The Structure of Braggite and Palladium Sulphide.

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The investigation of the structure of Palladium Sulphide PdS is of double interest. In the first place it is important in order to determine the coordination of palladium, and in the second, because the identification of Braggite $(Pt, Pd, Ni)\,S$, which is isomorphous with palladium sulphide, by F. A. Bannister[1]), was the first example of a mineral determination carried out solely by X-ray methods.

The structure of braggite was complicated by the large replacement of palladium by platinum and nickel (approx. 4 atoms Pt, $2\,Pd$, $2\,Ni$, $8\,S$). The best method of attack was clearly an investigation of the isomorphous synthetic compound PdS, of which, through the kindness of F. A. Bannister, two single crystals were available. These were small black, metallic, tetragonal crystals, with elongation along the c-axis, and a flattening perpendicular to one a-axis, producing a thick plate parallel to the (100) face. Oscillation photographs about the c and b axes give $a = 6.43 \pm 0.02$ Å, $c = 6.63 \pm 0.02$ Å. Assuming a density of 7, there are eight molecules of PdS in the unit cell, giving the X-ray density 6.69. Oscillation and Weissenberg photographs (CuK radiation) show a pseudo-cubic character, and the only regular absent reflections to be those for which 00l is odd. There are no planes of symmetry parallel to the principal axes ($hk0 \neq h\bar{k}0$ and $hk0 \neq kh0$), so that the space group is most probably $P4_2/m$ or $P4_2$.

The determination of the positions of the palladium atoms was made by the direct F^2 Patterson method[2]). The F^2's were obtained by estimating visually intensities on Weissenberg and oscillations photographs, and connecting these intensities by their respective polarisation factors $-\Theta = \frac{1 + \cos^2 2\theta}{\sin 2\theta}$. The measurement of intensities was made by fixing the strongest spot as 100 and estimating the intensities of others on this scale. Cross checks of one spot against another ensure that the right order of intensities is obtained, and an overlap of 2° on the oscillation photographs allows of comparison of different photographs. The results from oscillation and rotation photographs agreed well, as also the $F^2 hk0$ and $F^2 k\bar{h}0$, which should be equal. No account was taken of absorption, but this should not affect the $hk0$ reflections much, because the thickness

1) See preceding note.

2) Patterson, Z. Kristallogr. (A) 90 (1935) 517—542.

of the crystal in the b-direction is not much greater than that in the a-direction. With the $h0l$ reflections the larger c-direction will give an effective decrease of the low order reflections in the c-direction. This manifests itself as a slight elongation of the peaks in the $h0l\ F$ projection. The F's are obtained by taking the square roots of the F^2's and multiplying by a factor of 10. These were used for the Fourier projections, but are reduced by a factor $\frac{4}{5}$ for comparing F observed with F calculated.

For the $hk0$ plane the Patterson series may be written $\sum_{h=-\infty}^{\infty}\sum_{k=-\infty}^{\infty} F^2_{hk0} \cos 2\pi(hx+ky)$ — and this was summed by the method of Beevers and Lipson[1]) for the measured F's for the $hk0$ plane.

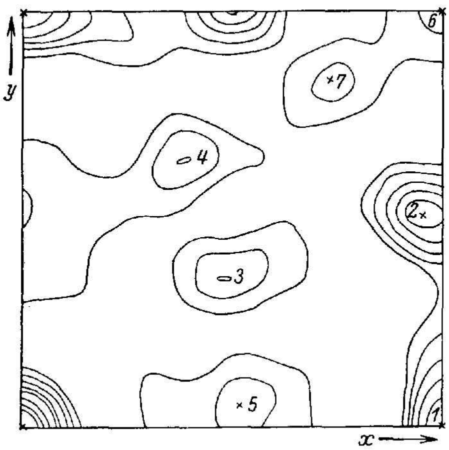

Fig. 1. $hk0$ Patterson (F^2) Projection. The contours are every 25 units (arbitrary) except the peak at the origin — which is marked every 50 units.

