CONTRIBUTION FROM THE NATIONAL PHYSICAL RESEARCH LABORATORY OF THE SOUTH AFRICAN COUNCIL
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Identification of Eckstrom–Adcock Iron Carbide as Fe_7C_3[1]

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The iron carbide first reported by Eckstrom and Adcock[2] has been identified as Fe_7C_3 by demonstrating its isomorphism with Cr_7C_3, Ru_7B_3, and related substances. A hexagonal $D10_2$ structure with $a = 6.882$ and $c = 4\,540$ Å., space group $P6_3mc$, and atomic coordinates taken from Ru_7B_3[3] gives calculated *d* values and intensities which agree satisfactorily with the observed (by diffractometer) powder pattern. However, the sensitivity of the present measurements is not sufficient to allow rejection of the superstructure proposed by Westgren.[4]

Introduction

A ferromagnetic iron carbide (Curie point 250 ± 3°) was found by Eckstrom and Adcock[2] in the catalyst charge of their fluidized-bed hydrocarbon synthesis plant. An X-ray diffraction pattern was obtained and the composition FeC was inferred from chemical analyses. The same carbide, identified by its X-ray diffraction pattern, was reported by Louw, *et al.*,[5] to form under similar conditions in the Kellogg fluidized-bed synthesis at Sasolburg, South Africa. This carbide does not form in the pilot plant at Sasolburg nor has it been found possible to synthesize it in the laboratory using accepted methods of carbide synthesis.[6] Eckstrom–Adcock carbide also occurs among the reaction products from the high-pressure, high-temperature synthesis of diamond when iron is used as solvent for carbon.[7] A crystal structure has not yet been proposed for this carbide nor has its chemical composition been determined unequivocally. We now wish to present X-ray diffraction evidence that shows that Eckstrom–Adcock carbide is isomorphous with the known phases Cr_7C_3[8] and Mn_7C_3[4,8] and that its chemical composition must therefore be very close to Fe_7C_3 and is not FeC as originally suggested. A crystal structure is also proposed by analogy with known structures; however the existence of a somewhat more complicated variant of the atom arrangement proposed cannot be ruled out on the basis of existing evidence.

A similar method of identification has recently been applied to Hägg carbide by Senateur, Fruchart, and Michel.[9] These authors have shown that Hägg carbide is isomorphous with Mn_5C_2 and therefore has the formula Fe_5C_2.

Identification from A.S.T.M. X-Ray Powder Data File

Reference of the powder data for "FeC" given by Eckstrom and Adcock[2,10] (or equally that given by Louw, *et al.*[5]) to the A.S.T.M Index showed at once that there was a close resemblance between the patterns of "FeC" and Cr_7C_3[11,12] in both line positions and relative intensities. Kohn and Eckart[7] have already pointed out that the Cr_7C_3 pattern has features in common with those obtained from 1:1 (*sic*) Mn and Fe carbides found in diamond synthesis reaction samples but they have not drawn any conclusions from this.

Confirmation of Identification by Comparison with Isomorphous Structures

The tentative identification made through the A.S.T.M. Index has been confirmed by comparing the *d* values and integrated intensities of the experimental powder pattern (redetermined here by diffractometer techniques—see Experimental section) with the pattern calculated from the crystal structure postulated for Fe_7C_3. Before giving these results it is necessary to consider the structure postulated for Fe_7C_3.

Westgren[4] has proposed a structure for Cr_7C_3 based on the examination of single crystals. This structure is closely related to the analogous structures Ru_7B_3[3] and Th_7Fe_3[13] (single-crystal methods) and Rh_7B_3[14] and Re_7B_3[14] (powder methods). The cell dimensions reported for these phases are compared in Table I. Westgren's structure for Cr_7C_3 can be described[4] as a slightly distorted superstructure of Ru_7B_3, with a doubled *a* axis and lower symmetry (trigonal instead of hexagonal). The powder patterns of Cr_7C_3 and Fe_7C_3

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(1) Work supported by South African Coal, Oil and Gas Corporation.

(2) H. C. Eckstrom and W. A. Adcock, *J. Am. Chem. Soc.*, **72**, 1042 (1950).

(3) B. Aronsson, *Acta Chem. Scand.*, **13**, 109 (1959).

(4) A. Westgren, *Jerkont. Ann.*, **118**, 231 (1935), and references therein.

