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The Crystal Structure of the High Temperature Phase Pd_3S

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The crystal structure of the high temperature phase Pd_3S, stable between 554° and 623°C, has been determined by X-ray methods. The crystal system is orthorhombic, probable space group $Ama2$, and the lattice dimensions are: $a = 6.088$, $b = 5.374$, and $c = 7.453$. Four palladium atoms are situated in (a) with $z = 0$, four in (b) with $y = 0.353$, $z = 0.193$, and four in (b) with $y = 0.843$ and $z = 0.301$. The four sulfur atoms are situated in (b) with $y = 0.683$ and $z = 0.000$.

The shortest Pd–S distance is 2.28 Å and the shortest Pd–Pd distance is 2.75 Å.

By thermal analysis of the palladium-sulfur system Weibke and Laar [1] found a high temperature phase with approximately 73 atomic-% palladium ($Pd_{2.7}S$–$Pd_{2.8}S$) stable between 554° and 623°C. The existence of this phase was later confirmed by Grønvold and Røst [2] by X-ray investigation of quenched samples. By slow cooling of the samples the two phases, $Pd_{2.2}S$ and Pd_4S, appeared.

EXPERIMENTAL

Palladium metal used in this investigation was a granulated sample of 99.99 % purity from Koch-Light Laboratories Ltd., England. The *sulfur* was a high purity sample from the American Smelting and Refining Company.

Batches of palladium and sulfur in proportions corresponding to $Pd_{2.5}S$, $Pd_{2.8}S$, $Pd_{3.0}S$, and $Pd_{3.1}S$ were sealed in evacuated silica tubes. The samples were melted, quenched in water and after having been ground finely, annealed for some days in evacuated silica tubes at 600°C. To obtain equilibrium conditions the grinding and annealing procedure had to be repeated some times.

The density of a powdered sample was determined at 25°C by the vacuum pycnometric method with kerosene as displacement liquid.

Som single crystals were obtained by the transport reaction method using small amounts of bromine as transport agent. The shapes of the crystals were irregular and the dimensions were in the range of 0.025 to 0.1 mm.

X-Ray powder photographs were taken in a Guinier-type focusing camera using Cu$K\alpha_1$-radiation ($\lambda = 1.54051$ Å) and KCl ($a = 6.2919$ Å) as calibration standard. Single crystal photographs were obtained in an integrating Weissenberg camera of 57.3 mm diameter using Mo$K\alpha$-radiation. The multiple film technique was used with

tin-foils placed between the films. Most of the intensities were measured photometrically, the weakest reflections were estimated visually.

Integrated intensity data were obtained with crystals rotating about the *b*- and *c*-axes, and the reflections from the layers *h*0*l* to *h*4*l* were used for three-dimensional least-squares refinements. Of a total number of 474 reflections 378 were observed. The unobserved reflections were omitted in the refinements.

Atomic form factors were taken from a paper by Hanson, Herman, Lea and Skillman.[3] The least-squares program used in the refinements was written by Gantzel, Sparks and Trueblood,[4] modified and adapted for UNIVAC 1107 by Chr. Rømming.

In the calculations no corrections were made neither for secondary extinction nor for absorption.

CRYSTAL DATA

Pd_3S, M = 351.3.
Orthorhombic.
$a = 6.088$, $b = 5.374$ and $c = 7.453$ Å.
The estimated standard deviations were of the order 0.001 Å.
Unit cell volum = 243.84 Å^3.
Observed density: 9.58 g cm^{-3}, $Z = 4.01$.
Calculated density assuming $Z = 4$: 9.57 g cm^{-3}.
$F(000) = 616$.
Systematic absent reflections:
hkl when $k + l = 2n + 1$.
*h*0*k* when $h = 2n + 1$.
Possible space groups: *Cmcm*, $Cmc2_1$, and *Ama*2.

Table 1. X-Ray powder pattern of Pd_3S. Cu$K\alpha_1$-radiation.

	$\sin^2\theta \times 10^5$		
$I_{obs.}$	obs.	calc.	*h k l*
w	3127	3122	0 1 1
w	4723	4722	1 1 1
w	6401	6401	2 0 0
m	9529	9524	2 1 1
m	9818	9817	1 2 0
st−	10675	10674	2 0 2
m−	11673	11667	0 1 3
m	12492	12489	0 2 2
st−	13272	13267	1 1 3
m+	14085	14089	1 2 2
w	14608	14618	2 2 0
vw	17079	17089	0 0 4
w	18895	18891	2 2 2
m	19555	19556	0 3 1

RESULTS

X-Ray powder patterns of quenched samples with gross composition $Pd_{3.0}S$ contained reflections from the high temperature phase only, whereas the patterns of $Pd_{2.8}S$ and $Pd_{3.1}S$ showed additional reflections from $Pd_{2.2}S$ and Pd_4S, respectively. As no variation in the lattice dimensions of the high temperature phase has been observed, the composition is assumed to be stoichiometric in accordance with the formula Pd_3S. The difference in composition from the result given by Grønvold and Røst [2] ($Pd_{2.8}S$) may be due to impurities, possibly hydrogen, in the palladium metal used by these authors.

