S to Co coordination in Co_9S_8 is that of the Rh(m) with the S(f), S(i) and S(j) atoms. The average distance for these is 2·33 Å (Geller, 1962b) compared with the average tetrahedral Co–S distance, 2·19 Å. Moreover, the relatively longer Rh(m)–Rh(m) than Co(f)–Co(f) distances (Table 4) would imply a relative shortening of Rh(m)–S distances. Thus we are able to conclude that the 4-coordination distances are relatively as one would have predicted.

It is possible that the more complex bonding and packing in the $Rh_{17}S_{15}$ results in the shortening of the bonds of the single Rh atom in the unit cell having octahedral coordination. By studying the systems in which Co replaces Rh in $Rh_{17}S_{15}$ and that in which Rh replaces Co in Co_9S_8, we hope to gain some further insight into the bonding and atom sizes as well as effects on the superconductive properties of $Rh_{17}S_{15}$.

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The Crystal Structure of the Superconductor $Rh_{17}S_{15}$

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Crystals of $Rh_{17}S_{15}$, isostructural with those of $Pd_{17}Se_{15}$, belong to one of three space groups O_h^1-$Pm3m$, T_d^1-$P\bar{4}3m$ or O^1-$P432$, have a lattice constant of 9·911 ± 0·001 Å, and two formula units per unit cell. The structure of $Rh_{17}S_{15}$ has been refined in $Pm3m$ from selected single-crystal X-ray data. It is shown that there are relatively short Rh–Rh contacts in $Rh_{17}S_{15}$.

Introduction

To date, only $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$ are known to crystallize with the structure to be described in this paper. A detailed account of the structural study of $Pd_{17}Se_{15}$ has already been given (Geller, 1962); it was mentioned that X-ray data from both $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$ were useful in the solution of the structural problem. The main purpose of the present paper is to report on the structural details of $Rh_{17}S_{15}$ and to point out how they differ from those of $Pd_{17}Se_{15}$.

The rhodium–sulfur system was first investigated by Juza, Hulsmann, Meisel & Biltz (1935). They found a compound that they designated Rh_9S_8, which appeared from X-ray powder diffraction data to have primitive cubic symmetry. The compound was found to be superconducting by Matthias, Corenzwit & Miller (1954). Recently, Kjekshus (1960) carried out X-ray studies over a temperature range on compounds alleged to be Rh_9S_8 and Pd_9Se_8. The structural study has conclusively shown, however, that the correct formulae of the compounds are $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$, as shown in the paper on the latter compound.

Experimental

The lattice constant obtained from a powder photograph (taken with a 114·6 mm. diameter Norelco Straumanis camera and using Cu K radiation) of a specimen with an originally intended composition Rh_9S_8 is 9·911 ± 0·001 Å. This value probably represents the lattice constant of $Rh_{17}S_{15}$ well within experimental error. A compound Rh_9S_8 would contain 78·31% Rh by weight while $Rh_{17}S_{15}$ contains 78·44% Rh by weight; the difference is small. Furthermore a specimen made up with intended composition Rh_8S_7 (78·58% Rh) contained elementary rhodium as shown by an X-ray photograph. Excess sulfur would be difficult to see in the 'Rh_9S_8.' The phase appears to be fairly sharply defined in the Rh–S system, but even *if* there were some solution of sulfur in the $Rh_{17}S_{15}$, there would probably not be a significant difference in lattice constant between 'Rh_9S_8' and $Rh_{17}S_{15}$.

With two $Rh_{17}S_{15}$ in the unit cell, the X-ray density 7·60 g.cm.$^{-3}$ is in good agreement with the value 7·68 g.cm.$^{-3}$ obtained pycnometrically on an 'Rh_9S_8' specimen.

An essentially* single crystal of irregular shape and less than 0·2 mm. each dimension, was photographed with a Buerger precession camera with the [100] direction as precession axis. Weissenberg photographs were also taken about both the [100] and [110] directions as rotation axes. Mo $K\alpha$ radiation was used throughout.

