Determination of minerals in platinum concentrates from the Transvaal by X-ray methods.

(With Plates VII and VIII.)

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[Read June 7, 1932.]

CONCENTRATES from the platiniferous norites of the Bushveld, Transvaal, are not completely soluble in aqua regia. The insoluble portion consists of steel-grey fragments first analysed chemically by R. A. Cooper [1] and considered by him to be a new platinum mineral represented by the formula $Pt(As,S)_2$. The name cooperite was proposed for the new mineral by F. Wartenweiller,[2] and after further work Cooper decided that the arsenic found in the early analysis was due to the presence of sperrylite, and he changed the formula [3] to PtS_2. H. Schneiderhöhn [4] observed simple twinning and, less frequently, polysynthetic lamellae on polished sections of mineral grains from the same deposits, and he suggested that cooperite is probably orthorhombic and isomorphous with marcasite. The latest account of the new mineral has been published by H. R. Adam [5] who gave several analyses of cooperite from the Rustenburg and Potgietersrust districts and concluded that the 'mineral is PtS_2 with a

[1] R. A. Cooper, Journ. Metall. Mining Soc. South Africa, 1928, vol. 28, p. 281. [Min. Abstr., 4–10.]

[2] In the discussion on Cooper's paper. See also Min. Mag., 1931, vol. 21, p. 618.

[3] R. A. Cooper, Journ. Metall. Mining Soc. South Africa, 1929, vol. 29, p. 230 (final discussion to the preceding paper).

[4] H. Schneiderhöhn, Centr. Min., Abt. A, 1929, p. 193. [M.A. 4–149.] H. Schneiderhöhn and P. Ramdohr, Lehrbuch der Erzmikroskopie, Berlin, 1931, vol. 2, p. 216.

[5] H. R. Adam, Trans. Geol. Soc. South Africa, 1931, vol. 33 (for 1930), p. 103. [M.A. 4–500.] See also discussion in Proc. Geol. Soc. South Africa, 1932, Trans. vol. 34 (for 1931), pp. xxxv and xlii.

small amount of excess metal (platinum, palladium, and nickel) present in solid solution'. G. V. White in the same paper figured a 1 mm. crystal picked out from fragments of cooperite from Potgietersrust, Transvaal. Perhaps influenced by Schneiderhöhn's results, White wrongly interpreted his accurate goniometric measurements as conforming with orthorhombic symmetry. In the abstract of this paper it was pointed out by L. J. Spencer that the crystal is 'clearly pyritohedral-cubic with the forms (100), (111), (210), and elongated along a cubic axis'. This crystal and a number of small fragments were then sent to Dr. Spencer for further investigation. At his suggestion X-ray methods have been applied and it has been possible by their aid alone to distinguish three different minerals amongst the fragments originally analysed and called cooperite. Moreover, through the kindness of Mr. H. R. Adam, who sent further supplies both of the cubic crystals and the cooperite fragments, sufficient quantities of each of the three minerals have been separated by X-ray methods to carry out more or less satisfactory chemical analyses. In addition to these three minerals the concentrates also contain flattened cubes of magnetic (iron-bearing) platinum, some sperrylite, and possibly two as yet undetermined minerals.

Cooperite.

Rotation and Laue photographs of the crystal no. 1 figured by White confirmed conclusively its cubic symmetry and also gave evidence that its structure must be of the pyrite type (pl. VII, fig. 4). A powder photograph of a few of the cooperite fragments from Rustenburg, however, cannot be interpreted on this basis. It is obvious that the lines to be expected for the cubic material or for sperrylite are not present. Most of the cooperite fragments are irregular flakes each weighing from 0·1 to 0·2 mg., but one elongated crystal no. 2 was picked out showing four good prism-faces. Neither the angles of the prominent prism-zone ([101], see p. 193) nor a rotation photograph parallel to the direction of elongation are compatible with cubic symmetry. The diffraction spots of this rotation photograph are, however, all superposable upon lines present on the powder photograph already mentioned, and all the prominent lines on the powder photograph can be accounted for in this way. This proves that crystal no. 2 represents the principal component present amongst the cooperite fragments. A complete X-ray study of this crystal was therefore proceeded with. A series of Laue and rotation

photographs shows that it possesses tetragonal symmetry (pl. VII, fig. 3). Having deduced the dimensions of the unit cell and indexed the rotation photographs it was possible to assign indices to all the prominent lines of the powder photograph. A few weak lines remained indicating the presence of at least one other mineral.

Further cooperite fragments were then selected and a rotation photograph taken of each one in succession. The photographs were taken in random orientation (pl. VIII, fig. 8), and the identity of a particular fragment with that of crystal no. 2 was proved if all the spots of its photograph were superposable upon the indexed lines of the powder photograph (fig. 7). For such work it is necessary to use a powder photograph taken with a pin-hole collimator and, of course, the same diameter camera with a wider film than usual. Seventeen fragments of so-called cooperite from the Rustenburg district were examined in succession by this method and fourteen shown to be identical with crystal no. 2 of the tetragonal mineral. The remaining three were found to be single crystals of a second tetragonal mineral (braggite, p. 198) with different cell-sides from the first. A powder photograph of Cooper's original material from the same locality also showed the presence of these two components in about the same proportions as in the last sample.

The fourteen fragments identical with crystal no. 2 weighed, together, 2·18 milligrams. A partial chemical analysis was carried out upon this material (table I). The metal remaining after chlorination was identified as platinum by microchemical tests. Further, one of the small metal blebs was rotated in an X-ray beam, and the powder photograph obtained was identical with one of finely divided platinum made for comparison. The sulphur content is closer to the figure for PtS than for PtS_2. The second consignment of cooperite from Potgietersrust contains much larger fragments. Four of them, weighing 8·28 milligrams, were selected by X-ray rotation photographs and the results of the chemical analysis are shown in table I. A separate analysis was made upon a further quantity of 5 milligrams to obtain the palladium content. This was found to be less than 3 %. Mr. H. R. Adam has kindly allowed me to print some new analyses[1] he has obtained on grains separated by colour difference under high-power magnification. A. B. Coussmaker[2] has found that the Rustenburg concentrates contain two components which exhibit

[1] Communicated in a letter.

