X-ray evidence for the interstitial position of carbon in α iron. By G. K. Williamson and R. E. Smallman, *Metallurgy Department, University of Birmingham, England.*

A study of the interstitial position of small atoms in solid solutions by conventional X-ray methods is generally impracticable, since even with the most advanced techniques the changes in intensity are too small to be detected. This is particularly true for the solution of carbon in α iron (maximum solubility about 0·04 atomic%) but an alternative X-ray method, based on the study of the line broadening due to the local strains about the occupied interstices, can be used.

Two types of interstitial sites are available for carbon in α iron as indicated in Fig. 1: the octahedral position at the mid point of a cell edge (co-ordinates 0, 0, $\frac{1}{2}$, etc.)

● Main lattice sites

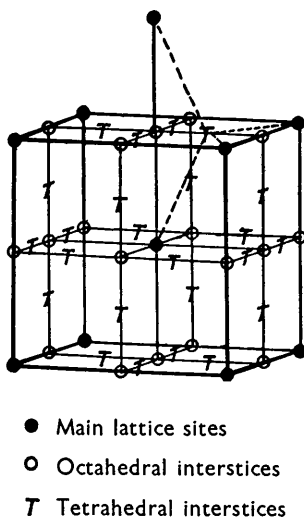○ Octahedral interstices

T Tetrahedral interstices

Fig. 1. Body-centred cubic Bravais lattice showing relative positions of main and interstitial sites. The tetrahedral symmetry of the surrounding lattice sites is shown for one of the tetrahedral interstices.
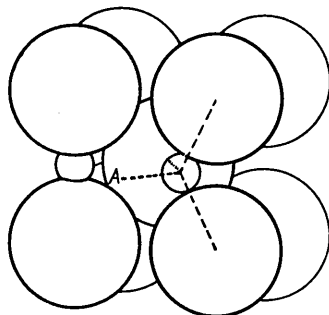

Fig. 2. Schematic representation of a structure cell of iron showing the different distortions produced by the two different interstitial sites. Large circles: iron atoms; small circles: carbon atoms. The octahedral position shown on the left indicates the severe stresses produced along the cell edge, while the tetrahedral position, on the right, produces a more uniform distortion by displacing four iron atoms (only three of which are shown, the fourth (centre *A*) having been omitted for clarity).

and the tetrahedral position midway between any two adjacent octahedral sites on a cell edge and a face centre (co-ordinates 0, $\frac{1}{4}$, $\frac{1}{2}$, etc.). Both sites produce a local distortion if occupied by a carbon atom. The octahedral site, being too small only along the cell edge containing it (Fig. 2), results in local distortion to a tetragonal lattice; tetrahedral siting, on the other hand, produces a more symmetrical distortion since all four nearest iron atoms are displaced equally away from the site. These differences in the symmetry of the distortion for the two sites results in characteristic and detectable variations in the strain broadening with the indices of reflexion in the Debye–Scherrer spectrum.

Measurements of the line breadths have been made in the spectra of annealed iron using a Geiger-counter spectrometer and monochromatized radiation. Specimens were prepared by filing and sieving Armco iron wire containing 0·03–0·06 weight% carbon, and from similar wire after decarburization by a 30 hr. wet hydrogen anneal sufficient to remove the yield point (Low & Gensamer, 1944). Annealing at 650° C. was carried out in a vacuum of better than 5×10^{-5} mm. of mercury to prevent the pick-up of nitrogen which has similar effects to those of carbon. After annealing each specimen was removed from the furnace and rapidly cooled in air. Integral line breadths, obtained using Simpson's rule and graphical resolution of the line shapes (Rachinger, 1948), were very reproducible and even for the lowest-angle reflexion (110), where the largest errors in graphical resolution were expected, the total scatter on the measured breadths was less than 0·05′ in 2θ. The physical broadening due to carbon has been taken as the difference between the breadths from the two samples, since experimental line shapes coincide closely with Cauchy curves. The very small broadening observed was 0·35′, 0·25′ and 1·30′ in 2θ for the 110, 200 and 220 reflexions respectively, this corresponding to strain breadths of $0·47 \times 10^{-4}$ perpendicular to the {100} planes and values of 1·04 and $1·01 \times 10^{-4}$ from the first- and second-order reflexions from the {110} planes. The differences in these last two values may be taken as a measure of the experimental scatter.

The {110} strain breadth due to carbon from a sample quenched in iced brine from 720° C. to retain the carbon in solution was not significantly different from the above value, although ageing at 200° C. for 18 hr. to allow the precipitation of most of the dissolved carbon as cementite (Fe_3C) resulted in a fall of the strain breadth to one-third of its original value. The measured physical broadening is thus due to carbon in solution in α iron and not due to precipitation.

