XIX.—*On a probably dimorphous form of Tin; and on some Crystals found associated with it.*

By C. O. Trechmann, Ph. D.

THE behaviour of tin under varying circumstances has frequently attracted the attention of chemists, and several authors have concluded that it is capable of assuming at least two different crystallographic forms, only one of which, however, has been thoroughly investigated. Since Miller* described the beautiful pyramidal crystals of tin obtained by galvanic deposition from a solution of its protochloride, the anomalous appearance of those obtained in the dry way has often been remarked upon. Brooke obtained octagonal needles on slowly cooling molten tin and pouring off the fluid part. Pajot† in a similar manner obtained rhombic prisms. Stolba‡ obtained quadratic plates, whilst Breithaupt§ saw tin crystals, from Cornish smelting furnaces, which had the form of short hexagonal prisms (Miller considered them to be $Cu\ Sn^2$). Lastly Rammelsberg‖ inferred from the varying specific gravity that a not yet determined dimorphic form existed. It is found for instance that electrolytic tin with a sp. gr.=7·18, after being melted and allowed to cool, assumes the higher sp. gr.=7·29, and yet retains a crystalline structure. Whether the crystals of tin to be described below, are the same as those observed by Breithaupt and others, though probable, cannot be decided, nevertheless the observations made on them may assist in solving the question of the dimorphism of this eminently crystallizable metal.

The crystals now to be described were brought to my notice by our able secretary Mr. Collins, who writes as follows respecting them:—"I have received the crystals in question at different periods from the Rev. Canon Rogers, of Gwennap, near Redruth; from Mr. A. T. Davies, of St. Agnes; and, lately, from Mr. A. K. Barnett, manager of the Chyandour Smelting Works at Penzance. They occur in cavities of "hard head," a highly arsenical slaggy

* Phil. Mag., iii Series, 22, 263.—Pogg. Ann. 58. 660—Brooke and Miller: Mineralogy, 1852, p. 127—Rammelsb: Handb. d. Kryst. und Chem. p. 14.

† Journ. de Phys. et Chim., t. 38, 52.

‡ Journ. f. pract. Chem. 96, 178. Berz. Jahresb. f. Chem. 1865, 161.

§ Schweigg. Journ., 52, 171.

‖ Ber. d. Deut. Chem. Ges. 3. 724.

material which is produced at a certain stage in the processes of tin-smelting. They also occur occasionally in the ordinary slags, also in cavities. They are formed with great rapidity, sometimes in a few minutes.

"In colour they vary from iron-grey to bright steel-grey, the lustre is occasionally almost exactly like that of the "kish" (graphite) formed on pigs of spiegeleisen in cooling. They are flexible but not elastic."

"When heated in a closed tube they give a *very* faint white sublimate but are not otherwise changed; in the open tube they suddenly glow, then deposit a thick white sublimate which is scarcely at all volatile on further heating; on charcoal they glow, deposit a white sublimate of oxide of tin, yielding at the same time faint arsenical and sulphurous odours, and a minute dark, brittle, magnetic bead. With borax bead the following are the results—

	HOT.	COLD.
OF	Brown, then yellowish-green	Pale clear blue
RF	Bluish	Violet-blue

In bead of microcosmic salt—

OF	Green	Very pale violet
RF	Bluish	Violet

"Treated with strong HNO_3 most of the crystals are changed to a white powder, red fumes being given off abundantly; a few minute dark crystals however are scarcely attacked after 10 days digestion in the acid.

"With HCl all the crystals are readily soluble.

"The above reactions shew that the crystals consist essentially of tin, with traces of arsenic, sulphur, iron, and cobalt.

By ordinary humid analysis the results obtained are

	a	*b*
Tin	98·7 p.c.	98·5
Iron ..	1·1 p.c.	1·0
S.As. Fe.Co.	traces	traces
	99·8	99·5
Sp. Gr.	6·5	6·4

"These analytical results shew that the crystals *taken as a whole* are composed of almost pure tin; the minute quantities of the other substances present being insufficient to form an alloy in any ordinary sense."

Their general appearance is that of a loose and irregular mass of very thin plates of different sizes, from about a quarter of an inch square, down to almost microscopical dimensions. The colour also varies, from a dark iron or graphite grey in the larger specimens, to a light bluish-grey in the smaller ones. Single plates and crystals, as seen under the microscope, appear still lighter, approaching to a bluish-tin colour. The lustre is bright metallic, though frequently the crystals are covered with a thin dull grey or slightly iridescent crust. The crystals are brittle when strained transversely, but against pressure they seem to be slightly ductile. A lamination seems apparent in the direction of their greatest length and breadth.

Two determinations of the specific gravity were made with carefully picked and washed crystals, and gave :—

(1) Sp. gr.=6·557 Weight of crystals used 0·1659 gramme.
(2) ,, =6·525 ,, ,, 0·8274 ,,

Temperature, 60·5 F (15·8 C).