[2] H. R. Adam, loc. cit., Proc., p. xxxv.

different colours on roasting in air. Adam has confirmed this result for material from Potgietersrust and, moreover, finds that the two components show a colour difference under high-power magnification before heating. By weighing each fragment before and after roasting he checks his preliminary colour separation and also discovers any associated sperrylite. Analyses III and IV of table I were carried out upon material separated in this way and provisionally labelled ' cooperite B '. In the meantime Mr. Hey had prepared a number of synthetic platinum sulphides by various methods and two of them gave powder photographs (pl. VIII, fig. 7) identical with those of the

TABLE I. Chemical analyses of cooperite and synthetic PtS and PtS_2.

No.	Pt.	Pd.	Ru, Ir, &c.	Ni.	S.	Total.	Density Observed.*	Density X-ray.
I.	[83·0]†	—	—	—	17·5‡	100·0	—	—
II.	[85·6]	trace	—	0·1	14·3‡	100·0	9·5	10·2
III.	82·2	2·6	—	trace	14·4	99·2	—	—
IV.	80·26	4·31	0·62	trace	14·36	99·55	—	—
V.	[82·7]	—	—	—	17·3	100·0	9·0	10·1
VI.	[84·6]	—	—	—	15·4	100·0	—	10·1
VII.	85·9	—	—	—	14·1	—	—	10·1
VIII.	[75·3]	—	—	—	24·7	100·0	7·2	7·86

I. Cooperite (2·18 mg.) from Rustenburg, Transvaal; analysed by M. H. Hey. Unit-cell edges $a = 4·91$, $c = 6·10$ Å.
II. Cooperite (8·28 mg.) from Potgietersrust, Transvaal; analysed by M. H. Hey. Unit-cell edges $a = 4·91$, $c = 6·10$ Å.
III. 'Cooperite B' from Potgietersrust, Transvaal; analysed by H. R. Adam.
IV. 'Cooperite B' from Potgietersrust, Transvaal; analysed by H. R. Adam.
V. Synthetic PtS (M. H. Hey); $a = 4·92$, $c = 6·12$ Å.
VI. Synthetic PtS (M. H. Hey); $a = 4·92$, $c = 6·12$ Å.
VII. Theoretical figures for PtS.
VIII. Synthetic PtS_2 (M. H. Hey); $a = 3·54$, $c = 5·02$ Å.

* The observed densities were obtained by the pyknometer method and are correct only to one or two units owing to the small amounts of material used.

† The figures in brackets are those obtained by difference.

‡ The sulphur content in these two cases was obtained by precipitation as $BaSO_4$. In the remaining analyses the figure given is for the loss of weight on ignition. The loss of weight on ignition for analysis II was also 14·3 %.

tetragonal component under discussion. Analyses of these powders are given, together with the calculated figures for PtS. Two other preparations of synthetic platinum sulphide proved to be hexagonal PtS_2 and identical with the PtS_2 prepared by Thomassen.[1] The data for one of these preparations are given in table I for comparison.

[1] L. Thomassen, Zeits. Physikal. Chem., Abt. B, 1929, vol. 2, p. 349.

W. Biltz and R. Juza [1] have also synthesized both platinum sulphides and given densities of 10·09 and 10·04 for two preparations of PtS, and 7·67 and 7·65 for two preparations of PtS_2. One of Mr. Hey's PtS preparations (analysis V, table I), contains a few small hexagonal flakes. A rotation photograph of a single flake identified it as hexagonal PtS_2, and faint PtS_2 lines were also observed on the powder photograph of this preparation. This presence of a small quantity of PtS_2 accounts for the high sulphur content and low density observed. It may be added that no hexagonal PtS_2 has been detected in the Transvaal concentrates. This compound has a perfect basal cleavage and it would probably be lost in the process of washing the concentrates.

The X-ray data show convincingly that the predominant tetragonal component of the so-called cooperite fragments both from Potgietersrust and Rustenburg is PtS, the material from the former locality only differing from the synthetic compound by a small palladium and nickel content. I propose, therefore, that the name cooperite be retained for this component, its ideal composition being PtS, not PtS_2.

It is possible now to combine the X-ray data obtained on cooperite crystal no. 2 with the chemical results and deduce the axial ratio, cell contents, and probable structure of this simple mineral. The approximate density and chemical analysis are consistent with a content of 4PtS per unit cell; the cell dimensions deduced from the X-ray photographs of crystal no. 2 being $a = 4{\cdot}91$, $c = 6{\cdot}10$ Å., $c/a = 1{\cdot}242$. All spots corresponding to indices (hkl) for $(h+k)$ odd, are missing, showing that a tetragonal cell has been chosen with the square end faces centred. In addition, all indices of the type $(0kl)$ for $(k+l)$ odd, and, of course, $(h0l)$ for $(h+l)$ odd, are absent. The only three space-groups consistent with these halvings are D^2_{2d}, C^7_{4v}, and D^9_{4h}. Assuming holohedral symmetry, the most probable space-group is D^9_{4h}. An optional setting of the unit cell with $a = 4{\cdot}91/\sqrt{2}$, $= 3{\cdot}47$, $c = 6{\cdot}10$ Å. is possible, but the face-centred setting has been retained because the probable structure of cooperite can be regarded as built up from expanded face-centred unit cells of platinum.

Having chosen a setting for the unit cell and therefore the axial ratio $a : c = 1 : 1{\cdot}242$, it is possible to assign consistent indices to the forms developed upon the crystal fragments of cooperite (PtS). The

[1] W. Biltz and R. Juza, Zeits. Anorg. Chem., 1930, vol. 190, p. 168.

only fragment so far separated showing definite faces is crystal no. 2 already studied in detail by X-ray methods. The fragment measuring $1{\cdot}0 \times 0{\cdot}26 \times 0{\cdot}26$ mm. is elongated parallel to [101]. The four elongated faces in this zone are of the form (111); the other four faces of the form being very small. In addition, the forms (110) and (001) are present as small faces, but the form (100) cannot be observed. Success in noting the small faces and measuring the interfacial angles was due to setting the crystal with the axes [100], [110], and [001] vertical in succession by X-ray methods. The angles measured were $(110):(1\bar{1}0) = 90° 5'$, $(111):(\bar{1}11) = 76°$, and $(001):(111) = 60° 18'$. The values of the latter two angles calculated from the X-ray axial ratio should be 75° 50′ and 60° 21′ respectively. The images of the faces (111) in the zone [101] are bright but very diffuse; the probable error of measurement is $\frac{1}{4}$ degree; hence the discrepancy between the measured and calculated values of the angle $(111):(\bar{1}11)$. Crystal fragments of cooperite from Potgietersrust frequently exhibit a cleavage parallel to (111), and they sometimes show distinctly rounded faces.