The diffraction symmetry was $m3m$. There were no systematic absences; thus the probable space groups are O_h^1–$Pm3m$, T_d^1–$P\bar{4}3m$ and O_1–$P432$.

The $hk0$ and $hk1$ intensity data used in the structure refinement were obtained from the precession photographs; the hkk data used in the refinement were obtained from the Weissenberg photographs, only those reflections for which $\sin\theta_{hkk} < 0{\cdot}790$ being included. The intensity estimates were made visually by comparison with a calibrated intensity strip. From the precession-camera data, 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.† Lorentz-polarization corrections were also applied to the Weissenberg data in the usual way. No corrections were made for absorption or extinction.

Refinement of the structure

It has been shown in the paper on $Pd_{17}Se_{15}$, that it is not possible to make a choice of the *most* probable of the three space groups to which the crystal might belong. The lowest standard errors were obtained in the centrosymmetric space group, but this in itself does not necessarily mean that it is the most probable one. In fact, as a result of the work on the $Pd_{17}Se_{15}$, the author is led to the speculation that if a structure truly belongs to a non-centrosymmetric space group but is only a very small perturbation on a centrosymmetric one, it is highly probable that it will converge more rapidly in the latter and have lower standard errors on the average. That is, the standard errors for like parameters will be about the same in the two groups, but those which arise from the additional degrees of freedom in the non-centrosymmetric group will have large standard errors associated with them (Geller, 1962). For $Rh_{17}S_{15}$, refinement was based only on the centrosymmetric space group $Pm3m$.

The total number of independent reflections within the precession camera range on the zeroth and first layer photographs about [100] and on the zeroth level Weissenberg photograph about [110] with $\sin\theta_{hkk} < 0{\cdot}790$ was 402. Of these, 128 were too weak to be observed.

Refinement was carried out using the IBM 704 Busing–Levy (1959) least-squares program adapted to the IBM 7090 with a compatibility program. At first all reflection amplitudes of observed reflections were given unit weight while those of reflections too weak to be observed were weighted zero. The starting positional parameters were the analogous final parameters of $Pd_{17}Se_{15}$ except for the Rh atoms in $24m$. These were taken as $x = 0{\cdot}360$ and $z = 0{\cdot}140$ as against 0·352 and 0·150 respectively for $Pd_{17}Se_{15}$. The change was based on examination of a number of the amplitudes. Starting values of isotropic temperature factors were 0·10 Å^2 for all Rh atoms and 0·25 Å^2 for all S atoms. In the calculation of structure amplitudes, the atomic scattering factors used for Rh were those of Thomas & Umeda (1957) and for sulfur, those of Dawson (1960). The real part of the dispersion correction (Dauben & Templeton, 1955) was applied to the Rh scattering factors.

Although after the first least-squares cycle there was little change in positional parameters, there was some difficulty with the temperature factors as was also found for $Pd_{17}Se_{15}$. In early iterations several of the amplitudes from reflections which suffered heavily from extinction were given zero weight and in subsequent iterations those for which $|\Delta F| \geq 30$ were given zero weight; the changes in positional parameters were not significant. The temperature factors were more reasonable but several were still negative* in the last cycle. Examination of the correlation matrix (Geller, 1961) indicates that interactions between the temperature factors and positional parameters are all small and therefore that we may have some confidence in the interatomic distances calculated from the latter. The final parameters and standard deviations based on the use of 219 amplitudes with unit weight are given in Table 1. Calculated and observed amplitudes with the positional parameters given in Table 1 but with values of B, 0·05 Å^2 for all Rh and 0·10 Å^2 for all S atoms are listed in Table 2. The discrepancy factor including considera-

Table 1. *Final parameters and standard errors*

Atom	Position	x	y	z	B	$\sigma(x)$	$\sigma(z)$	$\sigma(B)$
Rh	$24m$	0·3564	0·3564	0·1435	0·01	0·0001	0·0002	0·02
S	$12j$	0·1696	0·1696	$\frac{1}{2}$	−0·01	0·0006		0·09
S	$12i$	0·2310	0·2310	0	0·12	0·0008		0·11
S	$6f$	$\frac{1}{2}$	$\frac{1}{2}$	0·2643	0·14		0·0016	0·15
Rh	$6e$	0	0	0·2388	−0·05		0·0005	0·07
Rh	$3d$	0	0	$\frac{1}{2}$	0·00			0·07
Rh	$1b$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	−0·24			0·15

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* In some of the photographs, some extra spots appeared which were obviously from an occluded crystallite.