(5) J. D. Louw, J. P. van den Berg, L. C. Ferreira, and J. P. Pienaar, *J. Am. Chem. Soc.*, **79**, 5899 (1957). We are indebted to Dr. Louw for provision of some of this material (SASOL Code No. X-188) for the present investigation.

(6) J. D. Louw, private communication, Sept., 1963.

(7) J. A. Kohn and D. W. Eckart, *Am. Mineralogist*, **47**, 1422 (1962).

(8) K. Kuo and L. E. Persson, *J. Iron Steel Inst.*, **178**, 39 (1954).

(9) (a) J.-P. Senateur, R. Fruchart, and A. Michel, *Compt. rend.*, **255**, 1615 (1962); (b) J.-P. Senateur and R. Fruchart, *ibid.*, **256**, 3114 (1963).

(10) A.S.T.M. X-ray Powder Data Card No. 6-0686.

(11) A.S.T.M. X-ray Powder Data Card No. 6-0687. Results taken from W. Crafts and J. L. Lamont, *Trans. A.I.M.E.*, **185**, 957 (1949). The carbide was extracted electrolytically from a chromium steel but its exact chemical composition was not determined.

(12) A.S.T.M. X-ray Powder Data Card No. 5-0720. Results taken from H. J. Goldschmidt, *Metallurgia*, **40**, 103 (1949). The samples were mixed iron–chromium carbides $(Fe,Cr)_7C_3$, both extracted electrolytically from chromium steels and prepared synthetically. Mn_7C_3 gave a virtually identical pattern. There is another card in the Index (3-0975) which is labeled "Cr_7C_3 and Mn_7C_3" and cites Westgren[4] as reference. Comparison of this card with cards No. 6-0686, 6-0687, 5-072, and the present results shows that the *hk*0 reflections given by Westgren have been omitted from card No. 3-0975.

(13) J. V. Florio, N. C. Baenziger, and R. E. Rundle, *Acta Cryst.*, **9**, 367 (1956).

(14) B. Aronsson, E. Stenberg, and J. Åselius, *Acta Chem. Scand.*, **14**, 733 (1960).

TABLE I

CRYSTALLOGRAPHIC PARAMETERS FOR ISOMORPHOUS Th_7Fe_3 ($D10_2$) TYPE PHASES

Formula	*a*, Å.	*c*, Å.	Space group	Ref.
Th_7Fe_3	9.85	6.15	$P6_3mc$	13
Re_7B_3	7.504	4.882	$P6_3mc$	14
Ru_7B_3	7.467	4.713	$P6_3mc$	12
Rh_7B_3	7.471	4.777	$P6_3mc$	14
Cr_7C_3	13.90	4.54	P31c	6
	6.910	4.495	$P6_3mc$	*a*
Mn_7C_3	13.98	4.523	P31c	6
Fe_7C_3	6.882	4.540	$P6_3mc$	*b*

[a] Present indexing of A.S.T.M. pattern 6-0687. [b] Present indexing of diffractometer pattern recorded here (see Table II for experimental data).

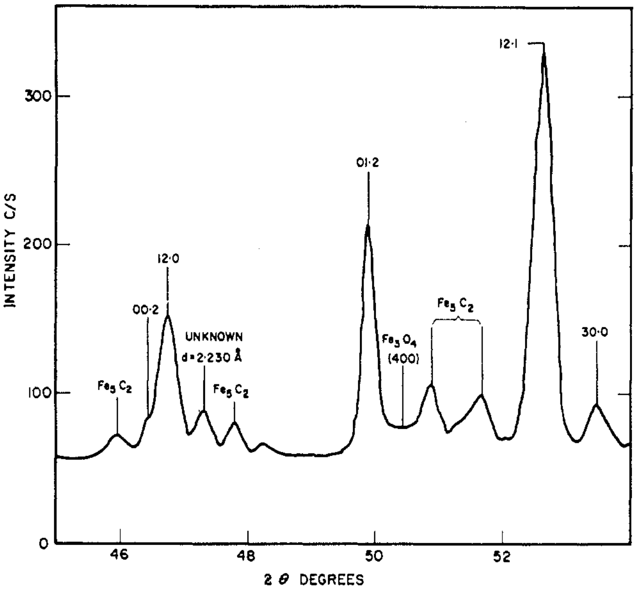

Fig. 1.—A portion of the diffraction pattern (Co Kα radiation with Fe filter) of Fe_7C_3 showing the presence of Fe_3O_4, Hägg carbide, and an unknown impurity.