A probable structure for cooperite will now be proposed consistent with the intensities of the spots observed on rotation photographs. If a crystal of cooperite be rotated about the axis [101] the odd layer-lines are weak, that is, all spots with indices of the type (hkl) where $(k+l)$ is odd, are weak. Thus the vertical faces (100) and (010) of the tetragonal cell are nearly centred. The atomic numbers of platinum and sulphur are 78 and 16 respectively. There is, therefore, strong evidence that the platinum atoms are arranged at the corners and face centres of the tetragonal cell. Of the six possible fourfold positions for platinum in the space-group D^9_{4h} only two lead to face-centred grouping. If either of these positions for platinum be associated with each of the five possible fourfold positions for sulphur in turn, only three different structures result. One of the three is a face-centred structure for sulphur as well as platinum. Since a number of spots corresponding to planes with mixed indices are observed on rotation photographs of cooperite this structure is excluded. A decision between the two remaining possibilities is afforded by the small differences between the intensities of certain strong spots (see below). The probable positions of the platinum and sulphur atoms are therefore:

Pt	...	...	$\frac{1}{4}\frac{1}{4}0$; $\frac{3}{4}\frac{3}{4}0$; $\frac{1}{4}\frac{3}{4}\frac{1}{2}$; $\frac{3}{4}\frac{1}{4}\frac{1}{2}$.
S	...	...	$00\frac{1}{4}$; $00\frac{3}{4}$; $\frac{1}{2}\frac{1}{2}\frac{1}{4}$; $\frac{1}{2}\frac{1}{2}\frac{3}{4}$.

These positions have been derived from the arrangements (*c*) and (*e*) of Wyckoff's tables[1] where equivalent twofold positions for the simple, not the face-centred, cell are given.

Using these parameters it can be shown that:

I. For planes with all indices odd the structure factor is twice the atomic number of platinum, viz. $F=156$. All observed spots with these indices are strong and, for a small range of spacing, equal in intensity.

II. For planes with mixed indices: (*a*) l odd, $F=0$; (*b*) l even, F is twice the atomic number of sulphur, $F=32$. All observed spots with these indices are very weak.

III. For planes with all indices even: (*a*) $(h+k+l)/2$ even: $F=156+32=188$; (*b*) $(h+k+l)/2$ odd, $F=156-32=124$.

	Structure factor F.	Indices of strong spots.								
III (*a*)	188	(202)	(220)	(224)	(004)	(400)	(404)	(422)	(206)	(440)
III (*b*)	124	(002)	(200)	(222)	(204)	(420)	(424)	(402)	(006)	(600)

All spots with indices in the top row have slightly greater intensities than those below, comparison being made, however, between spots of nearly the same spacing.

The alternative structure of cooperite would only differ in the indices of spots corresponding to structure factors given under III (*a*) and III (*b*) above. All planes with even indices and $(h+k)/2$ even would have a structure factor $F=188$, and those planes with $(h+k)/2$ odd would have $F=124$. Thus (002) should be stronger than (202), (402) than (206), &c., which is the reverse of what is actually observed. The intensity data decide against this alternative structure, which, in any case, is improbable, since the sulphur atoms would approach each other too closely.

The proposed structure is made up of planar groups of four sulphur atoms about each platinum atom, and tetrahedral groupings of platinum around sulphur. These groups are so linked that the sulphur atoms of the PtS_4 groups are arranged at the corners of a rectangle, almost a square, the sides being 3·05 Å. or half the cell-height, and 3·47 Å. or cell-side divided by $\sqrt{2}$. The smaller angle subtended at a platinum atom by two sulphur atoms is 82° 36′ and the Pt–S distance is 2·32 Å. The nearest S–S distance is 3·05 Å., and the nearest approach of the platinum atoms is 3·47 Å. The tetrahedral groups of platinum about sulphur are slightly flattened, so that although the Pt–S distance is the same for all four sulphur atoms the angle for a regular tetrahedron 109° 28′ is modified to angles of 128° 20′ and 97° 22′. The structure gives the appearance of a compromise between the almost square PtS_4 groups and the nearly regular tetrahedral SPt_4 groups. If the sulphur atom were moved

[1] R. W. G. Wyckoff, The analytical expression of the results of the theory of space-groups. Washington, 1922, p. 94.

within its tetrahedron of platinum towards the apex, until the tetrahedron became truly regular, the linked sulphur atoms of a PtS_4 group would be pulled out still farther from a true square, and vice versa. Fig. 1 shows the structure drawn to scale; the tetrahedral grouping of platinum about sulphur is clearly shown and also the good cleavage direction parallel to (111). Fig. 2 is a projection of the platinum and sulphur atoms upon the plane (110) and shows the

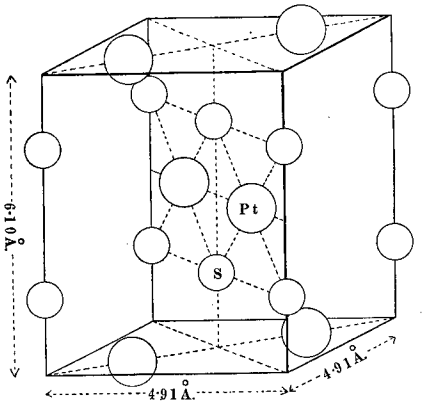

FIG. 1.

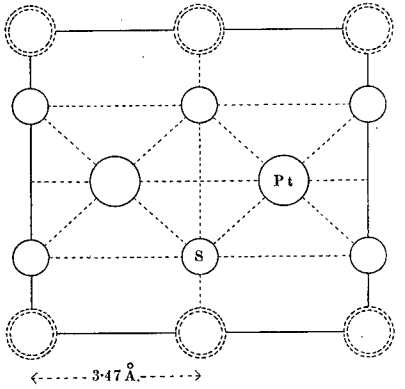

FIG. 2.

FIG. 1. Structure of cooperite. Large circles platinum, small circles sulphur.
FIG. 2. Projection of cooperite structure on the plane (110). Large circles platinum, small circles sulphur. Dotted circles represent platinum 1·735 Å. above and below the (110) plane.