The peaks of the F^2 projection indicate the positions of ends of vectors from the origin. These vectors represent interatomic distances. It will be seen that there are two very large peaks and several smaller ones. This rules out the possibility of one eight-fold position for the Pd atoms, because there should in this case be only one very large peak and one half the size for the Pd—Pd distances, and only smaller peaks for the Pd—S distances (F^2S approx $\frac{1}{9}F^2Pd$). Four-fold positions for the palladium atoms were tried, since two four-fold positions should give six equal large peaks and two half size peaks. No combinations of two peaks as the main Pd—Pd vectors for the two four-fold sets give the other calculated peaks in the observed positions. The restriction of the general positions, because the palladium atoms cannot approach a two-fold or four-foldscrew axis nearer than its atomic radius, helped to place the palladium atoms in three different sets, two special two-fold $(0, 0, \frac{1}{4})$ $(0, \frac{1}{2}, 0)$ and one four-fold with variable x and y parameters, $(x, y, 0)$, where $x = .48$, $y = .25$. The

1) Beevers and Lipson, Philos. Mag. (7) 17 (April 1934) 855.

(1) and (2) peaks are larger than the others because of the effect of two *Pd* atoms at (0, 0, $\frac{1}{4}$) and (0, 0, $\frac{3}{4}$) lying on the four-fold screw axis. The peak (4) is not accounted for with these positions for palladiums, and is therefore assumed to be due to sulphur atoms in eight-fold positions, the peak indicating $x = .19$ $y = .32$. Although the sulphur has an atomic scattering factor only one third that of palladium, a peak on the F^2 projection may arise because the vector represents the interatomic distance between two *S*'s (one vertically above the other) and two *Pd*'s (on fourfold screw axis).

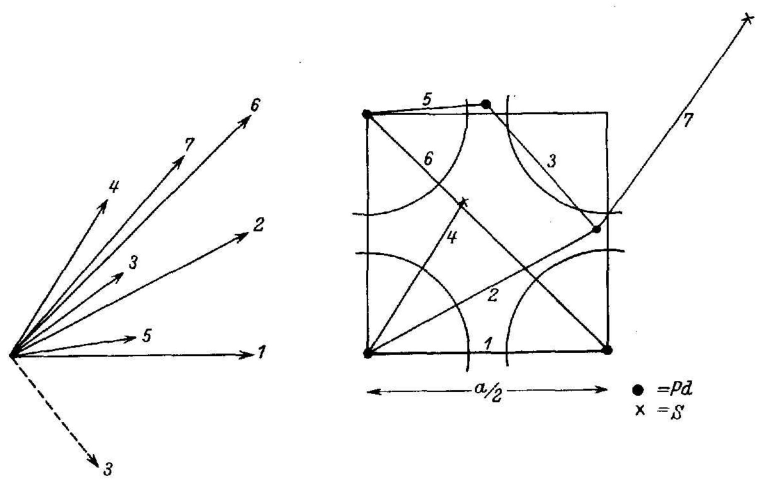

Fig. 2. (a), (b) Showing the vectors from the $hk0$ Patterson and the corresponding interatomic distances.

The $hk0$ F^2 projection shows that two two-fold positions are occupied by the palladium atoms. For these the z-co-ordinate is fixed. For the palladium atoms in the four-fold position the z-co-ordinate is fixed for the space group $P\,4_2/m$, but not for the space group without the plane of symmetry, $P\,4_2$. An F^2 projection on the $h0l$ plane was made, and to the limits of accuracy obtained the z-co-ordinates for the four-fold position were 0 and $\frac{1}{2}$, showing that there was no need to assume the lower $P\,4_2$ symmetry. All coordinates, will, therefore, be expressed as of the $P\,4_2/m$ space group. (The unit cells are $\frac{1}{4}c$ apart in the two space groups.) The F^2 projection on $h0l$ confirmed the results of the $hk0$ projection (its similarity showed the pseudo-cubic character) and indicated that the z-parameter for the sulphur was approximately 0.23, that is, just a little off the $z = \frac{1}{4}$ position.

