THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY.

No. 92. March, 1921. Vol. XIX.

Identity of Trechmann's 'β-tin' with stannous sulphide.[1]

By L. J. SPENCER, M.A., Sc.D., F.G.S.

Assistant in the Mineral Department of the British Museum.

[Read January 18, 1921.]

IN 1879 the late Dr. C. O. Trechmann[2] described in the pages of this Magazine some orthorhombic crystals from Cornish tin furnaces, which from the analyses of the late Mr. J. H. Collins were stated to be metallic tin. Shortly afterwards Baron Foullon[3] described similar crystals from tin furnaces in Bohemia, arriving at the same results, and thus apparently confirming the observations of the previous authors. At a later date, in 1898, Dr. W. P. Headden[4] analysed crystals of similar appearance, also

[1] Communicated by permission of the Trustees of the British Museum.

[2] C. O. Trechmann, On a probably dimorphous form of tin; and on some crystals found associated with it. Mineralog. Mag., 1879, vol. 3, pp. 186–192, pl. ix. The word 'probably' in this title has reference to an obscure relation noticed by the author between the angles of his crystals and those of tetragonal tin. He evidently had in mind the possibility of a pseudo-orthorhombic form produced by twinning, since twinning is common in tetragonal tin.

[3] H. von Foullon, Ueber krystallisirtes Zinn. Verh. geol. Reichsanstalt, Wien, 1881, pp. 237–244; Jahrb. geol. Reichsanstalt, Wien, 1884, vol. 34, pp. 367–884, pl. vii.

[4] W. P. Headden, Some products found in the hearth of an old furnace upon the dismantling of the Trethellen [Trethellan] tin works, Truro, Cornwall. Proc. Colorado Sci. Soc., [1901], vol. 6 (for 1897–1900), pp. 74–86. The same paper, but much abbreviated, also in Amer. Journ. Sci., 1898, ser. 4, vol. 5, pp. 93–96.

from Cornish tin furnaces, which he found to be stannous sulphide (SnS), but he stated that these crystals were monoclinic. Headden's crystals were afterwards goniometrically measured by Stevanović[1] and found to be orthorhombic.

These conclusions, especially the earlier ones of Trechmann, have been frequently quoted in chemical and crystallographical literature, and have found their way into many textbooks. As set out in Groth's 'Chemische Krystallographie' (1906, vol. 1, pp. 15, 150), under metallic tin and stannous sulphide respectively, the crystallographic details present a striking similarity; in fact one account is practically a duplication of the other. A comparison of Trechmann's and Stevanović's parameters and angles is given below (p. 117).

This similarity I noticed ten years ago when examining crystals from Cornish tin furnaces, which had been sent by Dr. Richard Pearce; and I then concluded that the two sets of crystals must be identical. It was puzzling at first to see where the error, if any, lay, and conclusive proof of the suggested identity could only be adduced by a re-examination of the original materials of the several authors. Fragments of these were in the course of time acquired for the British Museum collection (for preservation in the series of artificial minerals, including crystallized furnace products, etc.). Dr. Headden kindly sent, in 1910, the remainder of the material he had worked on; Mr. Collins sent, in 1913, fragments from his only remaining specimen; and Dr. Trechmann's original crystals and specimens, together with various other described materials selected from his collection, were presented by him only a few weeks before his death in 1917.

The minute crystals measured by Dr. Trechmann, and neatly mounted by him in tubes, were left intact, but other crystals of exactly the same appearance taken from his two small specimens were examined, and in every case found to contain much sulphur. Crystals heated on charcoal with sodium carbonate gave a good sulphur reaction on silver; they dissolved in hydrochloric acid with evolution of hydrogen sulphide (tested with lead acetate paper); and, finally, two separate lots fused with sodium carbonate and potassium nitrate yielded bulky precipitates with barium chloride. Mr. Collins's material also shows the same kind of soft, scaly, black crystals, and these were found to contain sulphur. But, in addition, it shows in considerable amount harder, blade-shaped crystals of another kind in which no sulphur could be detected. Crystals

[1] S. Stevanović, Zur Kenntnis einiger künstlich dargestellter Verbindungen. Zeits. Kryst. Min., 1905, vol. 40, pp. 321–331.

of this kind are not represented on Trechmann's specimens. Mr. Collins's analyses showed Sn 98·7 and 98·5, Fe 1·1 and 1·0, together with traces of sulphur, etc. Evidently what happened was that *Trechmann determined the crystallographic characters on crystals of one kind* (*viz. stannous sulphide*), *whilst Collins made the chemical analyses on those of another kind* (*viz. metallic tin*). Seeing that Collins was working in Cornwall and Trechmann in County Durham (on fragments of material sent to him by Collins) and that the material contained at least three kinds of crystals[1] as well as slag and globules of tin, this error is perhaps not altogether surprising.

