Crystalline forms of Carbides and Silicides of Iron and Manganese (' *Ferro-manganese*,' &c.).

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MALLARD[1], in 1879, noted that crystals of the metallurgical products 'Spiegeleisen' and 'ferro-manganese' are of two kinds. Both show a prism-zone of six faces, but when the percentage of manganese reaches a certain amount there is an abrupt change in the habit of the crystals and in the angles between their faces. Crystals containing from 11 up to 52 or 55 per cent. of manganese are lamellar, and were found to have a prism-angle ($mm''' = 110 : 1\bar{1}0$) of 67° 27′, while crystals containing a larger amount of manganese are acicular and have a pseudo-hexagonal prism-zone, the angular measurements of which varied between 58° 42′ and 61° 20′.

These observations have been confirmed by Rathke[2] and Brauns. Crystals with the composition given by the analysis quoted below under (1) were found to have a prism-angle[3] of 68° 5′, while crystals with more manganese, as shown in analysis (2), had angles of about 60° in the prism-zone.

	Fe.	Mn.	C.	Si.	P.
(1)	47·93	44·99	6·48	0·52	0·00
(2)	9·48	82·45	7·47	0·18	0·10

These differences in crystalline form are in correspondence with the metallurgical terms 'Spiegeleisen' and 'ferro-manganese'; the former

[1] E. Mallard, Sur la forme cristalline du ferromanganèse. Bull. Soc. Min. de France, 1878, vol. ii, pp. 47–50.

[2] B. Rathke, Ueber krystallisirtes Ferromangan. Liebig's Annalen der Chemie, 1890, vol. cclx, pp. 326–32. [With crystallographic determinations by R. Brauns.]

[3] This angle, 68° 5′, is the mean of readings which varied between 67° 40′ and 68° 30′. It is given by Brauns as the angle *bm*, since it was repeated four times on the same crystal; this repetition may, however, be explained by twinning on a prism-plane.

has a lamellar crystalline structure and contains less manganese, while the latter has an acicular structure and more manganese.

The absence of terminal faces has prevented previous observers from completely determining the crystals, and it has thus been impossible to state to which crystal-system they belong.

Crystals of two kinds, with prism-angles the same as noted above, and with well-developed terminations, have recently been sent to the British Museum for crystallographic determination by Mr. J. E. Stead, the well-known metallographer. In these crystals, however, the carbon is largely replaced by silicon, but their composition is expressed by the same general formula, $(Fe,Mn)_3(C,Si)$, as is that of ordinary 'ferro-manganese.' In the hope of elucidating the differences in crystalline form and chemical composition presented by this group of substances, other samples of material have been sent by Mr. Stead for crystallographic examination, but unfortunately none of the crystals on these show any definite terminal faces. Besides the material supplied by Mr. Stead, two other specimens, from French iron-furnaces and previously in the British Museum, were examined. I have to express my thanks to Mr. Stead for kindly supplying most of the material for examination, and also for his permission to publish separately the crystallographic results.

The physical characters are much the same in all the seven samples examined. The crystals are of a steel-grey colour, but are often tarnished bronze-yellow; unless covered with a dull, black crust, they have a brilliant metallic lustre. They are very brittle, and have a hardness on Mohs' scale of $6\frac{1}{2}$. They are non-magnetic.

The crystallographic characters of each sample, as far as could be determined, are separately described below under Nos. I to VII. For various reasons, such as the dullness, striation, or repetition of the faces, or the divergent grouping of the crystals, accurate measurements could be obtained only exceptionally. Nevertheless, by measurement of the crystals the different samples could be divided into two sharply defined groups:

(*a*) Crystals showing a rhombic prism-zone with a prism-angle of about $67\frac{1}{2}°$ ($mm''' = 67\frac{1}{2}°$, $bm = 56\frac{1}{4}°$). Terminated crystals (on sample No. I) belong to the orthorhombic system.

(*b*) Crystals showing a pseudo-hexagonal prism-zone with angles varying between 59° and 61°. Terminated crystals (on sample No. IV) belong to the anorthic system.

Carbo-silicide of Manganese and Iron.

I. This material, from the hearth of a blast-furnace at Blaina, Monmouthshire, has already been described in detail by Mr. Stead[1], and the original mass of crystals described and figured has been generously presented by him to the British Museum. Since then, Mr. E. Poulaine, the general manager of the Blaina Works, has presented to the Museum a finer specimen with much larger crystals, these reaching up to $4\frac{1}{2}$ cm. in length and 1 cm. in thickness. This larger specimen, however, shows nothing essentially different from the specimen already described, and I simply quote my crystallographic results from Mr. Stead's paper.

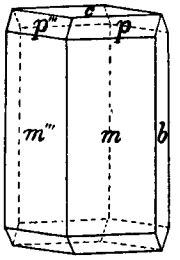

Fig. 1.—Carbo-silicide of manganese and iron.

