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DETERMINATION OF THE POSITION OF CARBON IN CEMENTITE BY THE NEUTRON DIFFRACTION METHOD

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The position of the carbon atoms in the crystal lattice of cementite Fe_3C (space group D_{2h}^{16}/P_{bnm}) has been determined by the neutron diffraction method. It has been found that the so-called *c* model is realized with the carbon parameters $\lambda = 0.46$ and $\mu = -0.146$, according to which each carbon atom is surrounded by six iron atoms, forming a trigonal prism with the following Fe–C distances: 2.16; 2.16; 1.90; 1.90; 1.93 and 1.85 A.

Introduction

The literature does not yet contain complete data on the structure of cementite (Fe_3C), one of the principal component phases of iron-carbon alloys. Existing data on the position of the carbon atoms in Fe_3C are far from reliable, in view of the fact that the x-ray method, by means of which these data were obtained, has low sensitivity in the determination of the coordinates of light atoms.

The unit cell of cementite was determined by Westgren and Phragmen as long ago as 1922 [1]. Hendricks [2] used these data to find the space group and the position of the iron atoms. It was found that Fe_3C has an orthorhombic lattice, described by the space group D_{2h}^{16}/P_{bnm}. The unit cell of Fe_3C contains 12 iron atoms and 4 carbon atoms, the former having the following coordinates:

$$r_1\,(x, y, z);\quad r_5\,(1/2 - x, 1/2 + y, z);$$
$$r_2\,(\bar{x}, \bar{y}, \bar{z});\quad r_6\,(1/2 + x, 1/2 - y, \bar{z});$$
$$r_3\,(x, y, 1/2 - z);\quad r_7\,(1/2 - x, 1/2 + y, 1/2 - z);$$
$$r_4\,(\bar{x}, \bar{y}, 1/2 + z);\quad r_8\,(1/2 + x, 1/2 - y, 1/2 + z);$$

$$r_9\,(u, v, 1/4);$$
$$r_{10}\,(\bar{u}, \bar{v}, 3/4);$$
$$r_{11}\,(1/2 - u, 1/2 + v, 1/4);$$
$$r_{12}\,(1/2 + u, 1/2 - v, 3/4).$$

As regards the position of the carbon atoms, both Hendricks and later Westgren [3] merely indicated their possible positions. Lipson and Petch [4] in their calculations used the values they had found for the reflection intensities. The authors give the following values for the parameters of the iron atoms:

$$8Fe \quad \text{for} \quad x = 0.333;\quad y = 0.183;\quad z = 0.065;$$
$$4Fe \quad \text{for} \quad u = -0.167;\quad v = 0.040.$$

From geometrical considerations, three models of the arrangement of the carbon atoms in Fe_3C are possible:

$$a - (000);\ (0, 0, 1/2);\ (1/2, 1/2, 0);\ (1/2, 1/2, 1/2);$$
$$b - (1/2, 0, 0);\ (1/2, 0, 1/2);\ (0, 1/2, 0);\ (0, 1/2, 1/2);$$
$$c - (\lambda, \mu, 1/4);\ (\bar{\lambda}, \bar{\mu}, 3/4);\ (1/2 - \lambda, 1/2 + \mu, 1/4);$$
$$(1/2 + \lambda, 1/2 - \mu, 3/4).$$

In calculating the electron density in the planes $z = 0$ and $z = 1/4$, Lipson and Petch came to the conclusion that the arrangement of the carbon atoms corresponds to model *c*. They give the following parameters for the carbon atoms:

$$\lambda = 0.47;\quad \mu = -0.14.$$

From the electron density diagrams given in [4], however, it is difficult to give the preference to either of the two models *a* or *c*. The inference made is unconvincing, since the mean difference between the calculated and observed structure amplitudes is 1.13, and the value of the mean carbon contribution to the structure amplitude of Fe_3C is 1.24. Thus, the carbon contribution to the structure amplitude lies within the limits of error of measuring the reflection intensities.