F values were calculated for the $hk0$ and $h0l$ reflections using the value:

2 Pd at $(0, 0, \frac{1}{4})$
2 Pd at $(0, \frac{1}{2}, 0)$
4 Pd at $(x, y, 0)$ where $x = .48$, $y = .25$
8 S at (x, y, z) where $x = .19$, $y = .32$, $z = .23$

These gave in most cases unambiguous values of the sign of F, so that the Fourier projection could be made on the $hk0$ and $h0l$ planes.

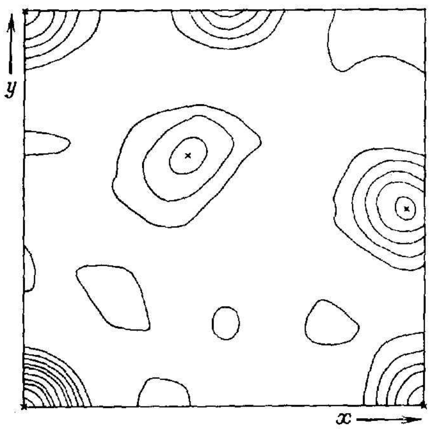

Fig. 3. Fourier projection on $hk0$. Contours every 25 units.

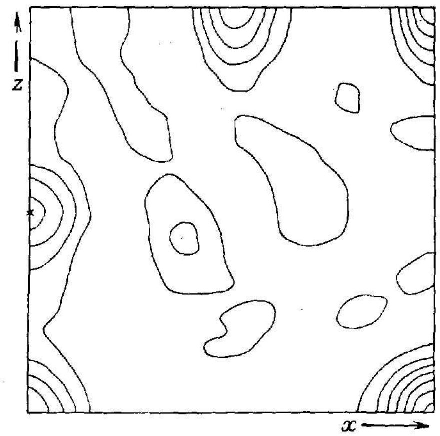

Fig. 4. Fourier projection on $h0l$. Contours every 20 units.

The $hk0$ gave very regular palladium peaks, and quite a good sulphur peak (due to $2S$ atoms), giving the parameters:

for Pd (4-fold) $x = .475$, $y = .250$
for S $x = .20$, $y = .32$

The $h0l$ projection is not so regular, the palladium peaks being elongated in the c-direction, due probably to absorption. It does, however, confirm the $z = 0$ parameter for the palladiums in four-fold positions. The two sulphur peaks are not so well defined as the single S peak in the $hk0$ projection, but are consistent with the parameters from the $hk0$ projection. The z parameter is indicated approximately as $z = .22$. It will be noticed that in both $hk0$ and $h0l$ projections slight diffraction maxima round the large peaks are observable, although most diffraction effects were removed by decreasing the effect of the higher order reflections by means of an artificial temperature factor ($F = F_0 e^{-B(\sin\theta/\lambda)^2}$, $B = 3$).

An attempt was made to obtain more accurate values of the parameters for the sulphur atoms—the exact position of the sulphur being required to give the distortion of the *Pd-S* co-ordinations. Very few reflections could be found for which the total F of the palladium atoms was zero. Those for which $F_{Pd} = 0$ were, further, found to be very insensitive to change of the S-position. However, the table I of intensities, (and more clearly the graphical representation of these Fig. 5) for $h00$ and $hk0$ reflections does show that the position of the sulphur atom indicated by the $hk0$ Fourier ($x = .20$, $y = .32$) is more probable than that for which the four *Pd-S* distances are equal. ($x = .20$, $y = .30$).