Crystal class: holohedral-orthorhombic.

Forms: $m\{110\}$, $p\{111\}$, $c\{001\}$, $b\{010\}$.

The faces of the crystals (fig. 1) are dull and drusy, and do not give any reflected image of the goniometer-signal. The mean of several readings taken in the position of maximum illumination gave the following approximate values for the angles:—

$$cp\ (001 : 111) = 51°,\ mm'''\ (110 : 1\bar{1}0) = 66°.$$

The corresponding axial ratios are:—

$$a : b : c = 0{\cdot}65 : 1 : 0{\cdot}67.$$

Carbide of Iron and Manganese ('Spiegeleisen').

II. More exact measurements in the prism-zone were obtained with crystals from a French iron-furnace. The specimen consists of a friable, cellular aggregate of blade-shaped and acicular crystals, which reach up to 10 cm. in length. The crystals, when not broken, have ragged terminations consisting of fine points, and no definite terminal faces could be found.

Measurement of four crystals, both blades and needles, showed that there is a rhombic prism-zone with the forms $m\{110\}$ and $b\{010\}$. The best crystal, from four of the faces of which single, sharp images were reflected, gave

$$mm'''\ (110 : 1\bar{1}0) = 67° 32'\ \text{and}\ mb\,(110 : 010) = 56° 14'.$$

[1] J. E. Stead, Crystals of carbo-silicide of manganese and iron. Journ. Iron and Steel Institute, 1901, No. 1, vol. lix, pp. 79–88. Here fig. 2 incorrectly represents the crystals as orthorhombic with inclined hemihedrism.

The crystals are deeply striated parallel to the length of the prism, and are often quite thin and blade-shaped parallel to the brachypinacoid, $b\{010\}$.

III. This sample shows smaller crystals of the same character as No. II thickly lining the walls of a cavity in compact material. No really good measurements were obtained; the means of all readings from five crystals are:—

$$mm''' = 67° 33' \text{ (limits, } 66\tfrac{1}{2}° - 68\tfrac{1}{4}°).$$
$$mb \quad = 56° 12' \text{ (} \quad \text{„} \quad 55\tfrac{1}{2}° - 56° 49').$$

The order in which these angles were repeated on one crystal suggested that it was twinned on a prism-plane.

From the above measurements (Nos. II and III) crystals of 'Spiegeleisen' may belong to either the orthorhombic or the oblique system; the agreement in the prism-angle with that of the carbo-silicide (No. I) makes it very probable, however, that the system is orthorhombic, and that the carbide and carbo-silicide are isomorphous.

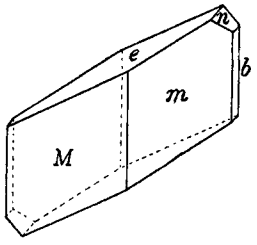

FIG. 2.

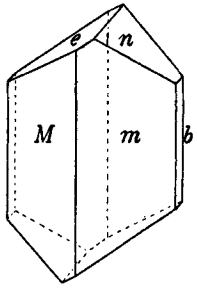

FIG. 3.

Silicide of iron and manganese.

SILICIDE OF IRON AND MANGANESE ('SILICO-FERRO-MANGANESE').

IV. The small and somewhat indistinct crystals line cavities in the crystalline material. The faces of the crystals are rather uneven and have the character of ground glass, but they sometimes give definite reflections; the measurements are therefore only approximate.

Crystal class: holohedral-anorthic.

Elements: $a : b : c = 0{\cdot}58 : 1 : 0{\cdot}66$; $\alpha = 85° 12'$, $\beta = 97° 43'$, $\gamma = 90° 39'$.

Forms: $m\{110\}$, $M\{1\bar{1}0\}$, $b\{010\}$, $n\{011\}$, $e\{0\bar{1}1\}$.

The usual habit of the crystals is illustrated in fig. 2; often n and b

are quite small or absent, and the crystals then closely resemble acute rhombohedra. On one crystal the faces n and those in the prism-zone are more largely developed, as shown in fig. 3. Figs. 2 and 3 represent the actual crystals, each about 1 mm. across, which were measured on the goniometer.

	Measured.	Mean.	Calculated.
bm, 010 : 110	58°–61½°	60° about	—
mM, 110 : 1$\bar{1}$0		,,	—
Mb', 1$\bar{1}$0 : 0$\bar{1}$0		,,	60° 0′
bn, 010 : 011	60° 16′, 60°	60° 8′	60 0
ne, 011 : 0$\bar{1}$1	66 42, 66 37′	66 39	—
eb', 0$\bar{1}$1 : 0$\bar{1}$0	53 13, 53½	53 21	—
nm, 011 : 110	69 29, 69	69 15	69 28
nM', 011 : $\bar{1}$10	81 19, 81½	81 25	—
eM, 0$\bar{1}$1 : 1$\bar{1}$0	66 8, 66 40, 67¼°	66 41	66 56
em', 0$\bar{1}$1 : $\bar{1}\bar{1}$0	78 8, 77, 78	77 43	78 10

Carbide of Manganese and Iron ('Ferro-manganese').