PtS_4 groups. Pauling [1] has shown theoretically that platinum, palladium, and nickel with fourfold co-ordination should form planar MX_4 groups. This prediction has been verified for anions [2] and cations [3] of various complex salts; cooperite is the first binary compound also shown to possess a structure in accordance with Pauling's principle.

LAURITE.

The work so far carried out upon the cubic crystal no. 1 (p. 189) figured by G. V. White has distinguished it from cooperite and sperrylite. Rotation and Laue photographs show that its cell-edge is 5·59 Å. and its space group T_h^6: therefore its formula is probably of the type

[1] L. Pauling, Journ. Amer. Chem. Soc., 1931, vol. 53, p. 1367.
[2] S. Sugden, Journ. Chem. Soc. London, 1932, p. 246.
[3] E. G. Cox, Journ. Chem. Soc. London, 1932, p. 1912.

AX_2. An X-ray examination of five further crystals (pl. VII, fig. 4), also from Potgietersrust, showed that they are all identical with the cubic crystal no. 1, and with one exception show the same development of forms and habit. They exhibit in order of importance (100), (210), and (111), faces of the last form being usually small. The crystals show also some variation in the relative development of the cube (100) and the pyritohedron (210), and they are elongated parallel to a cubic axis. The one exception is an elongated crystal of almost scalenohedral habit. Its identity with the others has been proved by rotation photographs about [100], and its axis of elongation, which proves to be [111]. All three usual forms are developed on this crystal but the cube faces have almost vanished. The pyritohedron faces are large and curved, while the octahedron faces are smaller and are truly plane. This crystal actually yields better angular measurements than the others. The average value obtained for (210) : (102) was 66° 24′ and for (210) : (100) 26° 36′ (theoretical values 66° 25¼′ and 26° 34′ respectively). Vicinal faces are often developed, particularly on crystal no. 1. In setting up this crystal for X-ray photographs it was found that the curvature of the two large faces (100) is due to vicinal faces, these being developed on one face about the zone [001], and on the other face about the zone [110].

The composition of the cubic crystals was obtained by a combination of physical and chemical methods. The crystals range in weight from 1½ to 2½ mg. and are, with one exception, rather smaller than crystal no. 1, which measures $1{\cdot}0 \times 0{\cdot}5 \times 0{\cdot}38$ mm. Approximate values of the densities of those crystals nearly rectangular in outline were calculated from the dimensions and weight. Values varying from 5·5 to 6·6 were obtained. Also a pyknometer determination of the density was made upon five crystals (9 mg.). The value 6 so obtained is subject to an error of one to two units. Indeed, the difficulties of the present work on all three minerals have been increased by lack of reliable density data. Available methods do not yield accurate values for small quantities of heavy minerals. The approximate data do, however, show that the cubic mineral has a density of the order of 6 rather than 10. This, in itself, is sufficient to throw doubt upon the metal being one of the three, osmium, iridium, or platinum ; their sulphides if isomorphous with pyrite would all possess densities of the order of 10. A preliminary partial analysis carried out upon one crystal weighing 2·27 milligrams showed that the mineral is a disulphide. Neither platinum nor palladium could

be detected, but there was some evidence for the presence of ruthenium. Microchemical tests for ruthenium are difficult, and it was decided to confirm its presence by X-ray methods. The metallic residue left over from the crystal analysed was applied to the surface of the anode of the X-ray tube. The amount available was so small, however, that the diffractions obtained from calcite were very weak, although they correspond in position to ruthenium K_α and K_β. The second partial analysis of another crystal is given under I in table II. This crystal was roasted in air at a red-heat and then a rotation photograph taken. The powder photograph obtained could be indexed on the basis of a tetragonal cell $a = 4{\cdot}51$, $c = 3{\cdot}11$ Å., agreeing with the dimensions of the cell of synthetic ruthenium dioxide prepared and studied by Zachariasen (pl. VII, fig. 5).[1] The oxide-coated crystal was then reduced in a current of hydrogen and the powder photograph obtained of the metal yielded measurements in exact agreement with the dimensions of the unit cell of ruthenium (pl. VII, fig. 6). Incidentally, this powder photograph reveals no trace of a cubic component of Group VIII and in itself reduces the six possibilities for the composition of the cubic mineral to two, RuS_2 or

TABLE II. Chemical analyses of laurite.

				Density	
	Ru.	Os.	S.	Observed.	X-ray.
I.	[67]	—	33	6	6·23
II.	65·2	[3·0]	31·8	6·99	6·23
III.	61·1	—	38·9	—	—

I. Crystal of laurite (1·78 mg.) from Potgietersrust, Transvaal; analysed by M. H. Hey. Unit-cell edge $a = 5{\cdot}59 \pm 0{\cdot}01$ Å. The ruthenium content was obtained by difference.

II. Crystals of laurite from gravel deposits, Borneo; analysed by F. Wöhler, Nachr. Gesell. Göttingen, 1866, p. 155; 1869, p. 327.

III. Theoretical values for RuS_2.

OsS_2. Osmium may be dismissed on the evidence of too low density and certainty of formation of OsO_4, at a red-heat when the crystal was roasted in air. Finally, microchemical tests on the metal showed the presence of ruthenium, but osmium could not be detected. The cubic crystals, insoluble in aqua regia, are therefore laurite, RuS_2, a mineral already known in the gravel deposits of Borneo. A sample of laurite sand mixed with platinum, gold, &c., from Pontijn,

[1] V. M. Goldschmidt, Skrifter Norske Videnskaps-Akad. I. Mat.-Naturv. Klasse, Oslo, 1926, no. 1, p. 9.

Tanah-Laut, Borneo, in the British Museum collection (B.M. 40504), was examined and found to contain small rounded crystals with the forms (110), (210), and (111); whilst a rotation photograph about a [110] axis gave $a = 5{\cdot}59 \pm 0{\cdot}01$ Å., confirming its identity with laurite from Potgietersrust. An X-ray study of synthetic RuS_2 has been made by two authors [1] and the structure is the well-known pyrite structure. The present work confirms that the natural mineral is identical with the synthetic compound. A careful study of Laue photographs of pyrite, sperrylite, and laurite has also been made, following Ewald's method,[2] and has shown that the parameter u for all three minerals is close to 0·39. For laurite from the Transvaal u lies between 0·39 and 0·395. The shortest Ru–S distance, assuming $u = 0{\cdot}39$, is 2·35 Å.

