Also, the stable conformation of both phosphorus and arsenic five-membered rings is intermediate between symmetries *m* and 2; whether this situation is also true for cyclopentane and its derivatives remains to be shown. Finally, the question of why PCF_3 forms a tetramer and a pentamer, $AsCH_3$ a pentamer, and AsC_6H_5 a hexamer is still open.

This work was aided by a Grant from the National Science Foundation. Mrs Maryellin Reinecke prepared all the figures. We wish to thank Prof. Lipscomb for furnishing the revised values for the bond angles in $(PCF_3)_5$, thus enabling us to make corrections to some of our corrections.

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The Crystal Structure of $Pd_{17}Se_{15}$

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(*Received* 11 *September* 1961)

The crystal structure of $Pd_{17}Se_{15}$, with which $Rh_{17}S_{15}$ (formerly alleged to be Rh_9S_8) is isostructural, has been determined from single crystal data. The crystal belongs to one of the three space groups O_h^1–$Pm3m$, T_d^1–$P\bar{4}3m$ or O^1–$P432$ with a lattice constant of 10·606 Å and two $Pd_{17}Se_{15}$ per unit cell. It is shown that the X-ray data do not lead to a choice of the most probable of the above space groups although refinement based on *Pm*3*m* leads to convergence with the lowest standard errors for all positional parameters. In *P*432, the *x* and *y* positional parameters of the palladium atoms in general positions do not converge with the data used; this is consistent with the large correlation between these two parameters.

The structure is described mainly on the basis of its belonging to space group *Pm*3*m*. There are four kinds of palladium and three kinds of selenium atoms in the structure. The palladium atom in 1*b* has a regular octahedron of selenium atoms about it at 2·58 Å. A palladium atom in 3*d* has a square of selenium atoms about it at 2·53 Å and two palladium atoms at 2·78 Å in a line perpendicular to the plane of the square. The palladium atoms in 6*e* have a square of selenium atoms at 2·44 Å about them and one palladium at 2·78 Å on a line perpendicular to the plane of the selenium square. The palladium atoms in 24*m* have a 'buckled' square or 'flattened' tetrahedron of selenium atoms about them at distances 2·43, 2·49 and 2·51(2) Å. Other than the metal–metal bonds mentioned, there are no others in the ideal structure.

Introduction

Some years ago, Juza, Hülsmann, Meisel & Biltz (1935) studied the rhodium–sulfur system and reported the existence of a compound 'Rh_9S_8'. The powder pattern of this compound indicated that it had primitive cubic symmetry. In a search for superconductors among compounds of the 4*d* transition metals, Matthias, Corenzwit & Miller (1954) prepared 'Rh_9S_8' as well as 'PdSe' at about the same time. The powder pattern of the latter melt indicated that the predominant phase present was isostructural with 'Rh_9S_8'. The compound allegedly Rh_9S_8 was found to be superconducting with a transition temperature of 5·8 °K. whereas the 'Pd_9Se_8' remained normal down to 1·4 °K. At the time, a small crystal of 'Rh_9S_8' was isolated from material prepared by Matthias *et al.* with intended stoichiometry RhS. Photographs taken with a Buerger precession camera confirmed the cubicity of the phase. A [100] Patterson projection misleadingly indicated a close relation to the Co_9S_8 structure (Lindqvist, Lundqvist & Westgren, 1936).

Since the time Matthias *et al.* first discovered that 'Rh_9S_8' was superconducting, short-lived attempts were made to solve the structure and as a result information was accumulated which has finally led to the solution. Because of the seemingly close relation to the Co_9S_8 structure, and because on this basis a solution could not be found, the Co_9S_8 structure was further examined. In this regard, crystals of Co_9S_8 were obtained from Dr J. R. Stubbles.[*] Data from a spherical crystal of Co_9S_8 led to the conclusion that the structure of Co_9S_8 as originally reported by Lindqvist *et al.* (1936) is correct. (A refinement of the structure will be reported eventually.)

In the case of intermetallic compounds, the fact that the Law of Definite Composition does not hold makes for some difficulties in structure determination. The measurement of densities is not always conclusive. The compound Co_9S_8 has a lattice constant of 9·928 Å whereas that of the compound with the alleged formula 'Rh_9S_8' has the lattice constant 9·911 Å (Matthias & Geller, 1958). This implies one of three alternatives: (1) It is expected that when Rh and Co are in the same coordination, Rh is larger than Co; thus, if its formula is Rh_9S_8, the compound cannot have only a simple superstructure of the Co_9S_8 structure; or (2) the packing in the 'Rh_9S_8' structure must be more efficient, implying higher coordination on the average for the rhodium atoms; or (3) the formula cannot be Rh_9S_8. The uncertainty regarding the formula of the compound also hindered the solution of the structure.

Recently the Pd–Se system was investigated by Grønvold & Røst (1956). They also found a compound with formula $Pd_{1\cdot 1}Se$, i.e., close to Pd_9Se_8, but their density measurements indicated a probable composition of 34 Pd atoms to 30 Se atoms in the unit cell. After the appearance of the paper by Grønvold & Røst we returned to an investigation of superconductivity in this system (Matthias & Geller, 1958). We concluded tentatively that the cubic phase richer in palladium than the 9:8 ratio was superconducting.

When the Pd–Se compounds were prepared by Matthias (Matthias & Geller, 1958), an extremely small essentially single crystal chip of the pertinent phase was isolated from one of the melts and three-dimensional data collected.

A powder photograph of $Pd_{1\cdot 1}Se$ taken with a Straumanis type 114·6 mm. diameter Norelco camera and Cu K radiation gave a lattice constant of $10{\cdot}606 \pm 0{\cdot}003$ Å, in good agreement with the value, 10·604 Å, reported by Grønvold & Røst (1956).

Determination of the structure

The present report is concerned mainly with the compound $Pd_{17}Se_{15}$ even though the work was initially begun on the rhodium–sulfur compound. (The structure of the latter is being refined; results will be published subsequently.) However, data collected from the crystal of the rhodium–sulfur compound aided in the solution of the structure.