Headden's material was found to agree with Trechmann's crystallographic description, and I was able to confirm the presence of tin and sulphur in his crystals. He was, however, in error, as already pointed out by Stevanović, in stating that the crystals were monoclinic. Foullon's material I have not seen, and the case against him is less clear. His paper commences with an account of Trechmann's work, and he was evidently prepossessed with the idea that his crystals were the same as those described by Trechmann. Only a qualitative chemical analysis was made, showing the presence of tin with traces of iron, copper, and carbon, no mention being made of sulphur. There can, however, be no doubt that the crystals which he measured and figured were really stannous sulphide.

The proof here adduced, and amplified by the description of other material in the following pages, of the non-existence of Trechmann's orthorhombic modification of tin must by no means be taken to suggest that tin is not dimorphous. As is well known, this metal possesses very curious properties due to its dimorphism. Ordinary 'white tin' can be infected with the 'tin plague' by contact with 'grey tin'—the crystal germs of which act, as it were, like a microbe—and the solid white metal becomes gradually reduced to a grey powder. This change sometimes takes place spontaneously, especially during very severe winters, and some very surprising results have been recorded. The phenomenon has been specially studied by E. Cohen[2]. The transition-point between grey

[1] The second kind of crystals measured by Trechmann, but not further determined, are identical with the iron arsenide, FeAs, described by Headden and Stevanović (loc. cit.).

[2] E. Cohen and others, in a long series of papers 'On the enantiotropy of tin'. Proc. K. Akad. Wetensch. Amsterdam, 1899-1902, vols. 2-4; 1913, vol. 15, p. 839; translations in Zeits. physik. Chemie, 1899-1909, vols. 30-68. A short popular account is given in my translation of R. Brauns's Mineral Kingdom, 1908-12, p. 183.

tin (cubic [1]) and white tin (tetragonal) he has fixed at 18° C., the former being stable below this temperature and the latter above. Trechmann's supposed orthorhombic modification appears always to have presented a difficulty. Curves representing certain physical characters of tin show a small break at about 161° C., and it has been incorrectly assumed by Cohen and others [2] that this marks the transition-point from tetragonal tin to Trechmann's supposed modification. O. Mügge [3] has recently failed to detect a crystallographic change at this temperature.

In the following pages are given the results which I obtained in 1910 from an examination of crystals of stannous sulphide from several sources. The publication of these results was purposely delayed during the closing years of the lives of the authors principally concerned. Of the four specimens previously in the Museum collection, one was acquired in 1865 as 'artificial antimony', and two others, acquired at some time previous to 1891, were labelled as 'Trechmann's tin'. In 1910 Dr. Richard Pearce sent a well-crystallized specimen from a Cornish tin furnace and many others from the new tin-smelting works of Messrs. Williams, Harvey and Co., at Bootle, near Liverpool. Samples from the Penpoll Tin Smelting Co., also at Bootle, were sent by Mr. Thomas Teague in the same year.

Through the kindness of Dr. Richard Pearce, and his son Mr. R. F. Pearce, manager of the works, I was enabled to visit the smelting works of Messrs. Williams, Harvey and Co. at Bootle at a time (in 1910) when these crystals were being produced in such quantities as to be a hindrance in the process. After reduction of the ore, the whole charge was run from the furnace into large iron pots or cauldrons, each holding about three tons of molten metal and slag. Here it was allowed to stand for two or three hours, when the metal (about $2\frac{1}{2}$ tons) was drawn off from the bottom of the pot. Beneath the crust of slag was a layer several inches in thickness consisting of a cellular mass of brilliant platy crystals; whilst at the bottom of the pot there was a deposit of a friable network of acicular crystals. This happened when pyritic tin-ores from Bolivia were being smelted. Evidently the sulphur of the pyrites combined with tin to form the lighter platy crystals of stannous sulphide, whilst the iron alloyed with tin to form the heavier acicular crystals of iron stannide. When these ores were roasted previous to smelting, the platy crystals

[1] Grey tin is cubic according to X-ray investigation of the crystal-structure by A. J. Bijl and N. H. Kolkmeijer, Proc. K. Akad. Wetensch. Amsterdam, 1919, vol. 21, pp. 405, 501.