In the case of the diffraction of neutrons, the scattering amplitudes for iron and carbon are already comparable ($0.96 \cdot 10^{-12}$ and $0.66 \cdot 10^{-12}$ cm, respectively), and consequently the carbon contribution to the structure amplitude of Fe_3C is substantially greater than the error in the determination of reflection intensity.

1. Fe_3C Specimen

The cementite powder was obtained from carbon steel U-12, water-quenched from 1000°C and tempered at 600°C for one h in an argon atmosphere. The tempered steel was subjected to anodic solution in a 5% aqueous solution of HCl. The powder was collected in colloid bags. The precipitate was carefully washed and dried. The x-ray photograph of the powder (exposure was in Cr radiation in 57.3 mm diameter camera) showed the presence of the same 15 primary reflections with the same intensities as in [4]. In contrast to [4], the (022) and (103) reflections were resolved. In addition, the intensities of the 14 succeeding reflections, corresponding to the extinction law for the group D_{2h}^{16}/P_{bnm}, to which cementite belongs, were determined.

The specimen for neutron structural analysis was a cylindrical duralumin container having a wall thickness of 0.1-0.2 mm, diameter 9 mm and height 55 mm, in which the cementite was placed. Plotting of the neutron diffraction curves was carried out by means of apparatus UNSA [5].

2. Method of Calculating the Fe_3C Neutron Diffraction Patterns

The intensity of the reflections I_{hkl} is written in the form

$$I_{hkl} = KA \frac{|F_{hkl}|^2}{\sin\vartheta \sin 2\vartheta} e^{-2M} H,$$

where K is a coefficient of proportionality denoting other generally accepted quantities. For the case of diffraction of neutrons by the cementite specimen, the factors A and e^{-2M} may be omitted, and the formula assumes the form

$$I_{hkl} = K \frac{|F_{hkl}|^2}{f(\vartheta)} H,$$

where $f(\vartheta) = \sin\vartheta \sin 2\vartheta$.

The structure amplitudes of Fe_3C for the case of nuclear scattering of neutrons for the three possible carbon positions have the form

$$\begin{aligned} F^a_{\text{nuc}\,hkl} = 2f_{\text{Fe}} \Big\{ &\cos 2\pi (hx + ky + lz) \\ &+ (-1)^l \cos 2\pi (hx + ky - lz) \\ &+ (-1)^{h+k} \cos 2\pi (-hx + ky + lz) \\ &+ (-1)^{h+k+l} \cos 2\pi (-hx + ky - lz) \\ &+ \cos 2\pi \left(hu + kv + \frac{1}{4} l\right) \\ &+ (-1)^{h+k} \cos 2\pi (-hu + kv + {}^1/_4 l)\Big\} \\ &+ f_c \{1 + (-1)^l + (-1)^{h+k} + (-1)^{h+k+l}\} \\ = F^{\text{Fe}}_{\text{nuc}\,hkl} &+ f_c \{1 + (-1)^l + (-1)^{h+k} + (-1)^{h+k+l}\}; \end{aligned}$$

$$\begin{aligned} F^b_{\text{nuc}\,hkl} = F^{\text{Fe}}_{\text{nuc}\,hkl} &+ f_c \{(-1)^h \\ &+ (-1)^{h+l} + (-1)^k + (-1)^{k+l}\}; \end{aligned}$$

$$\begin{aligned} F^c_{\text{nuc}\,hkl} = F^{\text{Fe}}_{\text{nuc}\,hkl} &+ 2f_c \{\cos 2\pi (h\lambda + k\mu + {}^1/_4 l) \\ &+ (-1)^{h+k} \cos 2\pi (-h\lambda + k\mu + {}^1/_4 l)\}. \end{aligned}$$

The theoretical article [6] gives the calculated values of $\frac{|F_{hkl}|^2}{f(\vartheta)}$ $(2\vartheta \leqslant 46°, \lambda = 1 \text{ A})$ for case c and for some reflections for cases a and b. We have calculated the values of $\frac{|F_{hkl}|^2}{f(\vartheta)}$ for these two cases and have corrected the erroneous values given in [6] for case c. The data obtained are given in the table, from which it will be seen that the carbon atoms make a considerable contribution to the total nuclear structure amplitude in the case of neutron diffraction.