A rigorous calculation of the strain breadth is difficult but an order-of-magnitude estimation is possible by extrapolating to low carbon contents the published data on martensite. The change in axial ratio in martensite, averaged over the three axes, would correspond to a strain breadth of 3×10^{-3} per atomic% carbon, and, taking the solubility of carbon at 650° C. to be 0·04

Table 1. *Calculation of the {100} and {110} strain breadths for the octahedral and tetrahedral sites*

N = number of nearest iron atoms to site.
p = multiplicity of plane.
l = displacement of nearest iron atom away from site.
a = interplanar spacing of {100} planes; $a/\sqrt{2}$ is spacing of {110} planes.
α = 26° 34′ (smallest angle between line of displacement in tetrahedral position and a $\langle 100 \rangle$ direction).
β = 45° − α = 18° 26′.

Site	Plane	Δp	No. of atoms with Δp	$\overline{\Delta p}$	Planes with $\overline{\Delta p}$	$\overline{\Delta d}$	$\overline{\Delta d}/d$	Ratio = B_{100}/B_{110}
Octahedral $N=2$	{100} $p=6$	l	2	l	2	$2l/6$	$l/3a$	
		0	2	0	4			1/2
	{110} $p=12$	$l\cos 45°$	2	$l/\sqrt{2}$	8	$8l/12\sqrt{2}$	$2l/3a$	
		0	2	0	4			
Tetrahedral $N=4$	{100} $P=6$	$l\sin\alpha$	4	$l\sin\alpha$	2	$\tfrac{1}{4}l(\sin\alpha+\cos\alpha)$	$0.4473\,l/a$	
		$l\cos\alpha$ / 0	2 / 2	$l\cos\alpha/2$	4			1/1·501
	{110} $p=12$	$l\sin\beta$ / $l\cos\beta$ / $l\sin\alpha\cos 45°$	1 / 1 / 2	$\tfrac{1}{4}l\left(\dfrac{\sin\beta+\cos\beta}{+2\sin\alpha/\sqrt{2}}\right)$	12	$\tfrac{1}{4}l\left(\dfrac{\sin\beta+\cos\beta}{+\sin\alpha\sqrt{2}}\right)$	$0.6710\,l/a$	

atomic % (Borelius & Berglund, 1951), the predicted strain breadth is $1\cdot 2 \times 10^{-4}$, comparing well with the observed value of $1\cdot 02 \times 10^{-4}$.

The ratios B_{100}/B_{110} of the strain breadths on the {100} and {110} planes for the two sites are readily found since all planes of one form contribute to the reflexion in the Debye–Scherrer spectrum. Thus each breadth will be proportional to the mean fractional perpendicular displacement $\overline{\Delta d}/d$ of the nearest iron atoms from all the planes of each form. In Table 1 this calculation is carried out in two stages by calculating first the mean perpendicular atomic displacement $\overline{\Delta p}$ from each plane of the form, and then the mean $\overline{\Delta d}$ of these values of $\overline{\Delta p}$ for all planes of the form.

For example, if the carbon atom occupies the octahedral position only two iron atoms suffer a direct displacement l, as indicated in Fig. 2, but as this displacement is along one of the cube axes, only two of the six {100} planes are affected; thus $\overline{\Delta d}$ is $2l/6$. Of the twelve {110} planes only the four forming a zone about this axis are unaffected, the two iron atoms having a perpendicular displacement $l/\sqrt{2}$ from the other eight, leading to $\overline{\Delta d} = 8l/12\sqrt{2}$.

Tetrahedral siting produces a displacement of the four nearest iron atoms having a $\overline{4}$ symmetry axis parallel to one of the cube edges. The displacements are not along a symmetry axis and thus the perpendicular displacements of the four neighbours from any one plane are not necessarily equal. Thus only for the two {100} planes perpendicular to this $\overline{4}$ axis are the four atomic displacements equal, and only two of the atoms suffer displacements out of the remaining {100} planes having the $\overline{4}$ axis as zone axis. All twelve {110} planes are distorted equally, although three different individual atomic displacements are involved.

The ratios of the {100} to {110} strain breadths given in Table 1 are significantly different for the two sites,

and the experimental results are sufficiently accurate for an analysis to be made. Since the 220 reflexion gives the greatest accuracy the {110} strain breadth may be taken as $1\cdot 01 \pm 0\cdot 02 \times 10^{-4}$; thus the {100} strain breadth will be $0\cdot 5 \pm 0\cdot 01 \times 10^{-4}$ for octahedral siting and $0\cdot 67 \pm 0\cdot 015 \times 10^{-4}$ for tetrahedral siting. The observed {100} breadth, allowing for an experimental scatter corresponding to $0\cdot 025′$ in measurement, is in the range $0\cdot 42$–$0\cdot 52 \times 10^{-4}$. This result indicates that at least 85 % of the carbon atoms occupy octahedral interstices, a result in agreement with the interpretation of internal friction measurements.

Body-centred cubic iron containing dissolved carbon thus contains many regions in which there is a local distortion to tetragonal symmetry. This fact has presumably been obscured in parameter measurements since the axial ratio changes very rapidly from cell to cell and because at room temperature the 'c' axis for each interstitial site is disordered, leading to a structure which is statistically cubic in an analogous way to the postulated cubic martensite discussed by Zener (1946).

This method of structure analysis has not so far been applied to other systems but as a supplement to existing methods it may be of value, particularly in systems where solubility is not as limited as in the above case.

References

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