[2] E.g., M. Werner, Zeits. Anorg. Chemie, 1913, vol. 83, p. 292.

[3] O. Mügge, Über die einfachen Schiebungen am Zinn und seine Zustandsänderung bei 161°. Centralblatt Min., 1917, pp. 233–239.

were formed only in small amount; the sulphur being then derived from the coal (containing about 1½ per cent. sulphur) used in the fire-box of the reverberatory furnace. Abundance of material was here available for examination, and the following description is based mainly on this material.

Orthorhombic Stannous Sulphide (SnS).

The material has the form of very thin scales, plates, or blades, and is of an iron-black or graphite-black colour with brilliant metallic lustre and quite opaque. It is loosely and confusedly aggregated as incoherent cellular masses on the surface of the slag, and resembles in appearance the flaky graphite ('kish') from iron furnaces. The streak is iron-black and shining; and being quite soft (H. = 2), the material marks paper. The plates are pliable, but not elastic, and when bent they have a tendency to break parallel to the face *r* (101), which is a direction of poor cleavage. They are not brittle,[1] and are difficult to reduce to powder; in the mortar the material grinds flaky and streaks out.

The plates are sometimes as much as 2 or 3 cm. across, but they are always paper-thin, about $\frac{1}{20}$ mm. Owing to this extreme thinness, it was not possible to obtain any clear evidence of the existence of a cleavage parallel to the surface of these plates, although their micaceous appearance rather suggests it. The plates are usually irregular in outline, and they show feathery markings on their surface. A characteristic feature is the frequent repetition of parallel growths, giving rise to comb-like and feathery forms, and to serrated edges of the plates (figs. 1 and 2; and Trechmann's fig. 6). Faces on the edges are quite inconspicuous, and only rarely can measurements be obtained on the goniometer. The plane angle of 95° on the face *b* (010) as measured under the microscope at the tips of crystals is, however, quite characteristic. Several crystals were measured on the goniometer for the purpose of identification, and the orthorhombic forms *b*(010), *m*(110), *n*(120), *o*(111), noted. No attempt was made to improve on the axial ratios deduced by Trechmann, which are probably the most accurate; on the other hand, Stevanović's letters for the forms may be retained as being the more suitable. Both authors adopted the same orientation and parametral plane:

Trechmann	$a : b : c = 0.3874 : 1 : 0.3558$
Stevanović	$0.3888 : 1 : 0.3566$

[1] Trechmann says 'Brittle to mild' (p. 191) and 'The crystals are brittle when strained transversely, but against pressure they seem to be slightly ductile' (p. 188). This 'brittleness' has been emphasized by some authors in their attempts to accommodate the crystals in the tin scheme.

The corresponding angles are:

	Trechmann (calcd.)	Stevanović (calcd.).	Measured on Bootle crystals.
(010) : (110).....	$ab = 68° 49\frac{1}{2}'$ ...	$bm = 68° 47'$ ...	$bm = 69°$
(010) : (120).....	$ae = 52\ 14$ ...	$bn = 52\ 10$ ...	$bn = 52$
(010) : (111).....	$ad = 75\ 19$ ...	$bo = 75\ 17\frac{1}{2}$ ...	$bo = 75$
(101) : ($\bar{1}$01).....	$cc' = 85\ 8$ ...	$rr' = 85\ 8$ ...	85[1]

The crystals from the works of Williams, Harvey and Co. at Bootle often show repeated twinning on r(101), as illustrated in fig. 1. Angles of 95° and 85° (calculated 85° 8′) between the edges of the prism-zones were measured under the microscope. Twinning was not noticed on any of the lots of material from other sources, nor is it mentioned by Stevanović, whilst Trechmann was careful to state that his crystals showed no signs of twinning (cf. foot-note on p. 113).

