures from nitrogen ferrite.

The iron–nitrogen system: the structures of ϵ-iron nitrides and $\epsilon \rightarrow \zeta$ transition

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 and the structure of which has previously 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. A detailed structural investigation over the whole range of compositions has now been completed. At compositions near Fe_3N and Fe_2N, the X-ray data are in agreement with the two structures proposed by Hendricks & Kosting with cell dimensions

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

where a and c are the dimensions of the approximately close-packed hexagonal unit of the iron-atom arrangement. Near Fe_4N, and between Fe_3N and Fe_2N, additional superlattice reflexions, unaccounted for by these previously proposed structures, are observed. Over the complete ϵ range, the true unit of structure has dimensions

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

and although ϵ-Fe_3N and ϵ-Fe_2N are the basic nitrogen-atom arrangements, nitrogen atoms are removed from or added to the Fe_3N structure in a perfectly ordered manner. The proposed 'intermediate' structures are correlated with observed unit-cell dimensional changes.

The ζ-Fe_2N structure is orthorhombic. 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. During the $\epsilon \rightarrow \zeta$ transition, additional superlattice reflexions, which can be indexed only on pseudo-hexagonal unit-cell dimensions

$$a' = (4\sqrt{3})\,a;\quad c' = c,$$

are observed. The transition can occur simply by movement of particular nitrogen atoms to empty interstices directly above or below those previously occupied. Details of such a mechanism account for all the observed X-ray effects.

Although the exact determination of phase boundaries was not one of the objects of the present work, a sufficient number of iron–nitrogen alloys have been examined to make possible the construction of a phase diagram. The general relationships of the phases are in accordance with those proposed by Lehrer (1930) rather than by Eisenhut & Kaupp (1930), but slight differences are found in the positions of phase boundaries. The ζ-phase has not previously been included in any accepted diagram.

Hexagonal nickel, nickel nitride and nickel carbonitrides

A specimen previously considered to be hexagonal metallic nickel (Rooksby, 1942) has now been shown to be nickel nitride, Ni_3N. Accurate intensity measurements and the observation of ten superlattice reflexions show that the structure is isomorphous with those of ϵ-Fe_3N and ϵ-$Fe_3(C,N)$ and is the same as was proposed, on inadequate experimental evidence, by Sachsze & Juza (1943). Anomalous superlattice reflexions observed by Marshall (1947) are unconfirmed. The unit cell dimensions,

$$a = 2{\cdot}6677 \pm 0{\cdot}0005,\quad c = 4{\cdot}3122 \pm 0{\cdot}0005\,\text{A.};\quad c/a = 1{\cdot}6165,$$

are identical for nitrides prepared by different methods and no range of composition is detectable. The nitrogen of nickel nitride may be partly replaced by carbon to form a nickel carbonitride with only small dimensional changes.

A review of available evidence suggests that the existence of a hexagonal allotrope of nickel has not yet been proved. The supposition that the abnormal structure is due to dissolved nitrogen, hydrogen or possibly carbon falls into line with results obtained by Snavely & Vaughan (1949) on the non-existence of 'hexagonal' chromium.

Full accounts of the above investigations are on record (Jack, 1949) and will be published later.

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References

Antia, D. P., Fletcher, S. G. & Cohen, M. (1944). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **32**, 290.

Arbusov, M. & Kurdjumov, G. (1941). *J. Phys. U.S.S.R.* **5**, 101.

Dijkstra, L. J. (1949). *J. Metals, A.I.M.E.* **1**, 252.

Eisenhut, O. & Kaupp, E. (1930). *Z. Elektrochem.* **36**, 392.

Hägg, G. (1934). *J. Iron Steel Inst.* **130**, 439.

Heidenreich, R. D., Sturkey, L. & Woods, H. L. (1946*a*). *Nature, Lond.*, **157**, 518.

Heidenreich, R. D., Sturkey, L. & Woods, H. L. (1946*b*). *J. Appl. Phys.* **17**, 127.

Hendricks, S. B. & Kosting, P. B. (1930). *Z. Krystallogr.* **74**, 511.

Hofer, L. J. E., Cohn, E. M. & Peebles, W. C. (1949). *J. Amer. Chem. Soc.* **71**, 189.

Honda, K. & Nishiyama, Z. (1932). *Sci. Rep. Tohoku Univ.* **21**, 299.

Jack, K. H. (1946). *Nature, Lond.*, **158**, 60.

Jack, K. H. (1948*a*). *Proc. Roy. Soc.* A, **195**, 34.

Jack, K. H. (1948*b*). *Proc. Roy. Soc.* A, **195**, 41.

Jack, K. H. (1949). Ph.D. Thesis, University of Cambridge.