V. This sample is almost pure carbide of manganese with very little iron. It is a compact aggregate of acicular crystals arranged approximately parallel to each other; in small interspaces, bright crystal-faces are developed. The six faces in the prism-zone are of about equal size, and are striated parallel to their mutual intersections. Six crystals were measured, and two or three very good readings obtained, the best being 59° 46′ and 60° 16′ (on the same crystal), while others varied between 59° 22′ and 59° 50′, and between 60° 15′ and 60° 29′. None of the crystals had good faces all round the zone, and no symmetrical or definite repetition of the angles could be detected; it is therefore probable that the crystals are twinned on a prism-plane, as is frequently the case with pseudo-hexagonal crystals.

VI. A friable, cellular network of acicular crystals confusedly arranged. Measurements in the prism-zone varied between 59° and 61°. On one crystal was noticed a rough terminal plane at about 90° to the prism.

VII. A confused aggregate of small needles, much intergrown, in a cavity of compact material. The best angles obtained from five crystals were 59° 34′ and 60° 23′; but again no definite order in the occurrence of the angles around the zone could be traced.

The measurements from samples Nos. V–VII, like those of Mallard and

Brauns, are insufficient to decide whether the crystals of 'ferro-manganese' belong to the orthorhombic, oblique, or anorthic system; but the occurrence of a similar pseudo-hexagonal zone on the anorthic crystals of 'silico-ferro-manganese' (No. IV) suggests that 'ferro-manganese' may also be anorthic, and that the two are isomorphous. It is to be noted, however, that neither the silicide nor the carbo-silicide follow Mallard's rule as to the relation between the size of the prism-angle and the amount of manganese present. It is possible that the difference in crystalline form does not depend on the amount of manganese, but that we have here an isodimorphous series. The present observations are thus still insufficient to determine the inter-relations of this group of substances, and more measurements from terminated crystals are required.

The following analyses, made in Mr. Stead's laboratory, give, under the corresponding numbers, the chemical composition of the material examined crystallographically. All agree fairly closely with the general formula $(Fe,Mn)_3(C,Si)$.

	Fe.	Mn.	C.	Si.	Prism-angle.
I.	34·80	56·80	3·90	3·31	66° about
II.	59·35 60·00	32·50 33·40	6·08 5·85	0·37 0·23	67° 32′
III.	48·10	44·05	6·40	1·35	67 33
IV[1].	67·40	20·10	1·63	10·50	60° about
V.	very little	—	—	very little	,,
VI[2].	29·80	61·98	6·83	0·26	,,
VII.	—	80	—	very little	,,

Crystals of 'silico-ferro-manganese,' from furnaces at Nijni-Tagilsk in the Urals, have been measured by Eremyeev[3], who found them to belong to the cubic system with the forms {102} and {100}, but distorted so as to simulate orthorhombic symmetry. These crystals are therefore quite distinct from those described above, but as Eremyeev does not give their chemical composition the two kinds cannot be further compared.

The meteoric mineral cohenite, $(Fe,Ni,Co)_3C$, has been proved by

[1] Of massive material, not of crystals. Also P, 0·17; S, trace.

[2] A small amount of graphite was detected between the crystals.

[3] Verhandl. russ.-kais. mineral. Gesell. St. Petersburg, 1879, ser. 2, vol. xiv, p. 246. A German abstract of this note is given in Zeits. Kryst. Min., 1879, vol. iii, p. 438, under the title: P. von Jeremejew. Krystalle des Ferromangansiliciums.

Hussak[1] to crystallize in the cubic system. This carbide of iron usually contains 2 or 3 per cent. of nickel and cobalt, but smaller amounts were found by Cohen[2] in the cohenite of terrestrial irons from Greenland. It is therefore probable, as pointed out by Groth[3], that the carbide of iron, Fe_3C, which is a constituent of steel and to which the name cementite has been given, is identical with cohenite.

The carbide (Fe_3C) and silicides (Fe_2Si, Fe_3Si_2, FeSi, and $FeSi_2$) of iron prepared in recent years by Moissan and other chemists, although frequently crystallized, do not appear to have been submitted to crystallographic examination.

[1] Archivos do Museu Nacional do Rio de Janeiro, 1896, vol. ix, pp. 130, 160.

[2] Meddelelser om Grønland, 1897, vol. xv, p. 293; Ann. k. k. naturhist. Hofmuseums, Wien, 1897, vol. xii, p. 58.

[3] Tabellar. Uebersicht der Mineralien, 4th edit., p. 16. Braunschweig, 1898.