The crystals when heated in a bulb-tube fuse (though not so readily as metallic tin) and give a small white sublimate in the bulb. Heated in an open tube or on charcoal, they glow (i.e. burn), emit a strong smell of sulphur dioxide, become white, and give a small white sublimate near the assay. On charcoal with sodium carbonate, they yield a bead of metallic tin and the fused mass gives a good sulphur reaction on silver.[2] The crystals dissolve slowly in hot strong hydrochloric acid with evolution of hydrogen sulphide. They are decomposed by nitric acid with the separation of a white insoluble residue.

A difficulty was presented in collecting material for analysis and determination of the specific gravity. The crystals are frequently intermixed with slag and metallic tin. When examined under the microscope the single crystals are seen to be dotted over with minute, shining white globules of tin, and attached to their surface are long, white needles of iron stannide. There are also present some minute hexagonal prisms, of short habit and terminated by the basal planes: these show an iridescent tarnish and could not be determined. A magnet attracts a few small clusters of minute ($\frac{1}{25}$ mm.) octahedra, which have the appearance of magnetite. It was therefore quite hopeless to collect pure material. All that could be done was to select

[1] From the plane angle, 95°, between the edges [(010) (111)] and [(010) ($\bar{1}$11)] as measured under the microscope.

[2] These blowpipe reactions agree with those given by Trechmann and by Collins, who, however, overlooked the sulphur. As pointed out by C. F. Rammelsberg in 1880, they are not those of metallic tin. Collins evidently did not make his blowpipe tests on the same kind of crystals that he analysed quantitatively.

a specimen in which these impurities were present in smaller amount. The best and cleanest crystals of typical habit were selected, and these were rubbed between sheets of paper, gritty specks being picked out.

The specific gravity determined on 1·6529 gram of the crystal plates from Bootle gave 5·62 at 21° C., but the same material after being powdered as far as possible gave the value 5·52. Two other lots of

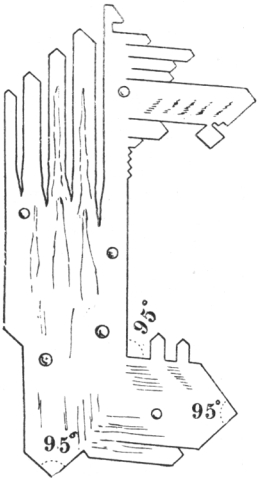

FIG. 1.

FIG. 2.

FIG. 1.—Twinned crystals of stannous sulphide (SnS) from a tin furnace at Bootle. Drawn on the face *b* (010). The circlets represent globules of metallic tin. × 7.

FIG. 2.—Photomicrograph [1] of a portion of a crystal plate of stannous sulphide (SnS) from a tin furnace at Bootle, showing comb-like forms at the edge, and impression-marks of detached globules of metallic tin on the surface. × 50.

crystals separately collected from a specimen from another source (B.M. 67471) gave the widely different values 6·31 and 6·45.[2] Such

[1] This photomicrograph was taken in the laboratory of Dr. J. E. Stead, and I have to thank him for his permission to use it in this place.

[2] A rough analysis made on this material of sp. gr. 6·45 showed about 17 per cent. of iron, in addition to tin and sulphur. The amount of iron exceeds that required for the iron stannide $FeSn_2$, and suggests that other stannides richer in iron (see p. 122) may also be present.

results are rather disconcerting—they seem almost too variable to be explained by admixed impurities (the density of fused tin is 7·29, and of iron stannide, $FeSn_3$, 7·77). But as given in the literature, the specific gravity of crystallized stannous sulphide ranges from 4·852 to 6·557.[1]

In the analysis, tin and iron were estimated in a portion (about 1 gram) dissolved in hydrochloric acid, the tin being precipitated as sulphide and weighed as oxide. Sulphur was estimated in another portion (1 gram) fused with sodium carbonate and potassium nitrate, and weighed as barium sulphate. The results given under I are compared with Headden's 1898 analyses (II and III) and the calculated percentages for the formula SnS. The loss in analysis I probably represents tin: arsenic was proved to be absent by Marsh's test.