Braggite.

The discovery of a third mineral, also tetragonal, but distinct from cooperite, was made when separating, by X-ray methods, the fragments of cooperite for chemical analysis (p. 190). The first crystal of this mineral was found amongst Cooper's original material from Rustenburg. Rotation photographs yielded a unit cell with sides $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å. The crystal, though less than $\frac{1}{2}$ milligram in weight, gives four good prism reflections at 90° intervals. Two larger crystals have also been received from Potgietersrust. These were associated with sperrylite crystals, but X-ray rotation photographs distinguished them readily (pl. VIII, fig. 9). These crystals are both tetragonal prisms, but the pyramidal planes are rounded and quite unsuitable for goniometric measurement. The prism-zone on each crystal yields values differing from 90° at the most by four minutes. The dimensions, weights, and rough density values calculated therefrom are given below:

Locality.	Dimensions.	Weight.	Density.
Potgietersrust ...	1·135 × 0·50 × 0·44 mm.	2·6 mg.	10·5
Potgietersrust ...	1·30 × 0·60 × 0·50	3·0	7·7

Four further fragments of this component were picked out by X-ray methods from Potgietersrust material also containing cooperite. The analysis carried out by Mr. Hey is given in table III. Below this, in the same table, an analysis of presumably identical material by H. R.

[1] W. F. de Jong and A. Hoog, Rec. Trav. Chim. Pays-Bas, 1927, vol. 46, p. 173. I. Oftedal, Zeits. Physikal. Chem., 1928, vol. 135, p. 291.

[2] P. P. Ewald and W. Friedrich, Ann. Physik, Leipzig, 1914, vol. 44, p. 1183.

Adam is reproduced.[1] This material he separated by colour difference under a high-power magnification, and he called it 'cooperite Y' (see p. 191). Both analyses show that the mineral is a sulphide of platinum and palladium containing 3 % to 5 % nickel. The number of sulphur atoms per unit cell is given by $[(x/32)d.a^2c]/1{\cdot}65$, where x is the sulphur percentage directly obtained from chemical analysis, d is the density, a and c are the cell sides given above, and 1·65 is the factor corresponding to the mass of a hydrogen atom. An accurate density value was unobtainable. The average of the values given on p. 198 and the pyknometer value of table III was used. Thence the numbers of sulphur atoms per unit cell calculated for analyses I and II of table III are 8·63 and 7·63 respectively. We may assume that the unit cell of this tetragonal mineral contains eight sulphur atoms. The calculated values depart from the ideal figure owing to errors in the density and sulphur determinations. It can be seen (table III) that the sum of the atomic ratios of the metals approximately equals the atomic ratio of sulphur.

TABLE III. Chemical analyses of braggite and synthetic PdS.

	Pt	Pd.	Ni.	S.	Density Observed.	Density X-ray.
I. Per cent.	[58·2]	18·1	4·7	19·0*	10	8·9
Atomic ratios	0·298	0·170	0·080	0·593		
Atoms per unit cell ...	4·35	2·48	1·17	8·63		
II. Per cent.	59·1	20·87	2·8	16·8	—	—
Atomic ratios	0·303	0·196	0·048	0·524		
Atoms per unit cell ...	4·42	2·86	0·72	7·63		
III. Per cent.	—	[80·2]	—	19·8	—	6·87
IV. Per cent.	—	76·9	—	23·1	—	—

I. Crystals of braggite (10·28 mg.) from Potgietersrust, Transvaal; analysed by M. H. Hey; platinum content by difference. Unit-cell edges $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å.

II. 'Cooperite Y', from Potgietersrust, Transvaal; analysed by H. R. Adam; also Rh, Ir, &c., 0·42, total 99·99.

III. Synthetic PdS (M. H. Hey). Unit-cell edges $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å.

IV. Theoretical values for PdS.

* Sulphur precipitated as $BaSO_4$.

The total number of platinum, palladium, and nickel atoms, therefore, also equals eight per unit cell. The ratio of Pt : Pd : Ni is roughly 4·5 : 2·5 : 1·0. No simple chemical formula that is consistent with the size of the unit cell can, therefore, be given to this mineral. The formula suggested by Coussmaker for the complex polysulphide

[1] Communicated in a letter.

existing in the Rustenburg deposits is 2PtS.2PdS.NiS;[1] but it is possible that he analysed a mixture or perhaps a mineral identical with one of the two unidentified minerals that I have separated from the Rustenburg concentrates (p. 189). It must be emphasized that in dealing with a mixture of opaque minerals reliable chemical data on the several components can only be obtained by analysing grains which have been separated and proved to be identical with each other by other methods.

This being the first new mineral to be isolated and determined by X-ray methods, it may very appropriately be named braggite in honour of Sir William H. Bragg and his son Prof. W. L. Bragg, the pioneers of the new method for the investigation of crystals.

The cell-dimensions of all the crystals and fragments of braggite so far examined are identical. Oscillation photographs have been taken around the axis [100]. The planes (001), (003), (005), and (007) are absent, otherwise there are no systematic halvings. A Laue picture along the *c*-axis also shows marked differences in intensities of the (*hkl*) and (*khl*) spots. Hence the space-group is C_{4h}^2 or C_4^3. The intensities of spots observed on the rotation photographs are not consistent with an approximately face-centred or body-centred lattice for the metal atoms. It is hoped to establish the structure of braggite shortly.

An attempt has been made to synthesize braggite from equimolecular proportions of platinum, palladium, and sulphur. Four preliminary preparations of palladium sulphide containing no platinum all yielded the same powder photographs. Moreover, no obvious relationship with PtS could be detected, the photographs being much more complicated. It was surprising to find, however, that the powder photograph of palladium sulphides is identical with that of powdered braggite (pl. VIII, fig. 10), and the relative intensities of the lines are the same for both. An analysis of one of these sulphides in table III yields the formula PdS, and approximate density values show that the tetragonal unit cell, with practically the same sides as braggite, contains 8PdS. It is probable, then, that braggite and synthetic PdS are isomorphous and that considerable replacement of the palladium by platinum and nickel can occur without disturbing the structure. Braggite may therefore be represented by the formula (Pt,Pd,Ni)S, the palladium and nickel contents being respectively about 20 % and 5 %. It has been noted that cooperite

[1] H. R. Adam, loc. cit., Proc., p. xxxv.

contains only very small quantities of nickel and palladium. A study of synthetic PtS and PdS compounds in which the platinum and palladium are replaced by varying amounts of palladium and platinum respectively is needed to reveal the limits of stability of both structures.