Unfortunately, the crystals used in the determination and the record of their sizes have been lost. The crystal of $Pd_{17}Se_{15}$ was barely visible to the naked eye and it is likely that it was no larger than 0·05 mm. in largest dimension. This crystal was photographed with a Buerger precession camera using Mo $K\alpha$ radiation. Photographs were taken with [100] and [110] directions as precession axes. Also a zero layer photograph about the [111] direction was taken to confirm the cubicity of the structure. The longest exposures were 100 hr. (at 45 kV. and 20 mA.) whereas to obtain estimates of the strongest reflections exposures of 4 hr. were necessary. The intensities of the $hk0$, $hk1$, hhl reflections were estimated visually by comparison with a calibrated intensity strip. Relative $|F_{hkl}|^2$ were obtained by applying the Lorentz-polarization corrections as obtained from Waser (1951, 1952) and Grenville-Wells & Abrahams (1952) charts supplied by Nies.

Patterson projections down [100] and [110] and the generalized projection using the $hk1$ data were calculated to be compared with analogous projections from the rhodium–sulfur crystal. Also the [100] Patterson projection from the Co_9S_8 crystal was calculated for comparison. As stated earlier, the latter comparison indicated that the structure in question was a superstructure of the Co_9S_8 structure.

An attempt was made to put the data from the Pd–Se and Rh–S compounds on an absolute scale (Wilson, 1942; Harker, 1948). Since rhodium and palladium have very nearly the same scattering factors it was felt that difference Patterson maps might lead to a solution. These of course must be made with due regard to the relative sizes of the structure amplitudes. If the data from both crystals were truly on an absolute scale, one should be able to obtain Patterson projections of the individual metal and metalloid 'substructures'. However if this is not the case or if there are significant differences in coordinates in the two crystals, the results would not necessarily be helpful.

Now, the symmetry of the diffraction effects from both the Pd–Se and Rh–S crystals was $m3m$, (see also Matthias & Geller, 1958) implying as most probable space groups O_h^1–$Pm3m$, T_d^1–$P\bar{4}3m$ and O^1–$P432$. The first, of course, is centrosymmetric, the second has a centrosymmetric [001] projection but the [110] projection is non-centrosymmetric; the last has both a [001] and [110] centrosymmetric projection. This structure could not have very many positional parameters and therefore statistical techniques were unlikely to produce conclusive results. Nevertheless, the tests of Howells, Phillips & Rogers (1950), and of Lipson & Woolfson (1952), that is, the evaluation of the $N(z)$ functions, were applied to the [001] and [110] zones

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and to the *hkl* data of $Rh_{17}S_{15}$. The results (Fig. 1) implied that the structure is centrosymmetric. However, a later discussion in this paper will point out that there is uncertainty in the space group determination.

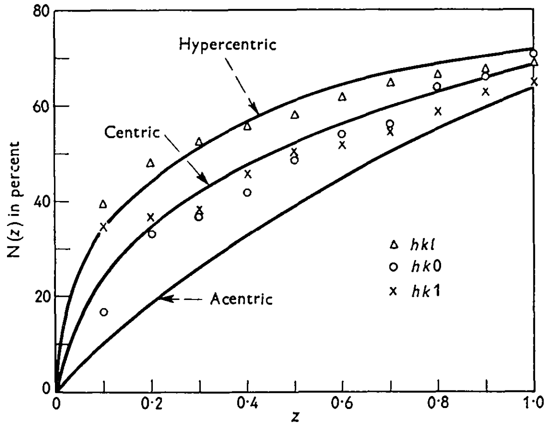

Fig. 1. Distribution of $|F_o|^2$: *hk*0, *hkl* and *hk*1 data of $Rh_{17}S_{15}$ compared with the curves for hypercentric, centric and acentric theoretical $N(z)$ functions.

All of the information from the Patterson maps indicated that there were 24 atoms in positions *m* of *Pm*3*m* or analogous positions of the non-centrosymmetric subgroups. It appeared highly improbable that metal atoms were in positions *k* and *l* of *Pm*3*m*, since these would put the metal atoms much too close to each other. Furthermore, after some least squares trials it soon became evident that the metal atoms could not be in positions *h*, *i*, or *j* of *Pm*3*m*. In particular, combinations involving the positions *h* through *j* could not give a relatively strong 440 reflection. Thus it appeared unequivocal that 24 metal atoms must be in *m* of *Pm*3*m* or in two sets of *i* in $P\bar{4}3m$ or in *k* of *P*432.

For simplicity of presentation we shall adhere to the *Pm*3*m* description temporarily. The Patterson maps, especially those of the Rh–S compound, indicated that the coordinates of the atoms in *m* were about $x = 0{\cdot}36$, $z = 0{\cdot}14$. Also there was indication that there were metal atoms in 1*b* and 3*d*. This much of the structure, (as well as the positions of six of the metalloid atoms) is indeed analogous to the structure of Co_9S_8.

The approach following this was to allow the computer to test trial structures using the Busing–Levy (1950) least squares programs. In the calculations, amplitudes of reflections which were actually observed were given unit weight, while those of reflections too weak to be observed were given zero weight. Of 269 observable reflections, only 177 were strong enough to be observed. Atomic scattering factors used were those of Thomas & Umeda (1957) corrected for dispersion (Dauben & Templeton, 1955).

Combinations of positions for other atoms were chosen in accordance with the Patterson projections. Some of the trial structures were also based on the non-centrosymmetric space groups and the ratios of metal to metalloid atoms of 37:32, 9:8 and 17:16. Now the structure of PdS has been known for some time (Gaskell, 1937) and it was felt that at least some of the metal atoms in this structure could easily have 'square' coordination as in PdS; also Pd in $PdSe_2$ and PdS_2 has essentially square coordination (Grønvold & Røst, 1957). But unit cell size considerations (see Introduction) and lack of knowledge of the exact formula also implied the possibility of octahedral coordination for a significant number of the metal atoms. Therefore, the models tried recognized these possibilities.

It became apparent, after several discouraging attempts, that there were probably no atoms in *g* of *Pm*3*m* (or of *P*432 or in *l* of $P\bar{4}3m$). Also the various trials were indicating that in the Pd–Se structure, the coordinates of the atoms in *m* (of *Pm*3*m*) were closer to $x = 0{\cdot}35$, $z = 0{\cdot}15$.