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* However, the standard errors (Table 1) indicate that none of these are significantly different from zero.

Table 2. *Observed and calculated amplitudes*

		hk0	
h	k	F_o	F_c
1	1	33	- 27
2	1	59	37
3	1	220	239
4	1	283	326
5	1	170	149
6	1	130	-115
7	1	152	-139
8	1	< 62	42
9	1	178	166
10	1	141	116
11	1	81	62
12	1	85	70
13	1	71	44
14	1	58	- 52
2	2	< 36	9
3	2	135	-111
4	2	254	313
5	2	< 51	- 4
6	2	101	- 91
7	2	< 59	25
8	2	< 61	18
9	2	< 64	- 20
10	2	110	111
11	2	65	- 54
12	2	110	100
13	2	51	34
3	3	82	- 68
4	3	139	-124
5	3	51	40
6	3	< 55	- 2
7	3	185	190
8	3	186	172
9	3	162	131
10	3	163	-167
11	3	144	-157
12	3	68	- 59
13	3	204	174
4	4	573	1002
5	4	162	144
6	4	207	-203
7	4	245	239
8	4	< 62	0
9	4	96	101
10	4	488	549
11	4	87	- 89
12	4	298	294
13	4	266	220
5	5	137	133
6	5	< 59	25
7	5	61	55
8	5	191	156
9	5	141	150
10	5	< 65	1
11	5	< 61	- 39
12	5	63	67
6	6	293	351
7	6	148	-164
8	6	283	320
9	6	65	- 46
10	6	213	-246
11	6	60	53
12	6	101	106
7	7	215	-219
8	7	65	- 53
9	7	83	93
10	7	106	126
11	7	70	76
12	7	< 51	36
8	8	365	407
9	8	114	141
10	8	106	-131
11	8	97	101
9	9	230	223
10	9	< 54	- 21

		hk1	
h	k	F_o	F_c
2	2	137	-110
3	2	193	-170
4	2	103	- 97
5	2	48	- 42
6	2	< 67	- 10
7	2	< 73	- 30
8	2	< 77	- 30
9	2	81	- 71
10	2	98	- 86
11	2	90	- 66
12	2	< 91	4
13	2	< 90	- 1
3	3	240	264
4	3	103	- 97
5	3	< 64	- 9
6	3	< 68	11
7	3	378	-447
8	3	101	78
9	3	< 83	- 6
10	3	149	-153
11	3	160	161
12	3	< 91	9
13	3	227	-206
4	4	20	- 21
5	4	126	126
6	4	57	81
7	4	144	144
8	4	121	122
9	4	84	78
10	4	89	- 99
11	4	72	- 61
12	4	73	52
13	4	189	168
5	5	74	- 81
6	5	72	- 52
7	5	199	-204
8	5	134	128
9	5	< 87	- 5
10	5	< 90	- 23
11	5	91	- 71
12	5	< 91	34
6	6	93	-101
7	6	142	-163
8	6	< 85	- 32
9	6	< 89	- 11
10	6	< 92	31
11	6	< 93	- 30
12	6	< 93	3
7	7	191	212
8	7	< 98	- 32
9	7	155	-151
10	7	< 73	44
11	7	366	-334
12	7	< 97	5
8	8	< 73	2
9	8	91	88
10	8	< 93	33
11	8	72	62
9	9	< 57	- 5
10	9	< 92	- 42