The powder photographs of Cooper's and Adam's original material show the predominance of cooperite and this is confirmed by the early analyses. The palladium figure ranges from 4·2 to 9·4 %,[1] and assuming palladium is present only as braggite the relative proportions of cooperite to braggite in the mixtures analysed varied from about 3 : 1 to 4 : 1. Laurite and sperrylite when present seem to show sufficient crystalline forms to make separation by eye possible. The proportion of ruthenium in Adam's analyses is small and accounts for the small number of laurite crystals so far found in these deposits. The sperrylite content in the early analyses ranged from 10 % to 30 %.

Sperrylite.

A crystallographic and X-ray study has also been made of sperrylite crystals from the Transvaal deposits. The identity of the two large crystals previously described by Dr. Spencer [2] has been confirmed by measuring the cell size. Oscillation photographs were taken to obtain the (200) diffractions from cube faces of both crystals. The data (together with density determinations) are given in table IV. Accompanying the crystal no. 1 of laurite figured by White was a tiny cubo-octahedron from Rustenburg readily identified by a rotation photograph as sperrylite. The spacing of this crystal (B.M. 1931,167) derived from oscillation photographs is also given in table IV. Six

Table IV. Measurements of oscillation photographs of sperrylite crystals from the Transvaal.

B.M. No.	Distance $2r$ between diffractions (200) on plate.	a.	Density X-ray.	Density Observed.
1926,445	8·105 cm.	5·926 Å.	10·90	10·46*
1926,261	8·085	5·934	10·88	10·58†
1931,167	8·100	5·927	10·90	—

Copper radiation $\lambda = 1{\cdot}539$ Å. was used, the distance from crystal to plate being 7 cm.

* The larger crystal, B.M. 1926,445, has some adherent limonite. Hence the figure 10·46 is only approximate.

† This figure was obtained by L. J. Spencer, Min. Mag., 1926, vol. 21, p. 95.

[1] H. R. Adam, loc. cit., Trans., p. 105.

[2] L. J. Spencer, Min. Mag., 1926, vol. 21, p. 94.

other additional crystals of this mineral from Potgietersrust have been selected by X-ray methods during the systematic study of the cooperite fragments. Apparently the colour difference test used by H. R. Adam to pick out the mineral components succeeds moderately well in separating cooperite from braggite, but it fails to distinguish laurite from cooperite, or sperrylite from braggite. Indeed, of five crystals labelled 'cooperite Y' three were found to be sperrylite by rotation photographs. These small crystals of sperrylite exhibit considerable variation in habit, and on them only the forms (100) or (111) have been detected. Their shape ranges from small prisms with the corners replaced by tiny octahedral faces to flat triangular plates which are simply flattened octahedra. The data in table IV show that the cell-size of large and small sperrylite crystals is fairly constant and that the observed density of the large crystals is considerably less than that calculated from X-ray measurements. In the absence of correlated physical and chemical data on the same crystal it can only be suggested that the discrepancy is due to assuming an ideal composition of $PtAs_2$; there may be some replacement of one or both elements by elements of lower atomic weight. The study of a Laue photograph of a crystal of sperrylite from Rustenburg shows that the parameter u lies between 0·385 and 0·390. The smallest distance Pt–As = 2·50 Å. for $u = 0{\cdot}39$.

Magnetic Platinum.

A number of small, bright cubes and dull, flattened prisms and plates of platinum from Potgietersrust can be separated into two lots by means of a bar magnet. The material that is readily attracted consists mainly of the dull prisms and plates, whilst the cubes giving good goniometric reflections are only feebly magnetic. A rotation photograph of one of the bright cubes about a cube axis gave a photograph typical of a face-centred cube lattice with spacing $a = 3{\cdot}91$ Å. In addition to the diffractions corresponding to planes with unmixed indices, the photograph shows definite though weak spots for planes with mixed indices. These, of course, should not appear with an ideal face-centred lattice and are perhaps to be referred to the iron-content. A rotation photograph of a dull plate yielded uniform Debye-Scherrer rings quite free from flecks. These rings correspond to the strong diffractions present on the platinum cube rotation photograph, and no other lines are present. If the plate be stationary during exposure, the same photograph is obtained; the rings are

uniform in intensity and no indication of orientation of the particles forming the plate is apparent. There is, however, a definite decrease in the spacing $a = 3{\cdot}87$ Å. For comparison, a powder photograph of finely divided platinum obtained by ignition of ammonium chloroplatinate was obtained which showed exactly the same lines as the photograph of the dull platinum plate and the same relative intensities. The spacing of platinum obtained by ignition is $a = 3{\cdot}93$ Å., and no lines could be detected corresponding to mixed indices.

In conclusion I should like to thank Dr. Spencer for his advice and encouragement during the course of the work. I am also indebted to Mr. Bernal for helpful suggestions on the structure of cooperite.

Summary.—X-ray rotation photographs have been used to distinguish and select for chemical analysis the various platinum- and palladium-bearing minerals present in concentrates of Bushveld platinum ore. The name cooperite is retained for PtS, tetragonal space-group D^9_{4h}. The face-centred unit cell with edges $a = 4{\cdot}91$, $c = 6{\cdot}10$ Å., contains 4PtS. The structure is a simple type of fourfold co-ordination built up from planar PtS_4 groups and tetrahedral Spt_4 groups, the Pt–S distance being 2·32 Å. Laurite (RuS_2) occurs as small pyritohedral-cubic crystals and has the pyrite structure with unit-cell edge $a = 5{\cdot}59$ Å., and parameter u between 0·39 and 0·395. The third mineral (Pt,Pd,Ni)S containing about 20 % Pd and 5 % Ni, is also tetragonal with unit-cell edges $a = 6{\cdot}37$, $c = 6{\cdot}58$ Å. The unit cell contains 8(Pt,Pd,Ni)S, and the space-group is D^2_{4h}. The name braggite is proposed for this mineral as being the first new mineral to be discovered by X-ray methods.