Then the following model with formula $Pd_{17}Se_{15}$ was tried, in which most of the Pd atoms had essentially square coordination:

Space group: *P*432. Pd in 1*b*; 3*d*; 6*e*, $x = 0{\cdot}220$; 24*k*, $x = 0{\cdot}355$, $y = 0{\cdot}350$, $z = 0{\cdot}153$. Se in 6*f*, $x = 0{\cdot}220$; 12*h*, $x = 0{\cdot}273$; 12*i*, $x = 0{\cdot}230$. This was the first model that showed a tendency toward convergence. However, the temperature factor of the 12*h* atoms went up to 5·1 while all of the others except that of the 6*f* atom went negative with values ranging from $-0{\cdot}6$ for the Pd atoms in *k* to $-1{\cdot}8$ to the Pd atom in *b*. This indicated strongly that atoms did not belong in 12*h*. Examination of the data and a ball model indicated that these atoms would be more properly located in positions 12*j* with $x \cong 0{\cdot}20$. This model turned out to be the essentially correct one. It turned out also, however, that the parameter for the atoms in *j* had a value more nearly equal to 0·17 as could have been seen from the [110] $Pd_{17}Se_{15}$ Patterson projection. Nevertheless, as would be expected, once all of the atoms were located in their proper space group positions, with most of the coordinates nearly correct, convergence was fairly rapid.

When the atoms formerly in *h* were located in *j* with $x = 0{\cdot}20$, two iterations brought the discrepancy factor (multiplicity neglected) from 0·44 to 0·25. The positions *a* through *j* of *P*432 are exactly the same (excluding point symmetry) as those in *Pm*3*m*. It was decided therefore to carry out further refinement on the basis of space group *Pm*3*m*. Subsequently refinement was based on the two other space groups and this will be a subject for later discussion.

In the space group *Pm*3*m*, the structure has only six positional parameters and 16 anisotropic thermal parameters. At first, refinement included the anisotropic thermal parameters and one over-all scale factor. The starting parameters for this refinement are listed in Table 1. Note that for atoms in *b* and *d*, $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$; for atoms in *e*

Table 1. *Starting parameters for refinement in Pm3m*

Atom	Position	x	y	z	$\beta_{11}\times 10^4$	$\beta_{33}\times 10^4$	$\beta_{12}\times 10^4$	$\beta_{13}\times 10^4$
Pd	24*m*	0·352	0·352	0·150	10·23	10·23	0·00	0·00
Se	12*j*	0·162	0·162	½	13·34	13·34	0·00	0
Se	12*i*	0·220	0·220	0	13·34	13·34	0	0
Se	6*f*	½	½	0·259	13·34	13·34	0	0
Pd	6*e*	0	0	0·241	5·56	5·56	0	0
Pd	3*d*	0	0	½	5·56	5·56	0	0
Pd	1*b*	½	½	½	5·56	5·56	0	0

and *f*, $\beta_{11}=\beta_{22}$ and $\beta_{12}=\beta_{13}=\beta_{23}=0$, for atoms in *i* and *j*, $\beta_{11}=\beta_{22}$ and $\beta_{13}=\beta_{23}=0$ and for atoms in *m*, $\beta_{11}=\beta_{22}$, $\beta_{13}=\beta_{23}$.

Four iterations with anisotropic thermal parameters were carried out, in all of which the temperature factors for the majority of atoms persisted in not being positive definite. This appears to be an inadequacy of the data, since the standard errors in the thermal parameters were in several cases larger than the absolute value of parameter. It should be kept in mind that the crystal used was of jagged shape and that although small, the absorption corrections could be significant (Mo $K\alpha$ radiation μ for $Pd_{17}Se_{15}=377{\cdot}6$ cm.$^{-1}$). Also some superficial inclusions which gave some extra reflections in the low angle region could have caused some incorrect intensities.

Another possibility is that the stoichiometry in the crystal from which the data were obtained was not 17:15. In such a case, the effect on parameters would depend on which atoms were in excess and of course on where they were. There was also some indication of the presence of double reflections (Renninger, 1937*a*, *b*) which could, of course, also lead to some incorrect intensities.

As to positional parameters, convergence to final values from those given in Table 1 was quite rapid. In the fourth iteration, changes in positional parameters in the order in which they appear in Table 1 were 0·00004, 0·00006, 0·00003, 0·00007, 0·0007 and 0·0002. Six of the seven temperature factors, however, were not positive definite with large standard errors and therefore not too meaningful. The discrepancy factor (multiplicity neglected) in the fourth cycle was 0·147.

Examination of the correlation matrix (Geller, 1961) indicated that the indeterminacy of the temperature factors was unlikely to have much effect on the accuracy of the positional parameters since all correlations between a thermal and positional parameter were relatively small.

Because the anisotropic temperature factors did not appear to be meaningful anyway, another cycle was carried out with isotropic temperature factors. All Pd atoms were assigned $B=0{\cdot}10$ Å^2 and all Se atoms 0·25 Å^2. Using the positional parameters and scale factor calculated in the previous cycle the discrepancy factor (multiplicity neglected) was 0·150. Calculated changes in the positional parameters in this cycle in order of appearance in Table 1 were 0·00009, 0·00006, 0·00018, 0·00035, 0·00021 and 0·00005. This calculation also indicated to some extent the negligibility of the effect of thermal on positional parameters. The final parameters and their standard errors are given in Table 2. The largest standard error, 0·017 Å, is that for the coordinate of Se in *f*. Next largest, 0·013 Å, is for the coordinate of Pd in *e*. The *x* and *z* coordinates of the Pd atoms in *m* have standard errors equivalent to 0·003 and 0·005 Å respectively, while the coordinates of the Se atoms in both *i* and *j* have a standard error equivalent to 0·007 Å. In comparison, while the absolute values of *B*'s are small, the standard errors in *B*'s are all large indicating the indeterminacy of the *B* values from the present data.

The values of observed and calculated amplitudes obtained in the last cycle based on *Pm*3*m* are listed in Table 3. Note that all calculated amplitudes for unobserved reflections are less than the minimum observable for the respective reflections. The discrepancy factor including consideration of multiplicity is 0·115.

Problem of the choice of space group

The crystals of $Pd_{17}Se_{15}$ and $Rh_{17}S_{15}$ cannot be tested for piezoelectricity because they are metals. Consequently, since the non-centrosymmetric groups allow some of the atoms in $Pd_{17}Se_{15}$ more degrees of freedom, the choice of the centrosymmetric one as most probable simply because it is compatible with the data or gives the lowest standard errors in parameters would seem to be essentially arbitrary.