		hkk	
h	k	F_o	F_c
2	0	36	- 9
3	0	214	226
4	0	195	-203
5	0	225	241
6	0	445	747
7	0	184	-181
8	0	474	709
9	0	127	127
10	0	262	-307
11	0	151	166
12	0	196	233
13	0	< 54	28
14	0	616	553
15	0	136	-120
16	0	83	63
17	0	222	216
18	0	77	- 86
19	0	< 64	15
20	0	275	293
21	0	63	- 47
22	0	327	272
2	1	40	- 32
3	1	324	-423
4	1	218	230
5	1	207	-191
6	1	157	-147
7	1	101	105
8	1	56	48
9	1	109	-102
10	1	58	41
11	1	270	-288
12	1	< 58	32
13	1	< 63	53
14	1	< 65	- 47
15	1	< 70	14
16	1	< 72	41
17	1	155	-168
18	1	< 77	24
19	1	110	- 88
20	1	< 78	- 8
21	1	63	86
2	2	23	24
3	2	< 30	18
4	2	< 34	4
5	2	109	-107
6	2	< 40	- 20
7	2	43	- 45
8	2	54	66
9	2	41	- 44
10	2	< 54	- 31
11	2	< 59	- 18
12	2	< 61	2
13	2	63	- 70
14	2	< 67	16
15	2	< 70	4
16	2	< 72	29
17	2	< 76	- 46
18	2	< 77	- 49
19	2	< 79	- 25
20	2	< 79	45
21	2	< 77	- 15
2	3	59	- 42
3	3	662	-813
4	3	200	202
5	3	251	-232
6	3	77	- 90
7	3	330	379

		hkk	
h	k	F_o	F_c
8	3	104	- 82
9	3	322	-292
10	3	89	80
11	3	378	-412
12	3	94	96
13	3	144	144
14	3	170	-153
15	3	41	47
16	3	42	42
17	3	308	-294
18	3	90	88
19	3	135	-105
20	3	79	- 62
21	3	152	146
2	4	62	48
3	4	247	266
4	4	41	- 58
5	4	155	150
6	4	372	435
7	4	123	-131
8	4	584	573
9	4	218	187
10	4	230	-193
11	4	124	98
12	4	184	139
13	4	< 67	33
14	4	514	455
15	4	< 71	- 35
16	4	85	71
17	4	202	157
18	4	110	- 88
19	4	< 78	15
20	4	279	256
21	4	< 76	6
2	5	< 42	- 11
3	5	94	- 88
4	5	217	183
5	5	77	- 73
6	5	69	- 54
7	5	110	- 97
8	5	145	134
9	5	< 56	- 2
10	5	< 59	20
11	5	119	-129
12	5	53	54
13	5	< 68	- 9
14	5	< 70	32
15	5	< 74	- 54
16	5	< 76	48
17	5	< 78	- 34
18	5	< 79	21
19	5	< 79	- 67
20	5	< 77	29
2	6	85	- 77
3	6	62	- 51
4	6	211	-182
5	6	51	- 37
6	6	204	196
7	6	90	- 94
8	6	128	131
9	6	109	-106
10	6	227	-178
11	6	< 66	40
12	6	67	53
13	6	108	- 84
14	6	146	116
15	6	106	- 92

		hkk	
h	k	F_o	F_c
16	6	< 77	- 10
17	6	< 79	17
18	6	< 79	- 83
19	6	< 78	- 30
20	6	< 76	83
2	7	< 52	- 3
3	7	487	-536
4	7	128	140
5	7	213	-216
6	7	173	-174
7	7	415	376
8	7	70	- 86
9	7	262	-190
10	7	84	79
11	7	480	-407
12	7	< 70	0
13	7	177	150
14	7	184	-147
15	7	132	136
16	7	< 78	30
17	7	403	-335
18	7	< 79	33
19	7	132	- 94
2	8	92	81
3	8	123	113
4	8	125	118
5	8	59	61
6	8	177	176
7	8	52	- 47
8	8	373	310
9	8	133	109
10	8	< 69	- 9
11	8	< 71	26
12	8	158	117
13	8	< 75	35
14	8	212	230
15	8	< 79	- 3
16	8	128	89
17	8	78	77
18	8	< 78	4
2	9	< 59	- 9
3	9	134	-139
4	9	149	163
5	9	< 64	- 1
6	9	66	58
7	9	< 67	- 39
8	9	111	110
9	9	< 70	- 45
10	9	< 72	34
11	9	105	- 79
12	9	151	128
13	9	< 77	27
14	9	< 78	24
15	9	78	- 82
16	9	< 78	57
17	9	< 76	4
0	10	354	361
1	10	114	-114
2	10	85	- 91
3	10	77	78
4	10	247	-252
5	10	< 68	- 24
6	10	184	171
7	10	154	-139
8	10	270	215
9	10	< 75	4
10	10	291	-268