Appendix.—Notes on the analyses, and on the synthesis of the sulphides of the platinum group. (By M. H. Hey.)

For those minerals in the Transvaal platinum concentrates which are insoluble in aqua regia, fusion methods are very unsatisfactory when small quantities have to be dealt with, as the amount of flux has generally to be quite disproportionate to the amount of material. It was found best to heat the minerals in a current of air, in a small silica-glass tube slipped into a wider one of the same material; the latter was bent and drawn down to a jet at the exit end, and the

sulphur oxides collected in ammoniacal hydrogen peroxide, and weighed as barium sulphate. Some difficulty was experienced in obtaining total absorption of the sulphur, as it is oxidized to sulphur trioxide, fumes of which can be seen in the tube, and this tends to give a troublesome fog (the oxidation to the trioxide is, of course, due to the catalytic action of the platinum metals).

The advantage of this process for the present purpose lay in the metal remaining as a bead instead of subliming as chloride, as it does if chlorine is used to attack the mineral; and an X-ray photograph of the metal bead may afford useful information. Cooperite and braggite leave beads of pure metal, readily soluble in aqua regia, but the laurite left a residue containing 9 % oxygen, due to superficial oxidation, and gave an X-ray photograph agreeing with RuO_2. This oxidized bead was reduced in hydrogen, to get the weight of the metal, and then heated in a current of chlorine to bring it into a soluble form for identification tests.

The small amount of material available limited the analyses to the principal constituents, and it was impossible to test accurately for the presence of osmium, iridium, ruthenium, or rhodium in the cooperite and braggite; but it could be shown that the laurite contained no appreciable amount of platinum, palladium, or iridium.

An accurate micro-balance was not available, but the analyses were carried out on a good analytical balance with the help of a reading microscope to follow the swing of the pointer. The weighings were probably accurate to about $\pm 0{\cdot}02$ mg., and the weight of material used for each analysis of the minerals is given in tables I–III. The synthetic products were available in larger quantity (0·2–0·4 gm.) and their analysis presented no difficulties.

The synthesis of the platinum sulphides was undertaken at a time when accurate analyses of any of the minerals seemed impossible owing to the minute amount of material available, and confirms the conclusion of W. Biltz and R. Juza[1] that PtS and PtS_2 are the only sulphides formed, processes supposed to give Pt_2S_3 or Pt_5S_6 leading to mixtures of mono- and disulphide. Biltz and Juza's work shows that the sulphide to be expected depends simply on the temperature and sulphur vapour-pressure, hence there seems no point in giving full details of all the processes tried.[2] But it may be noted that the

[1] W. Biltz and R. Juza, Zeits. Anorg. Chem., 1930, vol. 190, p. 161.

[2] The methods used were those of L. N. Vauquelin, Schweigg. Journ., 1817,

sodium and potassium platinum sulphides described by R. Schneider were not obtained, and the possibility of their existence requires re-investigation.

The syntheses of palladium sulphides were made mainly on the chance of one of them proving allied to one of the two rare, unidentified minerals in the Rustenberg concentrates, and it was surprising to find that PdS gives a powder photograph almost identical with that of braggite, which contains about 60 % platinum. So far as they go, the experiments show that PdS is the most stable of the palladium sulphides.[1] The stable existence of PdS_2 is doubtful, R. Schneider's process giving a mixture of PdS and sulphur. The reported insolubility of Pd_2S in aqua regia (both PdS and palladium are readily soluble) makes it probable that it can exist, but it was not obtained, and the exact conditions under which it is stable require investigation.

Laurite has been synthesized by H. Deville and H. Debray,[2] though the identity of the synthetic and natural product was not too firmly established. Indeed, Mr. Bannister's X-ray study of Borneo laurite forms the first satisfactory proof that the mineral is RuS_2, as Dana, L. J. Spencer and others believe [3], rather than Ru_2S_3, as it is given by H. E. Roscoe and C. Schorlemmer, and by A. J. Webb.[4]

vol. 20, p. 394; R. Böttger, Journ. Prakt. Chem., 1834, ser. 1, vol. 3, p. 267; R. Schneider, Journ. Prakt. Chem., 1873, ser. 3, vol. 7, p. 224; H. Deville and H. Debray, Compt. Rend. Acad. Sci. Paris, 1879, vol. 89, p. 587; and W. Knop, Chem. Centr., 1859, p. 18.

[1] The methods used were those of F. Roessler, Zeits. Anorg. Chem., 1895, vol. 9, p. 31; R. Schneider, Ann. Phys. Chem. (Poggendorff), 1870, vol. 141, p. 519; L. N. Vauquelin, Ann. Chem. Phys., 1813, vol. 88, p. 190; and Smith and Keller, Ber. Deut. Chem. Gesell., 1890, vol. 23, p. 3373.

[2] H. Deville and H. Debray, Compt. Rend. Acad. Sci. Paris, 1879, vol. 89, p. 587.

[3] Dana Syst. Min., 6th edit., 1892, p. 93; L. J. Spencer in Sir Edward Thorpe's Dictionary of Applied Chemistry, 2nd edit. (London), 1924, vol. 4, p. 38; W. F. de Jong and A. Hoog, Rec. Trav. Chim. Pays-Bas, 1927, vol. 46, p. 173.

[4] H. E. Roscoe and C. Schorlemmer, Treatise on Chem., 4th edit. (London), 1907, vol. 2, p. 1291; A. J. Webb, in Sir Edward Thorpe's Dictionary of Applied Chemistry, 2nd edit. (London), 1924, vol. 5, p. 721.

Explanation of Plates VII and VIII.

X-ray photographs of minerals from Transvaal platinum concentrates. All these photographs were taken with filtered copper radiation $\lambda = 1{\cdot}539$ Å., and with the same cylindrical camera, diameter 6·04 cm. A length of 15 cm. on all the original films is equivalent to 10 cm. on the reproduced figures.

Fig. 3. Rotation photograph of cooperite crystal no. 2 about the axis [100].

Fig. 4. Rotation photograph of a laurite crystal about a cube axis.

Fig. 5. Powder photograph of ruthenium dioxide.

Fig. 6. Powder photograph of ruthenium.

Fig. 7. Powder photograph of synthetic PtS.

Fig. 8. Rotation photograph of a crystal fragment in random orientation for identification. This photograph is completely superposable upon the powder photograph, fig. 7; the mineral fragment is therefore cooperite.