It is known that cementite is a weak ferromagnetic material. In this case, with scattering of nonpolarized neutrons, the structure amplitude has the form

$$F^2_{\text{tot}} = F^2_{\text{nuc}} + {}^2/_3 F^2_{\text{magn}},$$

where F_{nuc} and F_{magn} are the structure amplitudes for nuclear and magnetic scattering, respectively. The square of the structure amplitude for magnetic scattering, by analogy with nuclear scattering, may be written

$$F^2_{\text{magn}} = \Big[\sum_j p e^{2\pi i (hx_j + ky_j + lz_j)}\Big]^2,$$

where $x_j y_j z_j$ are the coordinates of the magnetic iron ions, which are basic, and p is the amplitude of magnetic scattering, equal to

$$p = \left(\frac{e^2\gamma}{mc^2}\right) Sf,$$

where $\frac{e^2}{mc^2} = 2.818 \cdot 10^{-13}$ cm, the radius of an electron, $\gamma = 1.91$, μ_B is the magnetic moment of a neutron, S, the spin quantum number, f, the magnetic form factor of the atom. Assuming that in Fe_3C, the iron is in the divalent state, for S = 2 we get

$$p = 1.075 \cdot f \cdot 10^{-12} \text{ cm}.$$

Data regarding the magnetic form factor for Fe^{++} have been taken from [7]. As will be seen below, the chemical and magnetic lattices of cementite coincide. The recurrence factors for magnetic reflections are therefore the same as for nuclear reflections. The combined integral intensity for nuclear and magnetic scattering has the form

$$I_{hkl} = K \frac{F^2_{\text{nuc}} + {}^2/_3 F^2_{\text{magn}}}{f(\vartheta)} H,$$

and in the case of superimposed reflections

$$I_{hkl} = K \sum_i \frac{F^2_{\text{nuc}\,i} + {}^2/_3 F^2_{\text{magn}\,i}}{f(\vartheta_i)} H_i.$$

hkl	H	I^a_{nuc}	I^b_{nuc}	I^c_{nuc}	I_{magn}	I^a_{tot}	I^b_{tot}	I^c_{tot}	I_{exp}	$\frac{I_{exp}-I^a_{tot}}{I_{exp}}$, %	$\frac{I_{exp}-I^b_{tot}}{I_{exp}}$, %	$\frac{I_{exp}-I^c_{tot}}{I_{exp}}$, %
020	2	1.84	1.84	11.69	2.31	4.15	4.15	14.0	16	74	74	13
112	8	69.67	322.25	22.68	38.01	107.68	360.26	60.69	57	89	532	6.5
021	4											
200	2	57.94	57.94	49.51	22.63	80.57	80.57	72.14	69	16.8	16.8	4.6
120	4											
113	8	205.4	205.4	343.28	21.42	226.82	226.82	364.7	348	34.8	34.8	4.8
202	4											
122	8											
212	8	50.12	50.12	75.27	3.71	53.83	53.83	78.98	85	36.7	36.7	7.1
004	2	89.64	89.64	116.2	2.41	92.05	92.05	118.61	110	14	14	10.8
023	4											
220	4											
221	8	17.08	17.08	79.79	0.84	17.92	17.92	80.63	72	75	75	12
130	4	115.93	16.58	104.82	2.39	118.32	18.97	107.21	104	13.8	81.8	3.1
123	8											
222	8	197.89	128.19	59.08	1.59	199.48	129.78	60.67	72	177	80.2	15.7
114	8											
310	4	118.11	91.96	62.88	0.74	118.85	92.7	63.62	60	98	54.6	6
311	8											
132	8											
024	4											
312	8	193.02	27.80	144.03	0.96	193.98	28.76	145	161	20.5	82.1	10
231	8											
						Reliability factor				59	98.4	8.5