The crystal structure of Pd_3S was found to be orthorhombic, and indexed front reflections of the powder pattern are listed in Table 1.

Of the space groups *Cmcm*, $Cmc2_1$, and *Ama*2 compatible with the systematically absent reflections the centrosymmetric *Cmcm* was first assumed during the refinement procedure. Two-dimensional Patterson projections along the *a*- and *b*-axes were computed, and on the basis of the approximate coordinates that were found, two-dimensional Fourier refinements were performed. Referring to the space group *Cmcm* the atoms are situated as follows:

Table 2. Positional parameters, temperature factors, and estimated standard deviations for Pd_3S calculated according to the three possible space groups.

		Space group *Ama*2							
		x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Pd_I	in 4(*a*)	0	—	0	—	0	—	0.49	0.02
Pd_{II}	in 4(*b*)	0.25	—	0.3533	0.0010	0.1933	0.0006	0.87	0.05
Pd_{II}*	in 4(*b*)	0.25	—	0.8428	0.0010	0.3013	0.0005	0.45	0.03
S	in 4(*b*)	0.25	—	0.6829	0.0015	−0.0001	0.0019	0.58	0.05
		Space group $Cmc2_1$							
		z	$\sigma(z)$	y	$\sigma(y)$	x	$\sigma(x)$	B	$\sigma(B)$
Pd_I	in 4(*a*)	0	—	0.0089	0.0011	0	—	0.47	0.01
Pd_{II}	in 8(*b*)	0.2549	0.0006	0.3474	0.0003	0.1960	0.0001	0.63	0.01
S	in 4(*a*)	0.2502	0.0025	0.6835	0.0015	0	—	0.55	0.05
		Space group *Cmcm*							
		z	$\sigma(z)$	y	$\sigma(y)$	x	$\sigma(x)$	B	$\sigma(B)$
Pd_I	in 4(*a*)	0	—	0	—	0	—	0.49	0.01
Pd_{II}	in 8(*g*)	0.25	—	0.3477	0.0003	0.1960	0.0001	0.62	0.01
S	in 4(*c*)	0.25	—	0.6836	0.0015	0	—	0.57	0.05

4 Pd_I in the (*a*), 8 Pd_{II} in (*g*), and 4 S in the (*c*) positions. The preliminary parameters determined by the two-dimensional Fourier syntheses were for the (*g*) positions: $x = 0.198$, $y = 0.346$ and for (*c*): $y = 0.685$. The *R*-index of the (0*kl*) and (*h*0*l*) reflections were 0.12 and 0.16, respectively.

Refinements by the least-squares method with the three-dimensional data set were then carried out. Anisotropic temperature effects were tentatively assumed in the calculations. The estimated standard deviations of the temperature factors exceeded however, the deviation from isotropy and, therefore, in the final calculations the thermal effects were regarded isotropic. The least-squares refinements proceeded until only negligible parameter shifts occurred, and a reliability factor *R* of 0.0639 was finally obtained.

Table 3. Interatomic distances (<3.5 Å), estimated standard deviations (σ) and $\delta l/\sigma$ (I: *Ama*2—*Cmcm*; II: *Ama*2—*Cmc*2_1, and III: *Cmc*2_1—*Cmcm*).