		hkk	
h	k	F_o	F_c
11	10	< 77	39
12	10	< 78	- 28
13	10	91	- 85
14	10	234	236
15	10	110	- 68
16	10	< 77	- 43
0	11	151	-148
1	11	92	82
2	11	< 70	- 2
3	11	327	-297
4	11	71	67
5	11	187	-156
6	11	147	-119
7	11	213	193
8	11	< 76	- 54
9	11	152	-129
10	11	< 78	39
11	11	301	-286
12	11	< 79	- 15
13	11	< 79	66
14	11	133	-100
15	11	132	78
16	11	< 75	17
0	12	251	201
1	12	< 75	30
2	12	< 76	58
3	12	< 76	- 19
4	12	123	130
5	12	44	41
6	12	152	112
7	12	< 78	11
8	12	168	122
9	12	< 78	1
10	12	64	59
11	12	< 78	18
12	12	173	133
13	12	< 77	33
14	12	115	66
0	13	77	78
1	13	77	75
2	13	< 79	23
3	13	155	-140
4	13	190	167
5	13	< 78	- 21
6	13	< 79	- 19
7	13	110	89
8	13	78	81
9	13	< 78	- 5
10	13	< 78	68
11	13	164	-148
12	13	86	75
0	14	292	323
1	14	91	- 96
2	14	45	- 65
3	14	64	70
4	14	191	-188
5	14	< 78	- 14
6	14	173	153
7	14	161	-131
8	14	216	211
9	14	< 77	22
0	15	< 77	- 29
1	15	< 77	- 8
2	15	< 77	- 38
3	15	172	-164
4	15	< 76	- 4
5	15	107	- 80

tion of multiplicity but excluding the 600, 800 and 440 amplitudes is 0·12. When the three amplitudes are included, the discrepancy factor is 0·13.

Description of the structure

The interatomic distances in $Rh_{17}S_{15}$ are listed in Table 3. For ease of comparison the analogous $Pd_{17}Se_{15}$ distances are also listed. The general features of the $Rh_{17}S_{15}$ structure are shown in Fig. 2 of the paper on $Pd_{17}Se_{15}$ (Geller, 1962). However, in detail, there are important differences in the $Rh_{17}S_{15}$ and $Pd_{17}Se_{15}$ structures.

The Rh(b)–S(f) are shorter than the Rh(d)–S(j) distances (Table 3), even though the former are octahedral whereas the latter *appear* to be square-coordination distances. This is reverse of the situation in $Pd_{17}Se_{15}$. On the other hand, Rh(d) also has two Rh(e) neighbors at 2·59 Å which together with the 4 S(j) atoms completes an octahedron about Rh(d). In $Pd_{17}Se_{15}$, the analogous Pd(d)–Pd(e) distance is 2·78 Å, which is 0·03 Å *longer* than the elementary Pd–Pd distance, 2·75 Å. In elementary Rh which has the same cubic close-packed structure as elementary Pd, the nearest neighbor Rh–Rh distance is 2·69 Å. Thus the Rh(d)–Rh(e) distance in $Rh_{17}S_{15}$ is 0·10 Å shorter than the elementary Rh–Rh distance, indicating considerably stronger bonding than between the analogous Pd(d)–Pd(e) neighbors. This would account for the longer Rh(d)–S(j) distances.