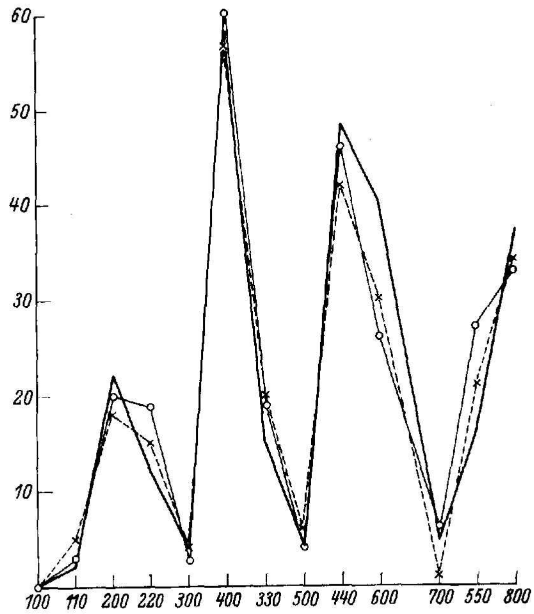

Fig. 5. Plot of $h00$ and $hh0$ observed and calculated intensities.
—— = observed F
—○— = calculated for S (.20, .30)
----×---- = calculated for S (.20, .32)

Table I.
F's observed and calculated for S positions
1. $x = .20, y = .30$; 2. $x = .20$, $y = .32$

$hk0$	F_1	F_2	$F_{obs.}$	$hk0$	F_1	F_2	$F_{obs.}$
100	0	0	0	700	6	1	7
200	18	20	28	800	33	34	62
300	3	4	5	110	3	4	2
400	60	57	73	220	19	15	15
500	4	6	9	330	19	20	19
600	26	30	50	440	47	42	60
				550	27	21	20

There is slightly better agreement here with the (.20, .32) position, indicating a certain amount of distortion. The (.20, .32) has also the weight of the $hk0$ Fourier result.

It will be seen, however, that the change in F values for 0.02 change in parameter is small, and in no case really significant. This must be expected, since the eighth order reflections are the highest obtainable, so that the resolving power of the crystal is small. The comparatively large palladium atoms also give a masking effect to the sulphur F contributions, especially as only half of the Pd atoms are in special positions, giving, therefore, no regularities in F contributions for palladiums. It will be assumed, then that the statistical result of the $hk0$ Fourier (which gives an almost regular sulphur peak) is correct, and that the sulphur parameters are $x = .20$, $y = .32$, $z = .22$. The z-parameter from the $h0l$ Fourier has a possible accuracy of $\pm$ 0.015 and the x and $y \pm$ 0.01. The parameters for the palladium atoms in $(x, y, 0)$ positions are estimated to be correct to $\pm$ 0.005, the Fourier peak (and the Patterson peak also) being very regular and sharply defined. A possible approach to a more accurate value of the sulphur parameters is the three dimensional method of Patterson[1]), which will bring in the extra weight of a large number of hkl reflections. A study of the selenide of palladium (which may be isomorphous with the sulphide) would be even more promising, because the selenium would give an F contribution comparable with that of palladium.

Table II. F's observed and calculated for $h0l$.

$h0l$	$F_{calc.}$	$F_{obs.}$	$h0l$	$F_{calc.}$	$F_{obs.}$	$h0l$	$F_{calc.}$	$F_{obs.}$
101	2	0	103	4	0	305	10	9
201	39	20	203	33	24	405	0	2
301	1	0	303	7	3	505	11	18
401	1	4	403	3	3	506	13	21
501	6	16	503	2	4	106	24	26
601	19	32	603	22	30	206	4	8
701	4	9	703	8	19	306	19	24
801	4	10	104	1	0	406	19	24
102	38	20	204	19	20	506	17	21
202	12	14	304	2	0	107	5	4
302	32	20	404	47	40	207	21	22
402	25	28	504	4	0	307	12	12
502	20	36	604	23	28	407	5	8
602	9	25	704	3	23	108	0	3
702	12	20	105	4	3	208	17	20
802	14	26	205	23	24			

1) Patterson, J. Phys. Chem. Soc. June 1936.

Table III. F's observed and calculated for $hk0$.