Table 2. *Final parameters and standard errors after refinement in Pm3m*

Atom	Position	x	y	z	B	$\sigma(x)$	$\sigma(z)$	$\sigma(B)$
Pd	24*m*	0·3521	0·3521	0·1501	0·15	0·0003	0·0005	0·07
Se	12*j*	0·1684	0·1684	½	−0·05	0·0007		0·15
Se	12*i*	0·2297	0·2297	0	−0·26	0·0007		0·17
Se	6*f*	½	½	0·2571	−0·30		0·0016	0·23
Pd	6*e*	0	0	0·2378	0·09		0·0012	0·17
Pd	3*d*	0	0	½	−0·21			0·23
Pd	1*b*	½	½	½	0·17			0·51

Table 3. *Calculated and observed amplitudes, Pm3m*

		hk0	
h	k	F_o	F_c
2	0	113	-102
3	0	< 48	3
4	0	155	96
5	0	342	307
6	0	943	1054
7	0	324	-270
8	0	793	761
9	0	72	112
10	0	314	-335
11	0	86	104
12	0	676	609
13	0	< 80	61
14	0	692	586
2	1	40	41
3	1	294	259
4	1	431	377
5	1	169	158
6	1	181	-180
7	1	179	-186
8	1	91	102
9	1	286	288
10	1	109	156
11	1	< 84	- 17
12	1	< 84	- 5
13	1	< 80	58
14	1	< 76	0
2	2	99	-103
3	2	237	-199
4	2	314	289
5	2	< 60	- 13
6	2	260	-232
7	2	< 72	34
8	2	< 76	- 15
9	2	74	- 70
10	2	82	84
11	2	< 83	- 72
12	2	< 83	44
13	2	< 79	45
14	2	115	-159
3	3	82	68
4	3	171	-162
5	3	105	116
6	3	163	-150
7	3	181	179
8	3	76	82
9	3	233	219
10	3	162	-212
11	3	107	-150
12	3	135	-124
13	3	274	259
14	3	91	112
4	4	1151	1146
5	4	259	257
6	4	247	-261
7	4	171	198
8	4	239	240
9	4	129	151
10	4	668	592
11	4	84	-113
12	4	284	229
13	4	362	309
14	4	74	-131
5	5	260	222
6	5	< 71	0
7	5	< 75	- 24
8	5	195	195
9	5	286	268
10	5	< 83	44
11	5	< 83	- 51
12	5	< 83	68
13	5	231	194
14	5	171	113
6	6	648	560
7	6	231	-245
8	6	239	284
9	6	149	-138
10	6	416	-395
11	6	< 83	46
12	6	437	315
13	6	99	-109
7	7	282	-266
8	7	< 83	- 39
9	7	117	151
10	7	127	149
11	7	< 83	- 13
12	7	< 80	- 86
13	7	84	-106
8	8	435	387
9	8	151	168
10	8	< 93	- 60
11	8	< 79	34
12	8	324	280
9	9	451	381
10	9	< 79	- 30
11	9	< 55	- 52
10	10	410	404
11	10	145	-128

		hkl	
h	k	F_o	F_c
2	1	< 40	- 31
3	1	485	-386
4	1	358	316
5	1	201	-183
6	1	251	-226
7	1	< 79	39
8	1	145	125
9	1	105	-121
10	1	<103	48
11	1	286	-285
12	1	<100	19
13	1	<100	73
14	1	< 87	- 35
2	2	54	- 63
3	2	278	-247
4	2	227	-202
5	2	62	- 51
6	2	119	120
7	2	< 79	0
8	2	125	- 97
9	2	181	-164
10	2	87	- 85
11	2	< 99	- 36
12	2	< 99	31
13	2	<103	- 7
14	2	<103	- 41
3	3	340	294
4	3	139	-129
5	3	< 68	- 49
6	3	< 75	0
7	3	457	-422
8	3	< 83	54
9	3	< 91	69
10	3	243	-213
11	3	145	139
12	3	<103	37
13	3	245	-271
14	3	<103	- 7
4	4	< 67	- 38
5	4	268	265
6	4	84	-104
7	4	139	158
8	4	< 83	44
9	4	135	87
10	4	103	-129
11	4	< 99	- 26
12	4	78	87
13	4	278	266
14	4	<103	44
5	5	105	-116
6	5	181	-146
7	5	207	-205
8	5	239	192
9	5	< 95	38
10	5	< 95	3
11	5	135	-164
12	5	<103	36
13	5	<103	- 50
14	5	<103	37
6	6	89	- 79
7	6	205	-210
8	6	< 87	- 6
9	6	< 95	- 18
10	6	99	116
11	6	<103	- 77
12	6	<103	- 37
13	6	114	-130
7	7	187	179
8	7	< 91	6
9	7	209	-233
10	7	< 99	49
11	7	235	-286
12	7	<103	- 20
13	7	<103	94
8	8	< 99	- 18
9	8	123	123
10	8	<103	- 12
11	8	<103	60
12	8	<103	42
9	9	99	83
10	9	103	-110
11	9	<103	11
12	9	<103	84
10	10	95	-121
11	10	<103	- 83