TABLE II

OBSERVED AND CALCULATED *d* SPACINGS, INTENSITIES, AND STRUCTURE FACTORS FOR Cr_7C_3 AND Fe_7C_3, ASSUMING HEXAGONAL SYMMETRY AND Ru_7B_3 STRUCTURE

Cr_7C_3[a]				Fe_7C_3[b]					
d_{obsd}, Å.	d_{calcd}, Å.	*hk.l*	I_{measd}	d_{obsd}, Å.	d_{calcd}, Å.	*hk.l*	I_{measd}[c]	$\lvert F_{obsd}\rvert$	$\lvert F_{calcd}\rvert$
				2.270	2.270	00.2	7	65	70
2.27	2.262	12.0	50	2.255	2.253	12.0	31	58	58
2.10	2.104	01.2	60	2.122	2.121	01.2	41	72	73
2.02	2.020	12.1	100	2.019	2.018	12.1	100	85	89
1.99	1.995	30.0	20	1.989	1.987	30.0	13	63	58
1.90	1.884	11.2	10	1.895	1.895	11.2	5	29	26
1.82	1.823	30.1	30	1.820	1.820	30.1	11	45	74
1.79[d]	1.797	02.2	50	1.807[d]	1.806	02.2	22	64	62
1.73[d]	1.728	22.0	30	1.720[d]	1.720	22.0	13	74	76
1.59	1.594	12.2	10	...	...	...	...	...	..
1.42[d]	1.420	40.1	30	1.417[d]	1.416	40.1	4	35	40
1.34[d]	1.340	02.3	30	1.349[d]	1.349	02.3	8	58	42
1.315	1.313	32.1	20	...	...	...	...	...	..
	1.305	31.0							
1.245	1.249	21.3	10	...	...	...	...	...	..
	1.245	04.2							
1.195[d]	1.198	30.3	50	1.204	1.204	30.3	14	68	65
	1.197	50.0			1.192	50.0		44	42
1.172	1.172	32.2	50	1.171[d]	1.171	32.2	15	54	49
1.159	1.157	50.1	30	1.153	1.153	50.1	11	66	66
1.154	1.152	33.0	30	1.146	1.147	33.0	13	104	90
				1.131	1.135	00.4	5		
					1.128	14.2			
				1.117	1.116	13.3	6		
					1.115	01.4			

[a] Cr Kα radiation. [b] Co Kα radiation. [c] Integrated intensities. [d] These reflections used to calculate *a* and *c* by least-squares method as described in the text. *a* and *c* values listed in Table I.

can be indexed in terms of hexagonal cells isomorphous with Ru_7B_3 (this is certainly true for Mn_7C_3 as well but the re-indexing has not been carried out because a separate pattern for Mn_7C_3 has not been published in the A.S.T.M. Index). Superstructure lines were not reported in the published patterns for Cr_7C_3[11,12] and Fe_7C_3[2,5] and we have not been able to detect any in our pattern for Fe_7C_3. The strongest superstructure lines reported by Westgren[4] are close to the detection limit in our diffraction pattern and our failure to observe them cannot be interpreted as unequivocal refutation of Westgren's structure. Nevertheless, *for our present purposes*, we shall consider Cr_7C_3 and Fe_7C_3 to be isomorphous with Ru_7B_3 as Westgren's superstructure would appear to give observable effects only in single-crystal patterns. (No single crystals of these phases were available to us for a check on the existence of the superstructure.)

Values of the observed structure factors $|F_{obsd}|$ for Fe_7C_3 are given in Table II together with values of $|F_{calcd}|$. Values of $|F_{obsd}|$ were placed on an absolute scale by comparison with $|F_{calcd}|$. The agreement between the two sets of values is sufficiently good to substantiate the proposed structure (the reflections omitted in Table II all have calculated intensities below the limit of observation) but there are significant differences for the reflections 03.1 and 02.3. These discrepancies probably are due to inadequacy of the atomic coordinates used in calculating structure factors; no attempt has been made to refine the coordinates because of the small number of $|F_{\text{obsd}}|$ values available.

The crystal chemistry of phases related to Fe_7C_3 has recently been discussed.[9b,15]

Experimental

Diffractometer Measurements.—The sample used was obtained from Dr. J. D. Louw[5] (S.A. Coal, Oil and Gas Corporation, Sasolburg, South Africa). The present X-ray measurements were made using a Philips PW 1010 highly-stabilized X-ray generator, a PW 1050 diffractometer, and associated counting equipment. The argon-filled Geiger counter used was linear to about 400 c.p.s. and this counting rate was not exceeded. Co Kα radiation (Fe filter, 36 kv., 10 ma.) was used; the specimen was contained in a PW 1064 specimen spinner; the angular velocity of the counter was 1/8° 2θ per minute. Integrated intensities were obtained by planimeter integration of chart records. The intensity measurements covered a period of 3 days and suitable checks were made on standard peaks to ensure that no drift in the apparatus had occurred during this time.