Fig. 9. Rotation photograph of a crystal of braggite about the axis [001].

Fig. 10. Powder photograph of braggite.

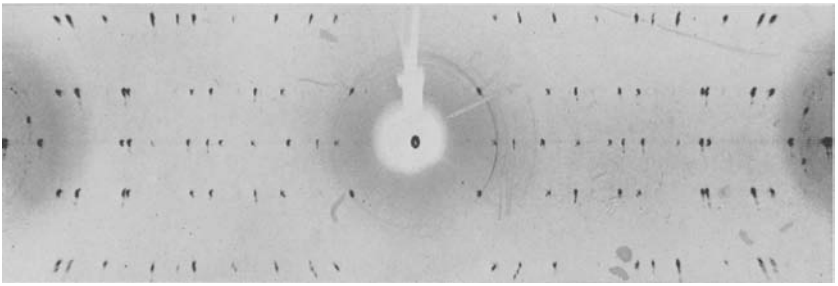

FIG. 3.

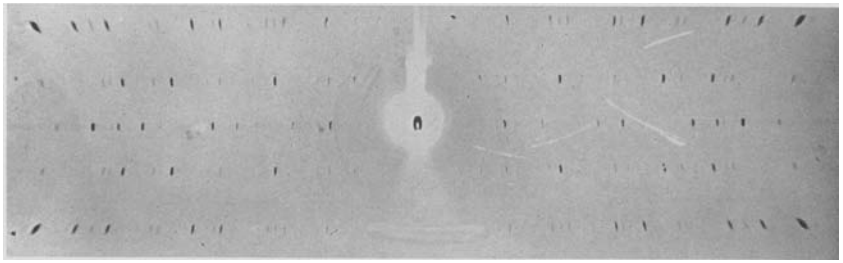

FIG. 4.

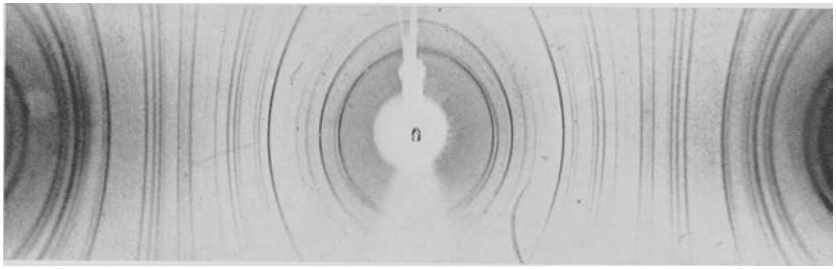

FIG. 5.

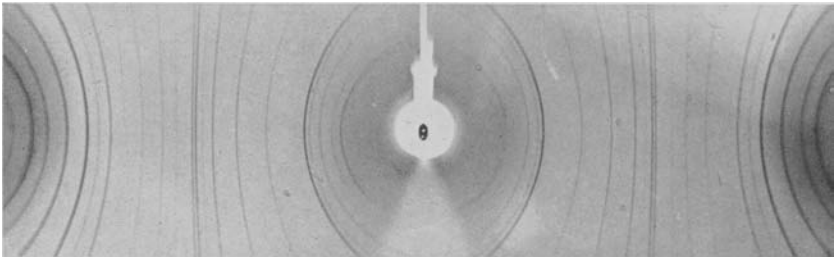

FIG. 6.

F. A. BANNISTER: X-RAY PHOTOGRAPHS OF TRANSVAAL PLATINUM MINERALS.

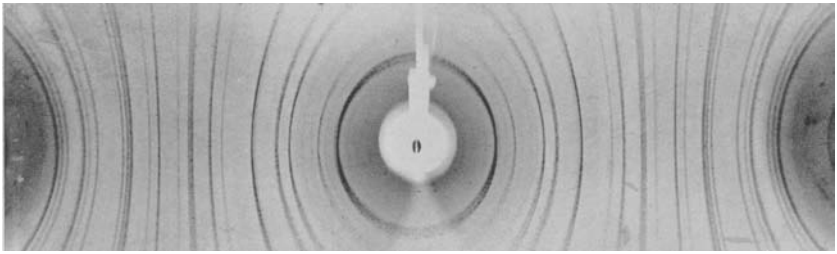

FIG. 7.

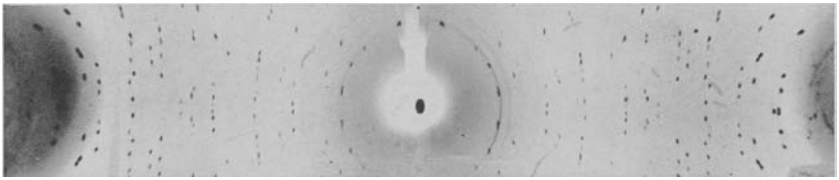

FIG. 8.

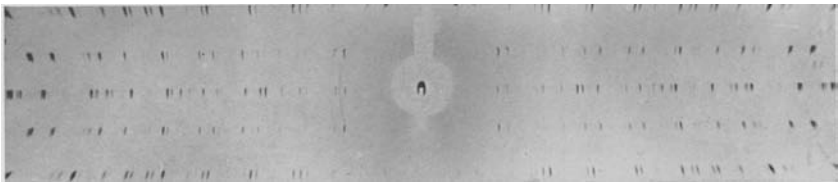

FIG. 9.

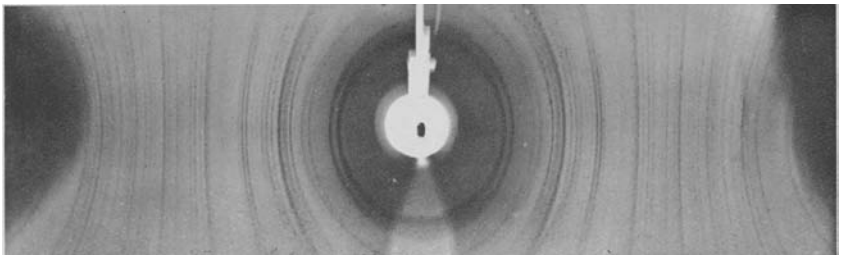

FIG. 10.

F. A. BANNISTER: X-RAY PHOTOGRAPHS OF TRANSVAAL PLATINUM MINERALS.