$hk0$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$hk0$	$F_{\text{calc.}}$	$F_{\text{obs.}}$	$hk0$	$F_{\text{calc.}}$	$F_{\text{obs.}}$
100	0	0	320	27	30	640	16	30
200	19	22	420	26	37	150	6	10
300	4	5	520	13	16	250	30	33
400	55	59	620	1	8	350	3	4
500	5	7	720	29	38	450	3	10
600	28	43	820	33	34	550	10	16
700	1	6	130	14	14	650	34	32
800	38	50	230	33	27	160	21	43
110	3	2	330	12	15	260	5	7
210	31	26	430	8	12	360	20	42
310	21	10	530	30	47	460	22	28
410	21	40	630	10	14	560	20	16
510	18	14	730	1	3	170	10	15
610	26	43	140	24	37	270	7	6
710	8	10	240	33	38	370	8	22
810	12	20	340	16	22	180	11	20
120	49	30	440	44	48	280	39	32
220	10	12	540	5	6			

The basis of the structure may be considered to be a cubic β-tungsten type lattice of palladium atoms. If the four palladiums in the general

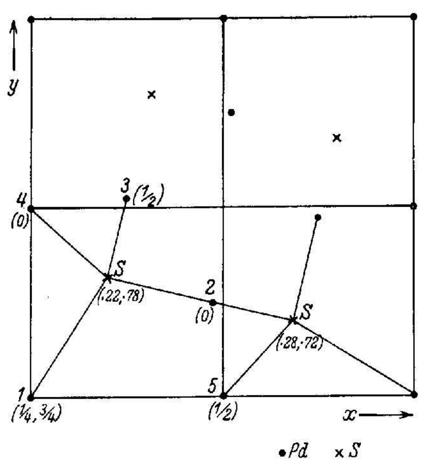

Fig. 6. Plan of structure on $hk0$. (The Pd-atoms are numbered as in the text.)

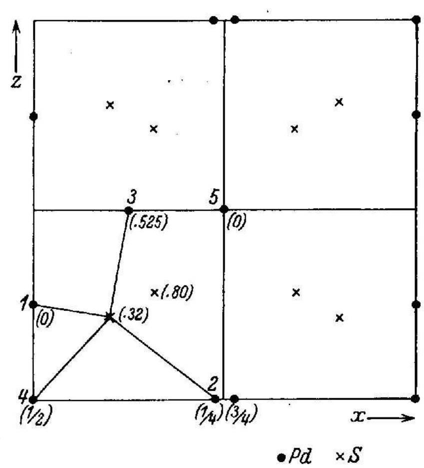

Fig. 7. Plan of structure on $h0l$.

position $(x, y, 0)$ are moved to $(\frac{1}{2}, \frac{1}{4}, 0)$ and the unit cell considered from the atom $(0, \frac{1}{4}, 0)$, as origin, a body centred cell, plus two atoms on each face, is at once apparent. This cubic arrangement, with the sulphur in the symmetrical position $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ (referred to the tetragonal axes to avoid confusion of diagrams) gives a five-fold coordination about the sulphur atom, there being three neighbours at $\sqrt{2}a/4$ and two at $\sqrt{3}a/4$. The arrangement of sulphurs is square about six of the palladiums, cubical about the other two. To avoid the five-fold coordination the sulphur in *PdS* has moved away from one palladium atom ((5) in the Fig. 6) and the four palladiums about the centre move slightly also. The cell elongates

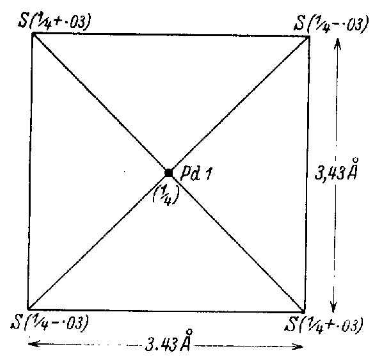

Fig. 8.
Arrangement of sulphur atoms about Pd (1), $(0, 0, \frac{1}{4})$.