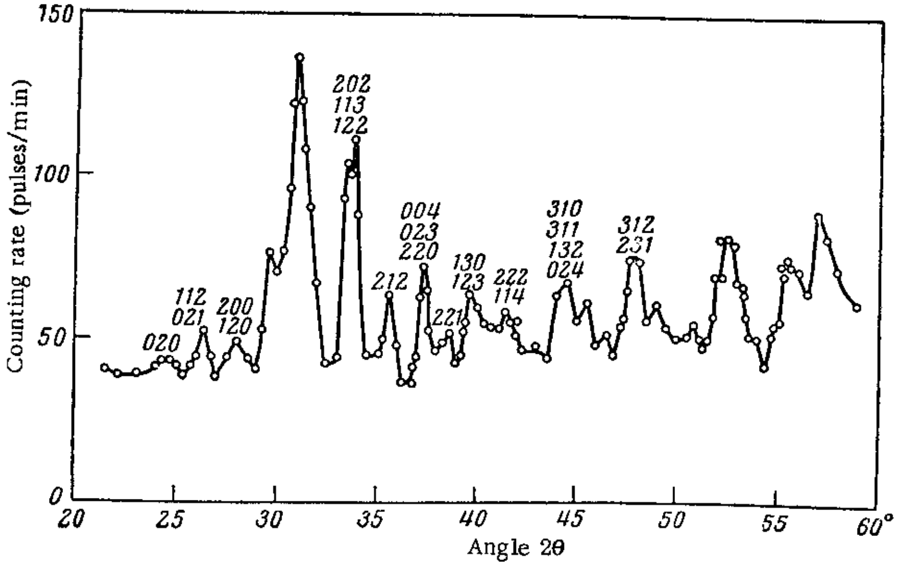

Fig. 1. Neutron diffraction curve of Fe_3C (λ = 1.07 A).

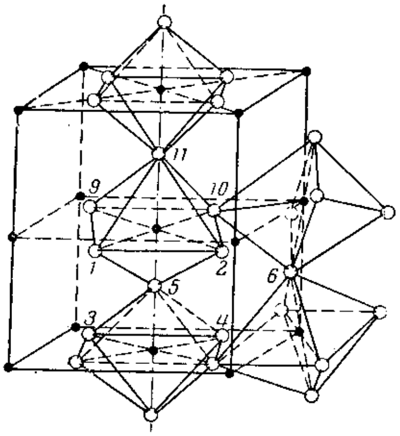

Fig. 2. Crystal lattice of Fe_3C according to model a. ○) Fe atoms; ●) C atoms.

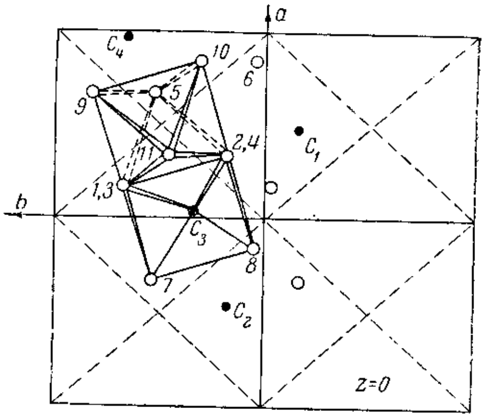

Fig. 3. Projection of lattice on the plane z = 0 according to model c. ○) Projections of Fe atoms; ●) projections of C atoms.

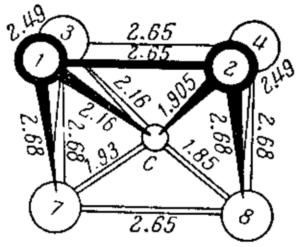

Fig. 4. Structural element of the Fe_3C crystal lattice.

3. Results and Their Discussion

Figure 1 shows the neutron diffraction curve of Fe_3C for radiation $\lambda = 1.07$ A, with a static counting error ~4% in the maxima and ~7% for the background. The positions of all the reflections coincide with the calculated positions. For comparison with the calculated intensities, 11 reflections marked on the diagram have been selected, most of which are not resolved or are only partly resolved.