		Headden (1898).		Calcd. for
	I.	II.	III.	SnS.
Sn	81·48	71·538	80·413	78·81
Fe	1·70	4·881	2·905	—
Cu	—	0·452	—	—
S	15·14	23·129	17·134	21·19
Insoluble ...	0·90	—	—	—
	99·22	100·000	100·452	100·00
Sp. gr.	5·52	5·782		5·0

The variations shown by these analyses amongst themselves and from the theoretical value are to be ascribed to the presence of impurities, mainly metallic tin and iron stannide. Analysis I corresponds to SnS 72·2, Sn 15·0, $FeSn_3$ 12·8 per cent. Calculated from this the specific gravity of the SnS portion is 5·0.

Tetragonal Iron Stannide ($FeSn_3$).

This was deposited in considerable quantity at the bottom of the baths of molten tin at the Bootle works. It forms loose, open aggregates of delicate, acicular crystals, confusedly matted together or sometimes with an approach to parallel or divergent grouping. The crystals are some-

[1] The actual values arranged in order of magnitude are: 4·852 (C J. B. Karsten, 1832), 4·973 (R. Schneider, 1855), 5·0802 (A. Ditte, 1883), 5·267 (P. Boullay, 1830), 5·52 and 5·62 (see above), 5·782 (W. P. Headden, determined on the material analysed by him in 1898; not previously published), 6·31 and 6·45 (see above), 6·525 and 6·557 (C. O. Trechmann, 1879). The first four lower values were determined on crystallized laboratory products and the remainder on impure furnace products. The value 5·0, as calculated above, is probably near the truth.

times tin-white with brilliant metallic lustre, but more often they show an iridescent tarnish, and sometimes are quite dull and black on the surface. They are $\frac{1}{2}$–2 cm. in length with a thickness of $\frac{1}{20}$–$\frac{1}{10}$ mm., and terminate in a fine point. On the goniometer they give angles of 45° all round the prism-zone, suggesting the forms a (100) and m (110) of a tetragonal crystal. The needles are brittle, breaking across when an attempt is made to bend them; and they are readily reduced to powder. The streak is iron-black and shining, and the hardness $3\frac{1}{2}$. They are not magnetic.

Associated with them are small, bright plates of stannous sulphide and globules of metallic tin. Under the microscope the needles are seen to be encrusted with numerous minute scales of stannous sulphide, giving them a frosted appearance. A magnet extracts a few black, magnetic grains and scales (of iron oxides?). Ideally pure material could therefore not be collected for analysis. The needles were rubbed between sheets of paper, and the dust and flakes blown away.

Heated in a bulb-tube, the needles fuse readily to a black bead and yield a small white sublimate. In an open tube, their surface becomes coated with rusty excrescences of ferric oxide. On charcoal in the reducing flame, they fuse to a black, magnetic bead, the interior of which consists of a white, malleable metal; and a white sublimate is formed near the assay. The needles are slowly soluble in strong hydrochloric acid with evolution of hydrogen. (At first hydrogen sulphide is also given off from the associated stannous sulphide.) The gas was passed through a heated tube and arsenic found to be absent (Marsh's test). The needles are not readily attacked by nitric acid. In the analysis, the tin and iron were estimated in a portion dissolved in hydrochloric acid, and sulphur in a separate portion fused with sodium carbonate and potassium nitrate. The loss is probably in the tin. A rough volumetric estimate of the tin made at the smelting works gave 81 per cent.

			Calculated for $FeSn_3$.
Sn	84·94	...	86·47
Fe.....	13·48	...	13·53
S	0·24	...	—
	98·66		100·00
Sp. gr.	7·77		

This material, being definitely crystallized, must therefore be regarded as a compound of tin and iron, rather than as an alloy. Further, the specific gravity calculated from the components, namely 7·36, is appreciably lower than the observed value of 7·77.

A series of ten alloys of tin and iron ranging in composition from Fe_9Sn to $FeSn_2$ were prepared in the laboratory by W. P. Headden.[1] Some of these showed imperfect crystals, which were examined by Stevanović[2]. He concluded that those near Fe_4Sn_5 in composition are hexagonal, whilst those near $FeSn_2$ are tetragonal. Earlier papers mention tetragonal needles of Fe_3Sn (J. L. Lassaigne, 1850), $FeSn_2$ (C. Noellner, 1860), and $FeSn_5$ or $FeSn_6$ (C. F. Rammelsberg[3], 1863).

Rhombohedral Tin arsenide (Sn_3As_2).