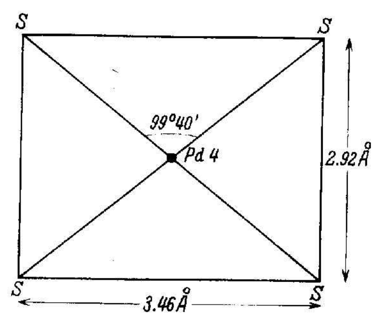

Fig. 9. Arrangement of sulphur atoms about Pd (4), $(0, \frac{1}{2}, 0)$. The S's and Pd are in the same vertical plane due to the symmetry.

slightly and the sulphur moves up, still further away from (5) at $(\frac{1}{2}, 0, \frac{1}{2})$ Fig. 7. We have for the *Pd-S* distances:

$d_1 = 2.43$ Å $\quad d_3 = 2.29$ Å $\quad d_5 = 2.94$ Å.
$d_2 = 2.34$ Å $\quad d_4 = 2.26$ Å

The sides of the palladium tetrahedron, with the angles subtended at the centre are:

(1) (2)	3.83 Å	106° 48′	(2) (3)	4.03 Å	121° 0′
(1) (3)	4.09 Å	119° 48′	(2) (4)	3.45 Å	95° 20′
(1) (4)	3.62 Å	100° 50′	(3) (4)	3.73 Å	110° 6′

The tetrahedron of palladium atoms about each sulphur is therefore much deformed. There are eight tetrahedra of palladiums in the unit cell, of similar shape because of the symmetry of the crystal. The arrangement of the tetrahedra is by sharing of one side (the short (4) (2) side in the notation above), and connecting with four tetrahedra at both of the other corners. The short edge common to both tetrahedra is that between the sulphur atoms of closest approach, and may be considered to be a consequence of the repulsion of sulphur from sulphur, and the consequent drawing in of the palladiums until the *Pd-S* attraction and the *Pd-Pd* repulsion give equilibrium. The presence of palladium atom (5), which was pushed away when the cubic structure was discarded, causes a flattening of the tetrahedron in its direction, so that the face (1) (2) (3) is quite the largest tetrahedron face. This is a forcing of the palladium atoms out of position by the attraction between *Pd* (5) and the sulphur atom.

The arrangement of sulphur atoms around palladium atoms is of three types. Type (1) $(0, 0, \frac{1}{4})$ has a "buckled" square of sulphurs about the palladium atom Fig. 8. The side of the square is 3.43 Å in projection on $hk0$, or $\sqrt{3.43^2 + (0.06c)^2} = 3.45$ Å in actual length. If the square is to be made flat the sulphurs have to be put on the same level. This would deform the tetrahedra even more than they are, since the distance between palladiums (4) and (2) would become shorter.

Type (4) $(0, \frac{1}{2}, 0)$ has a plane rectangle of sulphur atoms round it, this plane being vertical (c-axis vertical) Fig. 9. The sides are 2.92 Å (the nearest approach of sulphur atoms in the structure) and 3.46 Å. This is far removed from a square, and to make it a square large deformation of the palladium tetrahedron would be necessary.

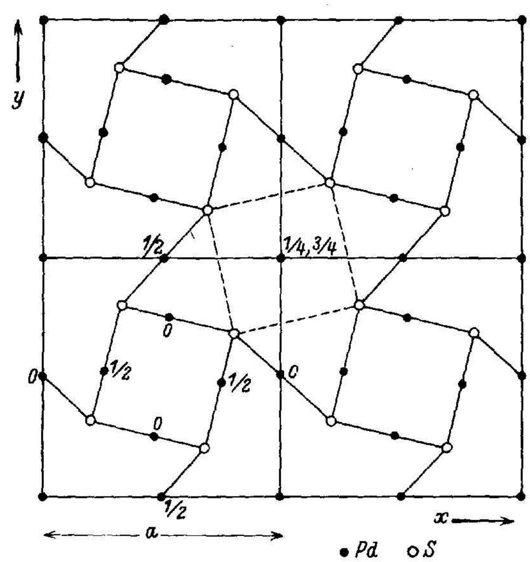

Fig. 10. Arrangement of sulphur atoms about *Pd* (2), (.475, .250, 0). The *S*'s and *Pd* are in the same vertical plane within the limits of measurement.