In the table, the experimental values of the intensities (corrected for the diffraction contribution by the duralumin container) are compared with the theoretical values for nuclear (I_{nuc}) and total (I_{tot}) scattering for the 11 reflections. The table shows that the experimental values of the intensities are in good agreement with the values calculated for case c. Calculation of the deviations $(I_{exp}-I_{tot})/I_{exp}$ and the reliability factors show quite clearly that the carbon atoms are in the c position. The data of Lipson and Petch on the carbon parameters were refined on the basis of the intensities of single (020), (212) and (221) reflections (the first reflection was measured with special care).

A number of authors, not relying on the results of x-ray diffraction determinations of the position of the carbon atoms in the Fe_3C lattice, have hitherto made use of purely theoretical notions. Thus, the textbook of Gulyaev [8] gives a model a, according to which the carbon atoms are situated at the center of an octahedron formed by six numbered iron atoms (Fig. 2).

By making use of the coordinates of the basic iron and carbon atoms (the latter according to the data of the present work), the projection on the plane z = 0 shown in Fig. 3 may be obtained. The positions (1, 3) and (2, 4) in Fig. 3 correspond to the iron atoms 1, 2, 3, 4 in Fig. 2. The octahedron situated at the center of the cell in Fig. 2 gives the projection 9, 5, 10, 2, 11, 1 on the plane z = 0 (Fig. 3). The carbon atoms C_1, C_2, C_3 and C_4 in Fig. 3, according to the data obtained, correspond to the positions of the basic carbon atoms. It can be seen that the carbon is situated in an environment of iron atoms 1, 3, 2, 4, 7, 8, forming a trigonal prism, which Lipson and Petch consider to be the structural element of the cementite lattice. The coordinates of the iron atoms 1, 2, 3, 4, 7, 8 and the carbon atom C_3, composing this structural element, are the following:

$$Fe_1\,(1/2-x;\;1/2+y;\;1/2-z);\quad Fe_4\,(x;\;y;\;z);$$
$$Fe_2\,(x;\;y;\;1/2-z);\quad Fe_7\,(\bar{u}-1/2;\;1/2+v;\;1/4);$$
$$Fe_3\,(1/2-x;\;1/2+y;\;z);\quad Fe_8\,(u;\;v;\;1/4);$$
$$C_3-(1/2-\lambda;\;1/2+\mu;\;1/4),$$

where $u = -0.167$, $v = 0.040$ [4] and $\lambda = 0.46$, $\mu = -0.146$ (refined values).

The spatial arrangement of the iron atoms in the prism is shown in Fig. 4. The Fe–Fe and Fe–C distances are as follows:

$$\left.\begin{matrix}\mathrm{Fe_1 - Fe_3}\\ \mathrm{Fe_2 - Fe_4}\end{matrix}\right\}2.49\ \mathrm{A};\qquad \left.\begin{matrix}\mathrm{Fe_1 - Fe_2}\\ \mathrm{Fe_3 - Fe_4}\\ \mathrm{Fe_7 - Fe_8}\end{matrix}\right\}2.65\ \mathrm{A};$$

$$\left.\begin{matrix}\mathrm{Fe_1 - C}\\ \mathrm{Fe_3 - C}\end{matrix}\right\}2.16\ \mathrm{A};\qquad \left.\begin{matrix}\mathrm{Fe_2 - C}\\ \mathrm{Fe_4 - C}\end{matrix}\right\}1.905\ \mathrm{A};$$

$$\left.\begin{matrix}\mathrm{Fe_1 - Fe_7}\\ \mathrm{Fe_3 - Fe_7}\\ \mathrm{Fe_2 - Fe_8}\\ \mathrm{Fe_4 - Fe_8}\end{matrix}\right\}2.68\ \mathrm{A};$$

$$\mathrm{Fe_7 - C} - 1.93\ \mathrm{A};$$

$$\mathrm{Fe_8 - C} - 1.85\ \mathrm{A}.$$

The mean value of the Fe–C distance is 1.985 A. The minimum Fe–C distance, 1.85 A, is much greater than the sum of the radii of the divalent iron ion (0.82A), according to Goldschmidt, and the carbon atom (0.77A). Thus, the cavity inside the trigonal prism is quite sufficient to accommodate a carbon atom.

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