		hkk	
h	k	F_o	F_c
2	2	199	142
3	2	324	231
4	2	60	- 42
5	2	133	- 112
6	2	< 83	6
7	2	89	67
8	2	78	80
9	2	< 99	- 7
10	2	< 103	- 28
11	2	< 107	86
12	2	< 107	5
13	2	86	- 104
14	2	< 86	20
2	3	< 75	- 16
3	3	1068	-1075
4	3	229	223
5	3	127	- 167
6	3	< 91	24
7	3	517	457
8	3	< 99	- 77
9	3	606	- 586
10	3	103	103
11	3	332	- 343
12	3	181	184
13	3	223	250
14	3	264	- 193
2	4	< 87	55
3	4	249	241
4	4	314	259
5	4	147	145
6	4	453	444
7	4	244	- 204
8	4	632	629
9	4	296	276
10	4	85	- 132
11	4	< 103	- 3
12	4	352	320
13	4	< 91	55
2	5	< 95	- 31
3	5	< 95	- 40
4	5	346	309
5	5	< 99	- 60
6	5	115	- 115
7	5	185	- 174
8	5	251	230
9	5	84	76
10	5	< 103	27
11	5	167	- 166
12	5	< 95	64
2	6	113	- 117
3	6	< 99	- 42
4	6	262	- 318
5	6	< 103	- 12
6	6	479	428
7	6	< 103	- 55
8	6	84	105
9	6	169	- 169
10	6	278	- 309
11	6	195	148
12	6	298	215
2	7	< 103	74
3	7	426	- 491
4	7	117	139
5	7	167	- 182
6	7	167	- 175
7	7	394	389
8	7	< 103	- 47
9	7	298	- 311
10	7	89	106
11	7	358	- 291
2	8	84	127
3	8	< 103	62
4	8	288	332
5	8	< 103	25
6	8	101	111
7	8	97	- 78
8	8	406	343
9	8	121	127
2	9	< 98	- 31
3	9	370	- 321
4	9	270	299
5	9	91	53
6	9	87	93
7	9	< 68	25
2	10	133	- 143
3	10	149	163
4	10	320	- 301

Thus refinements based on the two non-centrosymmetric space groups were also carried out. In *Pm3m*, $Pd_{17}Se_{15}$ has 16 anisotropic thermal parameters and 6 positional parameters. Including one scale factor the total number of parameters is 23. In $P\bar{4}3m$, $Pd_{17}Se_{15}$ has 24 anisotropic thermal parameters, 10 positional parameters and adding one scale factor, the total number of parameters is 36. In *P*432, there are 21 anisotropic thermal parameters, 7 positional parameters and one scale factor giving a total of 29 parameters. Mainly because of the difficulty with the thermal parameters seen in the *Pm3m* refinement, the refinements in the non-centrosymmetric space groups were carried out with isotropic temperature factors. However, the numbers of additional parameters were also becoming too large relative to the total number of observed data. With isotropic temperature factors the total number of parameters are: *Pm3m*, 14; $P\bar{4}3m$, 19; and *P*432, 15.

The refinement based on $P\bar{4}3m$ was carried out first. The very first result was a program stop which indicated a negative inverse matrix diagonal. This seemed to result from putting all atoms in the space group positions with the exact parameters obtained from the last iteration based on *Pm3m*. That is, the Pd atoms formerly in *m* of *Pm3m* were put into two sets of *i* in $P\bar{4}3m$ with parameters ± (0·352, 0·352, 0·150). The Se atoms in *i* and *j* of *Pm3m* were put into *m* with *z* exactly 0·000 and 0·500 respectively. After this stop, the values were changed somewhat and this difficulty did not occur again.

Four cycles were carried out to attain convergence. The results of the calculation are shown in Table 4. In the last cycle, structure amplitudes were calculated with the following *B* values in Å^2 given in the order in which the atoms appear in Table 4: 0·119, 0·05, 0·108, 0·05, 0·05, 0·137, 0·05, 0·05. The discrepancy factor (neglecting multiplicity) was 0·140, lower than but not a significant change from that obtained for the *Pm3m* calculation.

Five of the thermal parameters were negative, but again the standard errors in these parameters were all large. The standard errors for the coordinates in sixfold positions and for the *x*'s of the Se's in twelvefold positions were unchanged, but all of the others increased. Particularly noteworthy are the errors for the *z*-parameters of the Se atoms. Note that the average values of *x* and *z* for the twelvefold Pd atoms are equal to the *x* and *z* obtained from the *Pm3m* refinement and considering the errors on the *z*-parameters of the twelvefold Se atoms, the average interatomic distances obtained from the two refinements should not be significantly different.

The standard errors of the *x*-parameters in twelvefold positions indicate that these parameters do not

Table 4. *Parameters after refinement based on* $P\bar{4}3m$

Atom	Position	x	y	z	B	$\sigma(x)$	$\sigma(z)$	$\sigma(B)$
Pd	12*i*	0·3541	0·3541	0·1439	−0·03	0·0011	0·0015	0·21
Pd	12*i*	−0·3500	−0·3500	−0·1565	0·12	0·0011	0·0014	0·26
Se	12*i*	0·2301	0·2301	−0·0010	−0·12	0·0007	0·0054	0·17
Se	12*i*	0·1680	0·1680	0·5064	−0·11	0·0007	0·0029	0·19
Se	6*g*	½	½	0·2582	−0·35		0·0016	0·23
Pd	6*f*	0	0	0·2376	0·11		0·0012	0·17
Pd	3*d*	0	0	½	−0·27			0·24
Pd	1*b*	½	½	½	0·13			0·52

Table 5. *Parameters after the final cycle run based on P*432

Atom	Position	x	y	z	B	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
Pd*	24*k*	0·3461	0·3580	0·1502	0·34	0·0023	0·0023	0·0005	0·10
Se	12*j*	0·1681	0·1681	½	−0·01	0·0006			0·14
Se	12*i*	0·2299	0·2299	0	−0·19	0·0007			0·16
Se	6*f*	½	½	0·2578	−0·23			0·0015	0·21
Pd	6*e*	0	0	0·2378	0·02			0·0011	0·16
Pd	3*d*	0	0	½	−0·15				0·22
Pd	1*b*	½	½	½	0·01				0·46

* The parameters and standard errors for the x and y parameters of this atom are not meaningful because convergence was not attained.

differ significantly from the x-parameter obtained in the *Pm*3*m* refinement, but on cursory inspection, the z-parameters do look significantly different. This is not necessarily the case because the correlation between the two z-parameters is quite large, namely 0·62. The largest correlation coefficient, 0·81,* is that between the two x-parameters of the twelvefold Pd atoms. There is also a high correlation, 0·52, between the positive z-parameter of one of the twelvefold Pd atoms and the temperature factor of the other. The correlation between the z-parameter at 0·506 of the Se atom in i and the temperature factor of the same atom is −0·60. The correlation between the temperature factors of the two twelvefold Pd atoms is −0·73.

All in all, the results of the refinement based on $P\bar{4}3m$ make those obtained on the basis of refinement on *Pm*3*m* look more acceptable. However, one would have to admit, we think, that this would be an arbitrary decision, i.e., the X-ray data really do not eliminate the space group uncertainty.