Further corroboration of the preceding argument is obtained from examination of the Rh–S distances involving Rh(e), which is surrounded by a square of S(i) atoms (though Rh(e) is 0·08 Å out of the plane of the S(i) atoms) and one Rh(d) atom. The Rh(e)–S(i) distance, 2·29 Å, *is* shorter than that of Rh(b)–S(f), but not in the same proportion as the analogous distances in $Pd_{17}Se_{15}$. Again this is justified by the shorter Rh(e)–Rh(d) distance.

The average Rh(m)–S distance is 2·33 Å, not significantly different from the Rh(b)–S(f) distance. This appears to be somewhat anomalous, but again

Table 3. *Interatomic distances and standard error in* $Rh_{17}S_{15}$

Atom	Neighbors	Distance	σ	Analogous $Pd_{17}Se_{15}$ distance
Rh(*b*)	6 S(*f*)	2·336 Å	0·016 Å	2·576 Å
Rh(*d*)	4 S(*j*)	2·378	0·009	2·527
	2 Rh(*e*)	2·588	0·007	2·781
Rh(*e*)	4 S(*i*)	2·291	0·008	2·438
	1 Rh(*d*)	2·588	0·007	2·781
	4 Rh(*e*)	3·348	0·007	3·566
Rh(*m*)	1 S(*i*)	2·261	0·010	2·430
	1 S(*f*)	2·342	0·010	2·492
	2 S(*j*)	2·349	0·006	2·509
	1 Rh(*m*)	2·844	0·004	3·184
	2 Rh(*m*)	2·846	0·003	3·137
	2 Rh(*m*)	2·984	0·003	3·029
S(*f*)	4 S(*f*)	3·304	0·022	3·643
	4 S(*j*)	3·406	0·012	3·641
	4 Rh(*m*)	2·342	0·010	2·492
	1 Rh(*b*)	2·336	0·016	2·576
S(*i*)	4 S(*i*)	3·238	0·009	3·445
	4 S(*j*)	3·210	0·007	3·440
	2 Rh(*e*)	2·291	0·008	2·438
	2 Rh(*m*)	2·261	0·010	2·430
S(*j*)	2 S(*f*)	3·406	0·012	3·641
	4 S(*i*)	3·210	0·007	3·440
	2 S(*j*)	3·362	0·013	3·572
	1 Rh(*d*)	2·378	0·009	2·527
	4 Rh(*m*)	2·349	0·006	2·509

examination of the metal–metal distances indicates a possible reason. The three nearest Rh(*m*)–Rh(*m*) distances, although 0·16 Å longer than the elementary distances, are relatively considerably shorter than the analogous Pd–Pd distances; the nearest neighbor Pd(*m*)–Pd(*m*) distances average 3·15 Å which is 0·40 Å longer than the elementary distance. Thus it appears that in $Rh_{17}S_{15}$ the Rh–Rh bonds are in general stronger than the Pd–Pd bonds in $Pd_{17}Se_{15}$.

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Neutron Diffraction Study of Ammonium Perchlorate

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A neutron diffraction study of single crystals of NH_4ClO_4 at room temperature has indicated that the orientation of the ammonium ion in the crystal is random, and suggests that it is undergoing free or nearly free rotation.

Introduction

A room temperature single crystal study of ammonium perchlorate was undertaken in order to compare the structure of this compound with the 'isomorphous' compound hydronium perchlorate (also under investigation by the authors). A structure comprising an ordered, hydrogen-bonded arrangement of the ammonium ions had been suggested from X-ray difference Fourier projections by Venkatesan (1957). This arrangement, however, is not consistent with the present neutron data which suggests that the ammonium ion is undergoing essentially free rotation. The recent infra-red (Waddington, 1958), nuclear magnetic resonance (*NMR*) (Ibers, 1960, and Richards & Schaefer, 1961), heat capacity (Justice & Westrum, 1961) and cold neutron (Rush, Taylor & Havens, 1961) studies strongly support these results. The OH_3ClO_4 neutron diffraction study in which the OH_3^+ ion is disordered, but not rotating, will be reported at a later date.

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