Some crystals of electrolytic tin gave, at the same time and under the same conditions :—

(3) Sp. gr.=7·136 Weight of crystals used 0·3982 gramme.
(7·178, Miller)

On closer examination of the hand specimens it is found that there are two kinds of crystals intermingled ; the first kind, the thin plates already mentioned, very greatly predominating in quantity. They are bounded by six sides, of which two are generally wanting, where the crystal is affixed to its base. Of the enclosed plane angles four approximate to 133°, and two to 95°, and the plates represent either single individual crystals, or, as is more frequently the case, the edges at the ends are replaced by a number of smaller crystals, arranged in a parallel position, thus giving the plate a deeply serrated appearance, as of a double-sided comb, and showing it to be built up of a larger or smaller number of sub-individuals. Fig. 6, plate IX, is drawn from nature, and represents one of these plates.

The crystals of the second kind are very much smaller, of a lighter shade of colour, and generally disposed on the surface of, or among, those of the first kind. The single crystals form minute prisms, which are also arranged in parallel rows—like the teeth of a comb—and held together by a thinner central part, thus forming small plates, of about 1 mm. square, with protruding points. Fig. 7 shows one of these composite forms. They are probably some combination of tin with other substances, and seem to be of a later formation than the tin crystals, due probably to a change of temperature or an alteration in

the composition of the surrounding medium. A fuller description will be given below.

Both kinds have often small globules of what appears to be tin attached to their surfaces or in their serrations.

For the sake of distinction it is proposed to call the pyramidal tin, as described by Miller, the α modification or α tin, and the first kind of the above crystals the β modification or β tin.

(1) *β Tin.* As already stated the crystals form very thin plates with prismatic habit, and are frequently built up of a number of sub-crystals. The latter (fig. 2) are exceedingly well formed, rich in facets, with sharp well-defined edges, and though excessively small are well adapted for goniometrical measurement on account of the excellent polish of their surfaces. The planes were free from striations, but the larger ones frequently showed central depressions and lines of growth, such as are seen on artificial crystals of lead sulphide or bismuth, though in a much less marked degree. Five of the best developed crystals, the largest of which did not exceed 1·5 mm. in length, by 0·3 mm. in breadth and 0·1 mm. in thickness, were picked out and measured with very satisfactory results.

System: prismatic, with angles closely approximating to those of α tin.

The following angles, the mean of the best measurements, were used for the calculation of the axial ratio (the angles between the normals are given throughout.):—

$$a : b = 68° 49·5'$$
$$a : d = 75° 19'$$

Axial ratio*:—

$$\breve{a} : \bar{b} : \dot{c}$$
$$0·3874 : 1 : 0·3558$$

(Pyramidal or α tin:—$a : c = 1 : 0·3857$ (Miller)

The observed forms were—

$a=010$	.. ..	$\infty\breve{P}\infty$
$x=100$	.. ..	$\infty\bar{P}\infty$
$b=110$	.. ..	∞P
$e=120$	.. ..	$\infty\breve{P}2$
$d=111$	.. ..	P
$c=101$	.. ..	$P\bar{\infty}$
$n=021$	.. ..	$2P\breve{\infty}$

*In the description of the elements of a crystal we follow Groth's Zeitschrift f. Krystallographie, and designate the shorter lateral axis a, the longer one b, and the vertical axis c. This of course slightly modifies the symbols of Miller.

They were all well and fully developed, with the exception of x, which was exceedingly narrow and imperfect, and n, which was only observed on three crystals, and determined by a single approximate measurement (Fig. 2a.)

The following is a table of the angles calculated from the axial ratios, together with some of the measured ones, and some of the corresponding angles of α tin.

Calculated.		Measured, on Crystal No. 4.		Pyramidal or α tin (Miller.)	
$a : a'$	0° 0′	0° 0·5′			
$a : x$	90° 0′				
$a : b$	68° 49·5′	$a' : b$	68° 50·5′	$s : a$	68° 55′
		$a' : b''$	68° 51′		
		a'''	68° 43′		
		$a : b$	68° 46′		
$a : e$	52° 14′	$a' : e'$	52° 33′		
		$a' : e''$	52° 24·5′		
		$a : e'''$	52° 12′		
		$a : e$	52° 15′		
$a : d$	75° 19′	$a : d$	75° 19·5′		
		$a' : d''$	75° 21′		
		$a' : d'$	75° 21′		
		$a : d'''$	75° 16′		
$a : c$	90° 0′	(Crystal No. 1)	90° 0′		
$a : n$	54° 34′	(,, No. 5)	53° 49′		
$x : b$	21° 10·5′			s : (001)	21° 5·5′
$x : e$	37° 46′				
$x : c$	47° 26′	(,, No. 1)	47° 19·5′	t : (001)	49° 10′
$x : d$	49° 8′				
$b : b'$	42° 21′			$s : s''$	42° 11′
$b : e$	16° 35·5′				
$b : c$	50° 53·5′				
$b : d$	45° 26′	(,, No. 2)	45° 30·5′		
$e : e'$	75° 32′				
$e : c$	57° 40·5′				
$c : c'$	85° 8′	(,, No. 1)	85° 14′		
$c : d$	14° 41′				
$d : d'$	29° 22′				
$d : d'''$	81° 44·5′				
$d : e$	47° 44·5′				