A portion of the diffraction pattern is shown in Fig. 1. The impurities detected were Fe_3O_4, Hägg carbide (Fe_5C_2), and an unknown material giving a diffraction peak at $2\theta = 47.30°$ ($d = 2.230$ Å.). All the other reflections could be indexed in terms of the $D10_2$ structure. The following procedure was used. First systematic errors in d values were corrected by using the magnetite reflections as internal standards. Then values of a and c were derived for a hexagonal crystal, using the most accurately measured reflections. The five reflections used are marked in Table II; the best fit was achieved by using a least-squares program written here by Mrs. C. W. Pistorius for a Stantec Zebra electronic computer. Excellent agreement was obtained between the d values calculated on this basis and the measured d values of the reflections not considered in the derivation of a and c.

Calculation of Structure Factors.—The atomic parameters used in the calculation of structure factors were

6	Fe_I	in 6(c)	$u_I = 0.4563$	$w_I = 0.318$
6	Fe_{II}	in 6(c)	$u_{II} = 0.1219$	$w_{II} = 0$
6	Fe_{III}	in 2(b)	$u_{III} = 0.3333$	$w_{III} = 0.818$
6	C	in 6(c)	$u_c = 0.187$	$w_c = 0.580$

These are the coordinates of the Ru_7B_3 structure.[3] The atomic scattering factors were: Fe from Watson and Freeman.[16] Hönl correction $\Delta f' = -3.5$.[17] C from Berghuis, *et al.*[18] A single isotropic temperature factor $B = 3.0$ Å.^{2} was used.

The calculations were carried out on an IBM 704 computer, using Busing and Levy's program OR XLS.

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(15) B. Aronsson and S. Rundqvist, *Acta Cryst.*, **15**, 878 (1963).

(16) R. E. Watson and A. J. Freeman, *ibid.*, **14**, 27 (1961).

(17) M. J. Cooper, *ibid.*, **16**, 1067 (1963).

(18) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

Notes

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Fluoroalkyl Borate Esters[1,2]

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There are two reports of fluoroalkyl borate esters in the literature. The first, tris(2,2,2-trifluoroethyl) borate, was prepared by Abel and co-workers[3] by the low temperature reaction of trifluoroethanol and boron trichloride in *n*-pentane. These workers reported a boiling point at reduced pressure for the compound and noted that it formed a coordination complex with pyridine. Schroeder[4] attempted the chlorination of several α,α-dihydrofluorinated borates, $(R_FCH_2O)_3B$, prepared in petroleum ether solution from boron trichloride and the alcohols.

Discussion

Fluoroalkyl Borates.—In the work reported here, a series of fluoroalkyl borates, $(H(CF_2CF_2)_xCH_2O)_3B$, where $x = 1$, 2, 3, and 4, has been prepared in yields up to 95% by direct reaction of the corresponding α,α,ω-trihydroperfluoroalkanols, $H(CF_2CF_2)_xCH_2OH$, and boron trichloride. Physical properties are listed in Table I.

The inductive effect of fluorine atoms on the alkyl groups of the borate ester should decrease interaction of unbonded oxygen electron pairs with the vacant p_z orbital of the boron atom in the esters. This decrease in "back bonding" should decrease boron shielding and the B^{11} n.m.r. chemical shift for the fluoroalkyl borate esters might be expected to be at lower fields than that for the alkyl borates. The B^{11} n.m.r. chemical shifts of alkyl borates and fluoroalkyl borates were found to be approximately equivalent ($\delta = -16.5$ to -18 p.p.m.)[5] so that if this effect prevails, it is not mirrored in the n.m.r. spectra.

Reaction of Fluoroalkyl Borates and Amines.—In work previously reported from this laboratory[6] the

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(2) This work was presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(3) E. W. Abel, W. Gerrard, M. F. Lappert, and R. Shefferman, *J. Chem. Soc.*, 2895 (1958).

(4) H. Schroeder, *J. Org. Chem.*, **25**, 1682 (1960).

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(6) H. Landesman and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 2663 (1961).