Finally the refinement based on space group $P\bar{4}32$ was carried out. Particularly in view of the recent work by the author on parameter interactions in least squares refinement (Geller, 1961) and of the results of the attempts to refine the structure of guanidinium aluminum sulfate hexahydrate (Geller & Katz, 1962), the results were very interesting. In *P*432, all of the atoms have exactly the same positions as in *Pm*3*m* except for the 24-fold Pd atoms which are in 24*k* and therefore have one extra degree of freedom. Except for the x- and y-parameters of the Pd atoms in 24*k* all positional parameters converged to very nearly the same values as the analogous parameters in *Pm*3*m* and with very nearly the same standard errors (see Table 5 and compare with Table 2). However, although the z-parameter of the Pd atoms in 24*k* converged to *exactly* the same value as that obtained in the refinement based on *Pm*3*m*, the x- and y-parameters did not converge. In the cycle before the last one the changes in x- and y-parameters were 0·0060 and −0·0059 respectively, while in the last cycle run the changes were −0·0082 and 0·0081 respectively. This is a clear indication that at least with the present data, the x- and y-parameters will not converge in this space group.

Now, we examine the correlation matrix to see if this tendency is given by it. We should remember that the correlation matrix depends only on the particular model, that is, the parameters and atomic scattering factors, and in each iteration is *independent* of the data. The correlation coefficient between x and y is −0·96. We have seen (Geller, 1961; Geller & Katz, 1962) that such large correlations are indicative of this very kind of difficulty. They mean that the data and atomic scattering factors must be of *extreme* accuracy to attain convergence. This does not imply that the correlations will necessarily be reduced by accurate data, since the correlations depend on the structure model (Geller, 1961).

It is worth repeating (Geller & Katz, 1962) that since there is always the possibility of residual error in the observed amplitudes and in the atomic scattering factors, that is, since the *true* F_o's and F_c's are never really known, there exists the possibility that some structures may not from a *practical* point of view be completely determinate. Obviously if we could obtain *true* F's and exact atomic scattering factors all structures should be completely determinate provided that no correlation is exactly ±1·0, that is that a structure does not have one parameter completely dependent on another.

There are two other sizable correlations in the *P*432 space group. Aside from those involving the scale factor, the correlation between the Pd(k) x- and y-parameters and the B of the same atom are 0·63 and 0·62 respectively.

It should be noted also that along with the large correlation between x and y of Pd(k) the indicated standard errors (which are theoretically meaningless unless convergence is attained, see Geller, 1961) for these parameters are eight times that obtained for x in the *Pm*3*m* refinement.

Description of the structure

The preceding discussion of choice of space group presents the thesis that there appears to be some indeterminacy in this structure, despite the fact that convergence in *Pm*3*m* and in $P\bar{4}3m$ is attained and that the standard errors in coordinates in the *Pm*3*m*

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* In the *Pm*3*m* model, the largest correlation, 0·72, was between the scale factor and the B of the 12-fold Pd atoms. The largest correlation involving a positional parameter was 0·30 between x of Se in i and z of Pd in e. The correlation coefficient between the x- and z-parameters of the 24-fold Pd atoms was 0·26. All the remaining correlation coefficients involving positional coordinates were less than 0·19 and of these all but three were less than 0·10.

refinement are the lowest. It is possible that better or more representative data (see Geller, 1961) *could* result in convergence in the $P432$ refinement also. Even if this were the case, and it could be shown that differences among the three refinements were not statistically significant, there would then still be uncertainty in the choice of the most probable space group.

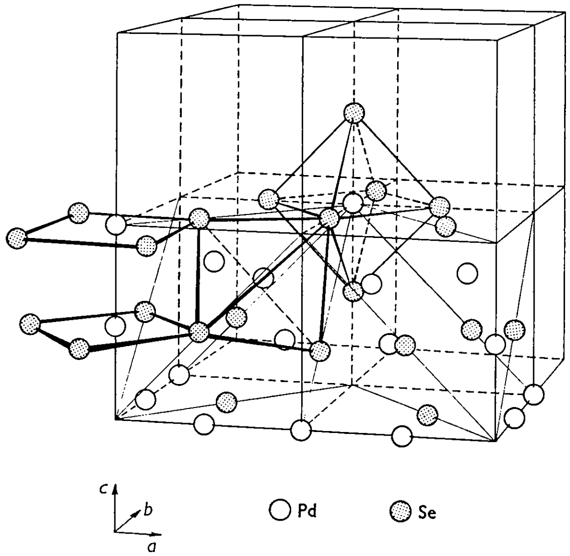

Fig. 2. The unit cell of $Pd_{17}Se_{15}$. The atoms in two octants and some needed to complete the four non-equivalent Se coordination figures are shown.

The atoms in two octants of the structure based on $Pm3m$ are shown in Fig. 2. Also shown are the four coordination figures of Se atoms about the four crystallographically different Pd atoms. The Pd atom in $b(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is surrounded by a regular octahedron of selenium atoms, all in f, at distances 2·58 Å. The remainder of the Pd atoms tend to have either square or almost square coordination as do the Pd atoms in $PdSe_2$ and PdS_2 (Grønvold & Røst, 1957) and in PdS (Gaskell, 1937). In $PdSe_2$ and PdS_2 the four Se or S atoms lie in the same plane with the Pd atom but do not form an exact square. In PdS, there are three kinds of coordination of sulfur to Pd atoms. One, Gaskell refers to as a 'buckled' square, which may also be thought of as a 'flattened' tetrahedron. Two sulfurs at opposite corners are 0·20 Å below and the other two 0·20 Å above the 'average plane' containing the Pd atom. Another type has four S atoms in the plane with the Pd atom at the corners of a rectangle of sides 2·92 and 3·46 Å. The third type is also a planar arrangement but it is far from square.

Based on $Pm3m$, in $Pd_{17}Se_{15}$ there is exactly square coordination of the Se atoms in $12j$ about Pd atoms in $3d$ at distances 2·53 Å. However the Pd atoms in $3d$ are also bonded to two Pd atoms in $6e$ at distances 2·78 Å, which is only 0·035 Å longer than the 12-coordination elementary diameter of Pd.