The close approximation of some of the angles of β tin to those of α tin would seem to suggest that the two are morphologically identical,

but the decided prismatic development and the peculiar physical properties make it extremely probable that we really have to deal with the prismatic system. In order to compare them one with another, the vertical axis of β tin must be multiplied by three, and the short lateral axis a placed in the vertical position, the similarity of the two axial ratios then demonstrates at once their close connection. The forms of β tin expressed as pyramidal ones, for comparison with those observed by Miller on α tin, would then be :—

β *Tin.*			α *Tin.*		
$a=010$	..	$\infty P\infty$	$m=110$	..	∞P
$x=001$	..	$0P$	$a=100$	..	$\infty P\infty$
$b=011$	..	$P\infty$	$p=111$	..	P
$e=021$	..	$2P\infty$	$r=331$	..	$3P$
$d=311$	..	$3P3$	$s=101$	..	$P\infty$
$c=301$	..	$3P\infty$	$t=301$	..	$3P\infty$
$n=320$	..	∞P_2^3			

Of the possible number of planes moreover only one half would be developed, and if we compare the projection of α tin upon its basal plane (Fig. 4,) with that of β tin upon the plane of the macropinacoid (Fig. 5) the absence of pyramidal symmetry becomes very apparent.

The hardness of β tin is somewhat greater than that of α tin. Cleavage very imperfect, parallel to a and also to c. Brittle to mild. Streak iron-grey, shining. The crystals melt easily, burn with a bluish-white flame, and leave a white ash. They are soluble in moderately concentrated HCl. as stated by Mr. Collins above.

The specific gravity given above is probably too low, on account of the admixture of the crystals of the second kind and other mechanical impurities.

(2.) The second kind of crystals referred to above are very sparingly distributed among the plates of β tin ; they seem to be of a complex nature, though containing apparently a large percentage of tin with smaller quantities of iron and other metals, but in what state the components occur cannot be determined until a larger quantity shall have been gathered and submitted to analysis. They are hard and very brittle, with a bright metallic lustre, almost insoluble in concentrated H Cl, and do not melt in the flame, but turn black and lose their form. More correct observations were precluded on account of their minute size and scarcity.

The crystallographic properties of these crystals are, however, not without interest, and may, as soon as their composition is known give rise to interesting comparisons. For the present we can only draw

attention to the fact that there is a close relation between these crystals and those of "iron-olivine" or artificial fayalite.

Despite their almost microscopical dimensions, the largest not exceeding 0·5 mm. in length by 0·15 mm. in thickness, it was possible to measure them with considerable accuracy.

System: prismatic.

Fundamental angles, the mean of the most reliable measurements of three crystals:—

$$m : r = 70° 45·5'$$
$$r : r' = 58° 57'$$

Axial ratio:

$\breve{a}$		$\bar{b}$		$\dot{c}$
0·9018	:	1	:	0·5652

Observed forms:—

$a=010$	..	$\infty P\breve{\infty}$
$b=100$	..	$\infty P\bar{\infty}$
$m=110$	..	∞P
$r=011$	..	$P\breve{\infty}$

The following are the principal angles:—

Calculated.		Measured.		No. of Crystal.
$a : a'$	0° 0′			
$a : b$	90° 0′		89° 57·5′	1
$a : m$	47° 57′	$a : m'$	47° 58·5′	1
		$a' : m'''$	47° 55·5′	1
$a : r$	60° 31·5′		60° 31′	2
$b : b'$	0° 0′			
$b : m$	42° 3′		42° 7·5′	1
$b : r$	90° 0′			
$m : m''$	84° 5·5′	$m' : m''''$	84° 14·5′	1
		$m' : m'''$	84° 8′	2
		$m'' : m'''$	(83° 58′)	2
$m : r$	70° 45·5′	$m' : r$	70° 44′	1
		$m''' : r'$	70° 47′	3
$r : r'$	58° 57′		58° 57′	2
			58° 57·5	3

No signs of twinning were observable in these crystals, nor in those of β tin.

In conclusion, I beg to acknowledge my great obligations to Mr. Collins for kindly placing the material for this paper at my disposal, and also for making me acquainted with the constitution of the crystals.