The palladiums in the general positions (atoms (3) and (2)) have within the limits of error a plane arrangement of sulphur around them (the *S-S* distance in the $hk0$ projection = 3.18 Å, Fig. 10 the sum $Pd - S + S - Pd = 3.19$ Å), the sulphurs being 2.92 Å and 3.71 Å apart at the two ends as shown in the diagram. The planes are vertical, and form a square prism around the central four-fold half screw axis. These prisms are joined by the vertical rectangle about the palladium atom on the two-fold axis, and by the horizontal square about the palladium on the corner four-fold axis (Fig. 11).

The structure is of considerable interest in showing that although square planar arrangements of sulphur about palladium are approached—these arrangements are readily deformed. This deformation is especially easy in the plane of the sulphur atoms, the angle between the *Pd-S* links varying from 77° 10′ to 99° 40′. This is slightly greater deformation than in cooperite for which the smaller angle subtended at a platinum atom by two sulphur atoms in a plane rectangular arrangement is 82° 36′. The deformation of the plane square out of the plane seems more difficult, the angle between the *Pd-S* link and the horizontal being only 4° 40′. The deformation out of the plane occurs by two sulphurs moving up, two moving down, as might

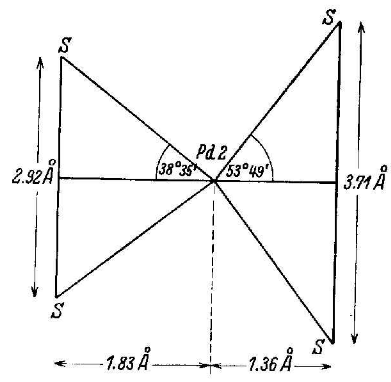

Fig. 11. Plan on $hk0$ plane, showing the arrangement of the PdS_4 groups. Four unit cells are shown.

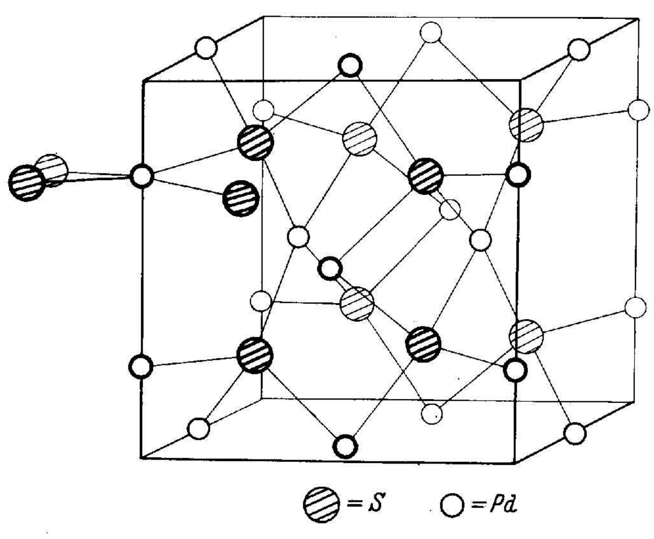

Fig. 12. Diagram of unit cell.

be expected if a structure rigid in the plane of the palladium atom were buckled by a large force. The palladium sulphur co-ordination is, then, the square type generally assumed, but this square can be easily deformed while kept plane, and deformed less easily out of the plane.

I wish to thank Mr. Bernal for giving me this problem and for his constant help in the work — also Dr. Fankuchen for taking the photographs and for much advice.

Summary.

Palladium sulphide is tetragonal, space group $P\,4_2/m$ $a = 6.43$ Å, $c = 6.63$ Å, eight molecules in the unit cell. The structure was determined by direct Patterson and Fourier analysis on visually estimated intensities of reflections. The arrangement of the palladium atoms closely resembles the β-tungsten structure. The sulphur atoms lie almost at the corners of a cube of half the linear dimensions of the unit cell, and twisted a little about the central half-screw axis. The structure shows deformed tetrahedra of palladium about sulphur atoms, and three types of deformed square in the arrangement of sulphur about palladium atoms. This latter deformation in two cases retains the plane arrangement, but is not square, in the third, retains the square arrangement but is not planar.

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