KURDJUMOV, G. & LYSSAK, L. (1947). *J. Iron Steel Inst.* **156**, 21.
LEHRER, E. (1930). *Z. Elektrochem.* **36**, 460.
MARSHALL, W. W. (1947). Ph.D. Thesis, University of Durham.
ROOKSBY, H. P. (1942). *J. R. Soc. Arts*, **90**, 673.
SACHSZE, W. & JUZA, R. (1943). *Z. anorg. Chem.* **251**, 201.
SNAVELY, C. A. & VAUGHAN, D. A. (1949). *J. Amer. Chem. Soc.* **71**, 313.
TROTTER, J. & MCLEAN, D. (1949). *J. Iron Steel Inst.* **9**, 163.

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A graphical method of indexing powder photographs of cubic substances and of determining unit-cell dimensions.

By J. C. DE WIJS, *Willem Smit and Co. Transformatorenfabriek N.V., Nijmegen, Netherlands.*

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This note describes a graphical method by means of which it is possible to determine, without any calculation, both the unit-cell dimension and the indices of the reflexions of cubic substances, when the positions of the diffraction lines on the powder photographs are known.

For the cubic system $\sin^2\theta=(h^2+k^2+l^2)\,\lambda^2/4a^2$, while, for a cylindrical camera, the Bragg angle in degrees is given by $\theta=90L/\pi R$. Here a represents the cell edge, L the distance between corresponding diffraction lines on opposite sides of the undiffracted X-ray beam, and R the diameter of the camera.

By plotting L as a function of a for a given value of $(h^2+k^2+l^2)$, we obtain a smooth curve, which gives for this particular choice of indices the relation between the position of the corresponding diffraction line on the photograph and the cell dimension. Doing so for many values of $(h^2+k^2+l^2)$, we obtain a chart consisting of a large number of curves, from which we can read, conversely, the indices and the unit-cell dimension of the substance under investigation.

The reading of such a graph is carried out very simply by tracing on a strip of paper the measured values of L and by shifting this strip parallel to the L axis across the chart until all marks coincide with the curves. Then for each reflexion the indices are known, while the intersection of the strip with the a axis gives the cell dimension.

Table 1 gives some unit-cell dimensions measured in this way on a graph of 60 × 30 cm. For these readings none of the usual corrections for the line positions has been made.

Table 1. *Results of measurements of cell dimensions*

	a(A.)	
	Graphical	Experimental
Cu	3·66	3·68
Al	4·05	4·04
Ni	3·50	3·52
NaCl	5·60	5·63
KI	7·05	7·05
CaF_2	5·45	5·45
$CaTiO_3$	3·85	3·84

In using this method for measurements of cell dimensions, diffraction lines with a Bragg angle up to about 45° are especially suitable. The accuracy obtainable is about 0·5 % of the measured value, and this method therefore cannot be used for very accurate unit-cell determinations.

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The crystal structure of α-D-glucose.

By T. R. R. MCDONALD and C. A. BEEVERS, *Dewar Crystallographic Laboratory, Edinburgh University, Scotland.*

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In a series of papers published between 1931 and 1935, E. G. Cox and his co-workers gave details of the space groups and unit-cell dimensions of a large number of sugars and sugar derivatives. On the basis of this work, it was suggested that the pyranose ring comprised a nearly planar group of five carbon atoms with one oxygen atom out of the plane (Cox, Goodwin & Wagstaff, 1935). Later work on glucosamine hydrobromide (Cox & Jeffrey, 1939) and sucrose sodium bromide dihydrate (Beevers & Cochran, 1947), however, proved the ring to be of the Sachse *trans* form. No other detailed structure determinations in the sugar series have been reported.

We have made a complete determination of the crystal structure of α-D-glucose. This work, though not yet sufficiently accurate for precise details of the bonding to be given, confirms the above findings relating to the *trans* configuration of the pyranose ring.

Crystal data

The crystals were grown from methanol solution at 18° C., the largest being about 2 mm. in length. Class, orthorhombic bisphenoidal; space group, $P2_12_12_1$; unit-cell dimensions,

$$a=10{\cdot}36\pm0{\cdot}02,\ b=14{\cdot}84\pm0{\cdot}03,\ c=4{\cdot}93\pm0{\cdot}05\text{ A.};$$

density, found 1·563 g.cm.$^{-3}$, calculated on the basis of 4 molecules of $C_6H_{12}O_6$ per unit cell 1·579 g.cm.$^{-3}$. The unit-cell measurements agree well with those of Hengstenberg & Mark (1930), and of Sponsler & Dore (1931). Sets of Weissenberg and oscillation photographs were taken about the three principal crystallographic axes, and the three Patterson projections and several sections at various z-levels were calculated. A correct interpretation of the projections led to the assignment of approximate x and y co-ordinates which were refined by successive Fourier syntheses. The z parameters were obtained very approxi-