These crystals were prepared by Dr. J. E. Stead, F.R.S., by slowly cooling an alloy containing 95 per cent. tin and 5 per cent. arsenic, and the crystallographic details respecting them may be repeated from his recent paper[4] to complete the present series of crystallized tin compounds. Analyses made in Dr. Stead's laboratory of several crops of crystals gave results approximating to the formula Sn_3As_2. The crystals measured were from a batch that gave Sn 70·22–70·62, As 29·78–29·38 per cent. (calculated for Sn_3As_2, Sn 70·41, As 29·59).

The crystals have the form of thin scales, about 2 mm. across, with much the appearance of flakes of graphite. The colour is steel-grey with a bright metallic lustre. They are quite soft (H. $2\frac{1}{2}$), readily marking paper; and are flexible, but not elastic. The outline of the flakes is usually irregular, but at times it is clearly triangular or hexagonal. Under the microscope these give angles of 120° and 60°, and lines on the surface of the scales are inclined to one another at the same angles. The edges of the scales are often deeply and regularly serrated, having quite the appearance of a saw with obliquely-cut, triangular teeth.[5] This is due to an alternate repetition of the faces of the rhombohedron which form the edges of the crystals. The crystals are rhombohedral (trigonal) and the only faces present are the large basal plane c (111), forming the surface of the scales, and the rhombohedron r (100) at the edges; the latter being represented by narrow planes or by a series of small, triangular facets. There is a perfect cleavage c (111)

[1] W. P. Headden, Proc. Colorado Sci. Soc., vol. 4 (for 1891–93), pp. 81–122; Amer. Journ. Sci., 1892, ser. 3, vol. 44, pp. 464–468.

[2] S. Stevanović, Zeits. Kryst. Min., 1905, vol. 40, pp. 327–331.

[3] C. F. Rammelsberg, Ann. Phys. Chem. (Poggendorff), 1863, vol. 120, p. 54.

[4] J. E. Stead, with notes by L. J. Spencer, The ternary alloys of tin-antimony-arsenic. Journ. Instit. of Metals, London, 1919, vol. 22 (no. 2 for 1919), pp. 127–144, pls. VIII–XVII; reprinted (from the uncorrected proofs) in Engineering, London, 1919, vol. 108, pp. 663–667.

[5] J. E. Stead, loc. cit., pl. X, fig. 4A.

parallel to the surface of the scales. The images seen in the goniometer are rather scattered and only approximate measurements can be obtained, viz.:

cr (111) : (100) = 55° 22′ (limits 55° 2′ – 55° 48′), corresponding with the axial ratio:

$$a : c = 1 : 1{\cdot}2538.$$

This angle approximates closely to the cubic angle (111) : (100) = 54° 44′; and it might be suggested that the crystals are really cubic, being flattened parallel to a pair of octahedron faces and with cube faces at the edges. If this were the case we should expect to find some trace of the six suppressed octahedron faces at the edges in the zones [111,100]. Again, the cleavage would be octahedral instead of basal, but no indication of a cleavage across the plates was detected.

The crystals agree closely in their characters, and are no doubt identical with those described by W. P. Headden [1] from Cornish tin works. His analysis gave the formula Sn_6As, but he mentions a difficulty in separating the crystals from globules of tin. He believed the six-sided plates to be rhombohedral. Headden's crystals were subsequently measured by S. Stevanović,[2] who determined them to be trigonal with $cr = 54° 51'$, corresponding with $a : c = 1 : 1{\cdot}2299$.

If the formulae Sn_3As_2 and Sn_6As correctly represent the composition of the crystals, there is, perhaps, some relation between their angles and those of arsenic (which also is rhombohedral with a perfect basal cleavage), since those of Sn_3As_2 lie between the corresponding values for Sn_6As and As:

	Sn_6As.	Sn_3As_2.	As.
cr (111) : (100) ...	54° 51′	55° 22′	58° 17′
$a : c$ ...	1·2299	1·2538	1·4013

[1] W. P. Headden, Proc. Colorado Sci. Soc., [1901], vol. 6 (for 1897–1900), p. 80; Amer. Journ. Sci., 1898, ser. 4, vol. 5, p. 95.

[2] S. Stevanović, Zeits. Kryst. Min., 1905, vol. 40, p. 326. His error in stating the chemical formula is corrected by P. Groth, Chemische Krystallographie, 1906, vol. 1, p. 66.