The Pd atoms in $6e$ are each also bonded to an exact square of selenium atoms in $12i$ at distances 2·44 Å, but the Pd atom is 0·09 Å above the plane of these Se atoms. Each Pd atom in $6e$ is also coordinated to one Pd atom in $3d$ at 2·78 Å. The Pd atoms in $24m$ are coordinated to four Se atoms in a distorted or 'flattened' tetrahedron. The distances are Pd–Se(i), 2·43 Å; 2 Pd–Se(j), 2·51 Å; Pd–Se(f), 2·49 Å. The average is 2·48 Å about 1·6% larger than the Pd(e)–Se(i) distance. Actually it would appear that the Pd(e)–Se(i) distance should be a little longer than it is because of the additional Pd neighbor. The longer Pd(d)–Se(j) distances are consistent with the two additional Pd(e) neighbors.

Aside from the Pd(e)–Pd(d) distances of 2·78 Å, the remainder of the Pd atoms do not form bonds with other Pd atoms. This is unlike the case of Co_9S_8 in which a Co atom in an f position not only has a tetrahedron of S atoms surrounding it but also three Co atoms at 2·50 Å. Other Pd–Pd distances in $Pd_{17}Se_{15}$ are Pd(m)–Pd(m), 3·03, 3·18 and 3·14 Å; Pd(e)–Pd(e), 3·57 Å; Pd(b)–Pd(m), 4·33 Å, and Pd(d)–Pd(m), 4·34 Å.

As would be expected, as in PdS and unlike $PdSe_2$ or PdS_2, there are no close approaches among metalloid atoms. The Se atoms about the Pd atoms in b are at distances 3·64 Å (i.e., the length of a side of the octahedron). The length of a side of the Se(i) square is 3·45 Å and of the side of the Se(j) square 3·57 Å. About the Pd(m) atoms there are two Se(i)–Se(j) distances of 3·44 Å and two Se(f)–Se(j) distances, 3·64 Å.

Each Se atom in i is at the corner of four coordination figures; two squares about Pd(e) atoms and two flattened tetrahedra about Pd(m) atoms. Each Se atom in j is at the corner of five coordination figures: four flattened tetrahedra about Pd(m) atoms and one square about a Pd(d) atom. Each Se atom in f is at the corner of five coordination polyhedra: four tetrahedra about Pd(m) and one octahedron about Pd(b).

Within a single octant no edges are shared between any two Se coordination figures. However the Se tetrahedra about Pd(m) atoms in adjacent octants do share edges.

The interatomic distances and standard errors obtained in $Pm3m$ (based on the particular weighting scheme, of course) are listed in Table 6.

The average Pd(m)–Se distance is 2·485 Å, somewhat longer than the 2·44 Å found in $PdSe_2$. The Pd(e)–Se(i) distance of 2·44 Å compares more favorably with the distance found in $PdSe_2$ but Pd(e) does have a Pd(d) neighbor at 2·78 Å unlike the Pd atom in $PdSe_2$. Perhaps the distortion in $Pd_{17}Se_{15}$ is responsible for the longer distances about the Pd(m) atom.

Based on the $P\bar{4}3m$ space group, the Pd(i)–Se(i) distances are 2·41 and 2·45 Å ($z_{Se} \simeq 0$) and 2·56 and 2·55 Å ($z_{Se} = 0{\cdot}506$). Averages are 2·43 and 2·55 Å. Considering the large errors in the coordinates, these distances do not differ significantly from those ob-

Table 6. *Interatomic distances and standard errors*

Atom	Neighbors	Distance	σ
Pd(*b*)	6 Se(*f*)	2·576 Å	0·017 Å
Pd(*d*)	4 Se(*j*)	2·527	0·011
	2 Pd(*e*)	2·781	0·013
Pd(*e*)	4 Se(*i*)	2·438	0·008
	1 Pd(*d*)	2·781	0·013
	4 Pd(*e*)	3·566	0·018
Pd(*m*)	1 Se(*i*)	2·430	0·014
	1 Se(*f*)	2·492	0·014
	2 Se(*j*)	2·509	0·011
	1 Pd(*m*)	3·184	0·011
	2 Pd(*m*)	3·137	0·006
	2 Pd(*m*)	3·029	0·014
Se(*f*)	4 Se(*f*)	3·643	0·024
	4 Se(*j*)	3·641	0·014
	4 Pd(*m*)	2·492	0·014
	1 Pd(*b*)	2·576	0·017
Se(*i*)	4 Se(*i*)	3·445	0·010
	4 Se(*j*)	3·440	0·010
	2 Pd(*e*)	2·438	0·008
	2 Pd(*m*)	2·430	0·014
Se(*j*)	2 Se(*f*)	3·641	0·014
	4 Se(*i*)	3·440	0·010
	2 Se(*j*)	3·572	0·015
	1 Pd(*d*)	2·527	0·011
	4 Pd(*m*)	2·509	0·011

tained from the *Pm*3*m* refinement. The over-all average is 2·49 Å which is equal to the average Pd(*m*)–Se distance from the *Pm*3*m* refinement.

As to the refinement based on *P*432, all parameters other than those for the Pd atoms in 24*k* converge to very nearly the same values as in the *Pm*3*m* case and the important distances in pairs of these atoms will be the same in both cases. Little can be said about the distances involving the atoms in 24*k* of *P*432 other than that if convergence had been attained the *average* distances would be expected to be the same as those obtained in the *Pm*3*m* refinement.

Another interesting feature of the structure is the apparently large vacancies in the *c* positions $(\frac{1}{2}, \frac{1}{2}, 0, \circlearrowright)$. Based on the *Pm*3*m* structure, each of these points is surrrounded by eight Pd atoms in *m* at distance 2·73 Å and two Se atoms at distance 2·73 Å. It would appear possible that some atoms would enter these sites. From a size point of view, either Pd or Se would be satisfactory. From a coordination point of view the Pd atoms would probably be preferred. Furthermore, there was the possibility that the exclusion of such atoms in the calculation might be the cause of the negative temperature factors of some of the atoms.

