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Comparison of X-ray and neutron-diffraction refinements of the structure of cementite Fe_3C*.

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New X-ray intensity measurements have been made (see Experimental) on a powdered sample of cementite and used for a three-dimensional least-squares refinement of the structure. The intensities of 49 peaks were measured, encompassing 77 different Bragg reflexions. 29 peaks could be assigned to individual reflexions. The coordinates given by Lipson & Petch (1940) were used as starting point for refinement. (Although recent electron-diffraction results (Gardin, 1963) have suggested that the carbon atom is at the origin of the cell, this possibility is unequivocally eliminated by two independent sets of neutron-diffraction measurements (Meinhardt & Krisement, 1962; Lyaschenko & Sorokin, 1963)).

The refinement was carried out with only the 29 resolved reflexions, and the final coordinates and e.s.d.'s obtained on this basis are given in Table 1. Observed and calculated structure factors for resolved reflexions are in Table 2 while the corresponding quantities for the unresolved reflexions are in Table 3. The weighted R index ($\{\Sigma w(F_o-F_c)^2/\Sigma wF_o^2\}^{\frac{1}{2}}$) for the 29 resolved reflexions decreased from 7·4% for the Lipson–Petch coordinates to 4·4% for the present final coordinates.

We have also further refined the coordinates derived by Meinhardt & Krisement from their neutron-diffraction measurements. Using only the 10 resolved reflexions (Table 2) the weighted R index based on input parameters was 6·4% and that based on the refined parameters

Table 2. *Structure factors of resolved reflexions calculated for the coordinates of Table* 1, *references* 1 *and* 3

Unobserved reflexions are not included; their calculated intensities are all below the observation threshold

	X-rays		Neutrons	
hkl	$\|F_o\|$	F_c	$\|F_o\|$	F_c
011	8	4	0	−0·16
111	8	5	0·82	−0·70
200	29	−31	1·22	−1·28
002	77	−80	3·40	−3·45
201	56	−56	2·40	−2·48
211	74	74	4·44	4·36
102	105	104	5·72	5·75
220	126	−128		
031	141	−146		
112	76	77	5·75	5·53
221	76	76		
122	49	52	4·30	4·33
212	33	31	3·79	3·65
311	27	−34		
113	26	−27		
240	47	44		
241	30	19		
322	32	−39		
401	95	98		
133	70	−74		
411	32	23		
332	81	−82		
303	100	−94		
313	31	27		
104	75	−70		
143	36	−37		
114	30	−24		
214	21	22		
261	20	16		

Table 1. *Atomic coordinates and e.s.d.'s for* Fe_3C *according to various authors*

Crystallographic parameters for present work: $a=5·090$, $b=6·748$, $c=4·523$ Å
Space group *Pnma* (No. 62) with 8Fe in (*d*), 4Fe in (*c*) and 4C in (*c*)

Atom	Reference*	u	v	w
Fe in (*d*)	1	0·186 ± 0·002	0·063 ± 0·002	0·328 ± 0·002
	2	0·183	0·065	0·333
	3	$0·18_9$ ± 0·011	$0·06_1$ ± 0·005	$0·32_9$ ± 0·009
Fe in (*c*)	1	0·036 ± 0·002	$\frac{1}{4}$	0·852 ± 0·004
	2	0·040		0·833
	3	$0·03_6$ ± 0·008		$0·84_5$ ± 0·012
C in (*c*)	1	0·89 ± 0·02	$\frac{1}{4}$	0·45 ± 0·01
	2	0·86		0·47
	3	0·90 ± 0·02		0·45 ± 0·01
	4	0·854		0·46

* X-ray diffraction

1. Present work.
2. Lipson & Petch (1940).

Neutron diffraction

3. Refined coordinates based on intensity measurements of Meinhardt & Krisement (1962).
4. Lyaschenko & Sorokin (1963): these authors retained the Lipson–Petch iron coordinates but refined their carbon coordinates.

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Table 3. *Structure factor data for unresolved reflexions*

F_c from coordinates of Table 1, reference 1

	$\Sigma(_jF^2)^{\frac{1}{2}}$	
hkl	obs.	calc.
101	31	20
020		
121	167	169
210		
022	180	192
131		
202	142	159
040		
230		
301	151	161
231		
132	130	138
222		
141		
302	64	60
042		
232		
312	185	195
123		
203	56	88
331		
051		
151	63	65
033		
410		
242	138	133
250		
420		
341	184	215
251		
421		
004	146	189
152		
060	159	144
233		
402	142	187
430		
323	49	67
161		
342	91	117
252		
422		
351	57	86
260		
243		
333	55	64
062		
053		

was 3·0%. The new coordinates with their e.s.d.'s are also listed in Table 1. No refinement could be based on the results of Lyaschenko & Sorokin who give intensity values for only three resolved reflexions.

The refined X-ray and neutron-diffraction coordinates agree well among themselves. The only significant difference from the Lipson–Petch results is in the *w* coordinate of the iron atom on the mirror plane. The X-ray and neutron diffraction results for carbon have very similar e.s.d.'s but the X-ray results for the iron atoms are considerably better than the neutron values. Thus the larger number of X-ray reflexions and their greater extent in $\sin\theta/\lambda$ more than compensate for the more accurate neutron-diffraction intensity measurements and their greater sensitivity to the carbon-atom coordinates.

The standard deviations of interatomic distances are about 0·015 Å for Fe $\cdots$ Fe and 0·08–0·14 Å for Fe $\cdots$ C. The limited accuracy of the results from polycrystalline samples does not warrant discussion of the carbon-atom environment beyond that already available in the literature (see the reports of the three earlier structure analyses and also Aronsson & Rundqvist, 1962). The computer program available did not permit the inclusion of the unresolved intensities (due to groups of reflexions) in the refinement process, so that the experimental data obtained have not been fully exploited. However, use of all the measured intensities would only be expected to reduce the e.s.d.'s to about three-quarters of their present values. Evidently measurements on single crystals (Westgren & Phragmén, 1922), preferably by neutron diffraction, are needed to establish the detailed structure of cementite.

Experimental

The present sample was prepared by heating Hägg carbide in a nitrogen stream at 800 °C for 20 minutes. It contained traces of free iron and 12 wt.% of free carbon (non-crystalline). Intensities were measured with a Philips PW1010–PW1050 stabilized generator–diffractometer combination using Co $K\alpha$ (Fe filter) radiation. Standard precautions were taken to ensure accurate results. Integrated intensities of the stronger peaks were measured from chart records while step-scanning was used for the weaker peaks. The cell dimensions and the intensities of some high-angle reflexions were determined from powder photographs (114·6 mm camera, Co $K\alpha$).

The refinement was carried out on an IBM 704 computer with the Busing–Levy program ORXLS. Scale factors were refined but not temperature factors. The scattering factors used were:

f_{Fe} from Watson & Freeman (1961) with Hönl correction $\Delta f' = -3{\cdot}4$ (Cooper, 1963);

b_{Fe} $= 0{\cdot}96 \times 10^{-12}$ cm (*International Tables for X-ray Crystallography*, 1962);

f_{C} from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955);

b_{C} $= 0{\cdot}66 \times 10^{-12}$ cm (*International Tables for X-ray Crystallography*, 1962);

$\langle B \rangle = 0$ and 0·25 Å² for X-ray and neutron diffraction refinements respectively.

X-ray structure factors were weighted according to the accuracy of the experimental measurements; neutron structure factors were given equal weights, more appropriate weights not being available.

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