The value of $\varrho_o(0, 0)$ is 1·076 e.Å^{-2}. Because three Pd atoms project on this point, the peak density per Pd atom is then 359 e.Å^{-2}. The plot of $\varrho_o(\frac{1}{2}, y) - \varrho_c(\frac{1}{2}, y)$ is shown in Fig. 3; the residual density is given in terms of the fraction of a Pd atom. It is seen from this plot that there are probably very few atoms in the *c* sites. Examination of the individual calculated and

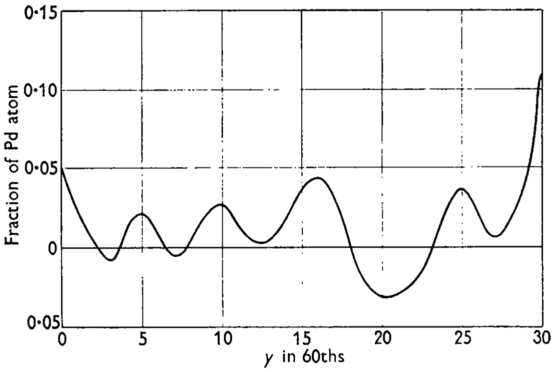

Fig. 3. The difference synthesis $\varrho_o(\frac{1}{2}, y) - \varrho_c(\frac{1}{2}, y)$. Density is given in terms of the fraction of the peak density of one Pd atom at (0, 0).

observed amplitudes also corroborate this conclusion.

Now it seemed possible, however, that the inclusion in the least squares calculations of the atoms in the *c* sites might produce changes in the parameters of the other atoms. In such a case, the difference synthesis shown in Fig. 3 would not be meaningful. Therefore, least squares calculations were made in which one Pd atom distributed over the *c* sites was included. All other atoms had the positional parameters obtained in the final *Pm*3*m* refinement. All Pd atoms were assigned a *B* value of 0·10 Å^2 and all Se atoms, 0·25 Å^2. In the first cycle, the *B* value of the Pd atom distributed over the 3*c* sites increased to 2·09 Å^2 indicated standard error, 0·63). The only substantial change of a positional parameter was that of the Pd atom in *e*: it changed by −0·0009. The thermal parameters of the other atoms are shown in Table 7. Note that there was some improvement in the *B* values for three of the Se atoms but the *B* value of the Pd atom in 6*e* became slightly negative.

A second cycle was run using the positional parameters of the first cycle and a *B* value of 0·10 Å^2 for all atoms except that of the Pd atom distributed over the 3*c* sites which was taken as 2·09 Å^2. The largest change in positional parameter was 0·0001 in that of the Pd atom in *e*. There was another large increase, to 3·82 Å^2, in the *B* value of the Pd atom distributed over the 3*c* positions, but the other *B*

Table 7. *B values of atoms when one* Pd *atom distributed over positions* 3*c was included in calculation*

		B (Å^2)		
Atom	Position	Cycle 1	Cycle 2	OPd in 3*c*
Pd	24*m*	0·12	0·13	0·15
Se	12*j*	−0·07	−0·05	−0·05
Se	12*i*	−0·20	−0·19	−0·26
Se	6*f*	−0·20	−0·19	−0·30
Pd	6*e*	−0·01	0·00	0·09
Pd	3*d*	−0·11	−0·12	−0·21
Pd	1*b*	0·09	0·10	0·17
Pd	3*c*	2·09	3·82	

values returned (Table 7) very nearly to those obtained at the end of the previous cycle.

There appeared to be no good reason to carry the calculations further. All the results indicated that there are probably few atoms in the *c* sites and their exclusion from the calculation is not the main cause of the negative thermal parameters. Examination of Table 3 now indicated that the source of the difficulty was error in the observed data. There are a number of calculated amplitudes which are considerably larger than the observed which lead to a larger factor by which the observed amplitudes are multiplied to put them on an absolute scale. This, however, makes a sizable number of the observed amplitudes especially at high angles too large relative to the calculated amplitudes which in turn tends to reduce the thermal parameters. When the *true* values of these parameters are small, the calculations can, as in this case, produce negative values. This case shows also that the scale and thermal parameters tend to absorb measurement errors. Because as stated earlier, the correlations between thermal or scale and positional parameters are small it is probable that the effect on the positional parameters is small.

Finally we give the X-ray density of the compound with ideal composition $Pd_{17}Se_{15}$, 8·34 g.cm.$^{-3}$.

The IBM 704 programs used in the calculations other than those of the least squares refinement were those of Dr R. G. Treuting. The drawing of the structure (Fig. 2) was made by Mr H. J. Seubert.

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The Crystal Structure of Yoderite

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(*Received* 28 *August* 1961)

Yoderite is a hydrous magnesium iron aluminosilicate discovered by D. McKie in 1956. The approximate empirical formula is $[Mg_{2\cdot0}Ca_{0\cdot2}(Fe''Fe''')_{0\cdot5}Al_{5\cdot3}]Si_4O_{17\cdot6}(OH)_{2\cdot4}$. There are weak subsidiary reflections with unitary structure factors $\leq 0\cdot03$ (McKie, 1959). The average structure, ignoring these, has been determined and refined by two-dimensional Fourier methods. It is monoclinic with space group $P2_1/m$ and cell dimensions

$$a = 8\cdot035 \pm 0\cdot003,\ b = 5\cdot805 \pm 0\cdot001,\ c = 7\cdot346 \pm 0\cdot002\ \text{Å};\ \beta = 105^\circ\ 38' \pm 4'.$$

Chains of AO_6 octahedra, sharing edges, run parallel to the y-axis, linked by isolated SiO_4 tetrahedra and AO_5 trigonal bipyramids in which A sites are mainly occupied by Al and Mg. The packing of oxygen atoms resembles (but is not identical with) that in kyanite with which the mineral intergrows. Two of the 2·4 hydrogen atoms per unit cell have been located. Consideration of the causes of the subsidiary reflections is left to a later paper.

Introduction and summary of previous work

Yoderite is a hydrous magnesium iron aluminosilicate of composition $Mg_2Al_{5\cdot3}Fe_{0\cdot5}Ca_{0\cdot2}Si_4O_{20}H_{2\cdot4}$. It was discovered by McKie in 1956 occurring in a quartz-yoderite-kyanite-talc schist in grains containing relicts of kyanite in a fixed orientation. McKie (1959) made an X-ray study of the mineral and showed that it had a primitive monoclinic lattice with cell dimensions similar to those of the triclinic kyanite lattice. The

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