Atom (no.)	– Atom (no.)	Ama2 Dist.	Ama2 σ×10²	Cmc2₁ Dist.	Cmc2₁ σ×10²	Cmcm Dist.	Cmcm σ×10²	δl/σ I	δl/σ II	δl/σ III
S(1)	– Pd_I (5)	2.284	0.6	2.381	1.3	2.282	0.7	0.3	2.4	2.4
	– " (6)	"	"	2.246	1.3	"	"	"	2.7	2.4
	– Pd_{II} (8)	2.283	1.2	2.323	0.7	2.322	0.7	2.8	2.9	0.1
	– " (9)	2.351	1.2	"	"	"	"	2.1	3.5	"
	– " (10)	2.405	1.4	2.431	0.3	2.432	0.4	1.9	1.8	0.2
	– " (11)	2.461	1.4	"	"	"	"	2.0	2.1	"
	– " (12)	3.373	0.7	3.406	1.4	3.380	0.1	1.0	2.1	1.9
	– " (13)	3.387	0.7	"	"	"	"	1.0	1.2	"
	– " (15)	"	"	3.354	1.4	"	"	"	2.1	1.9
	– " (16)	3.373	0.7	"	"	"	"	1.0	1.2	"
Pd_I(1)	– S (3)	2.284	0.6	2.246	1.3	2.282	0.7	0.3	2.7	2.6
	– S (4)	"	"	2.318	1.3	"	"	"	2.4	2.4
	– Pd_I (2)	3.044	–	3.045	0.1	3.044	–	–	1.0	1.0
	– " (7)	"	–	"	"	"	–	–	"	"
	– Pd_{II} (8)	2.827	0.5	2.802	0.5	2.818	0.2	1.7	3.5	3.0
	– " (22)	"	"	2.833	0.5	"	"	"	0.9	2.8
	– " (9)	2.811	0.4	2.802	0.5	"	"	1.6	1.4	3.0
	– " (21)	"	"	2.833	0.5	"	"	"	3.4	2.8
	– " (17)	2.857	0.4	2.880	0.3	2.850	0.1	1.7	4.6	9.5
	– " (19)	"	"	2.820	0.3	"	"	"	7.4	9.5
	– " (18)	2.841	0.4	2.880	0.3	"	"	2.2	7.8	9.5
	– " (20)	"	"	2.820	0.3	"	"	"	4.2	9.5
Pd_{II}(8)	– S (1)	2.283	1.2	2.323	0.7	2.322	0.7	2.8	2.9	0.1
	– S (5)	2.461	1.5	2.431	0.3	2.432	0.4	1.9	2.0	0.2
	– S (2)	3.373	0.7	3.354	1.4	3.380	0.1	1.0	1.2	1.9
	– S (3)	"	"	3.406	1.4	"	"	"	2.1	1.9
	– Pd_I (1)	2.827	0.5	2.802	0.5	2.818	0.2	1.7	3.5	3.0
	– " (2)	"	"	2.833	0.5	"	"	"	0.9	2.8
	– " (3)	2.857	0.4	2.880	0.3	2.850	0.1	1.7	4.6	9.5
	– " (4)	"	"	2.820	0.3	"	"	"	7.4	9.5
	– Pd_{II}(10)	2.751	0.8	2.804	0.3	2.805	0.3	6.3	6.2	0.2
	– " (18)	2.859	0.8	"	"	"	"	6.3	6.4	"
	– " (9)	2.921	0.6	2.922	0.1	2.922	0.2	0.2	0.2	0.0
	– " (14)	3.320	0.3	3.318	0.5	3.319	0.1	0.3	0.3	0.2
	– " (20)	"	"	"	"	"	"	"	"	"
	– " (12)	3.428	0.4	3.457	0.5	3.456	0.1	6.8	4.5	0.2
	– " (16)	"	"	"	"	"	"	"	"	"

Table 4. Observed and calculated structure factors of Pd_3S. The columns contain $h\ l$, $|F_o|$ and $|F_c|$, respectively.

k = 0			13	1	-	14	5	15	39	34	9	10	46	49	10	5	33	38	9	2	54	56
h	l		14	1	40	38	6	15	56	56	10	10	54	54	11	5	19	18	10	2	-	1
2	0	202	204	0	3	265	263	0	17	43	39	11	10	33	38	12	5	84	88	11	2	34	42
4	0	370	375	1	3	222	227	1	17	28	26	0	12	64	60	0	7	-	2	12	2	59	64
6	0	97	103	2	3	16	19	2	17	22	16	1	12	64	60	1	7	24	22	0	4	50	60
8	0	206	205	3	3	185	187					2	12	33	38	2	7	148	149	1	4	-	21
10	0	51	53	4	3	177	186	k = 2				3	12	57	56	3	7	22	20	2	4	107	115
12	0	117	111	5	3	145	143	h	l			4	12	57	55	4	7	-	1	3	4	-	20
0	2	38	39	6	3	13	15	0	0	-	21	5	12	54	50	5	7	-	17	4	4	58	50
2	2	308	326	7	3	103	109	1	0	258	242	6	12	34	30	6	7	115	113	5	4	-	18
4	2	30	26	8	3	100	110	2	0	239	250	7	12	43	42	7	7	-	14	6	4	85	84
6	2	177	182	9	3	88	82	3	0	207	197	8	12	44	41	8	7	-	4	7	4	-	17
8	2	19	12	10	3	19	12	4	0	22	17	9	12	34	34	9	7	-	11	8	4	41	35
10	2	103	105	11	3	59	60	5	0	143	147	10	12	24	20	10	7	68	74	9	4	-	15
12	2	-	8	12	3	57	62	6	0	162	147	11	12	27	26	0	9	95	94	10	4	44	53
14	2	46	56	13	3	37	42	7	0	104	110	0	14	38	33	1	9	-	11	0	6	32	24
0	4	205	222	0	5	33	28	8	0	15	12	1	14	16	13	2	9	33	36	1	6	25	28
2	4	37	35	1	5	144	145	9	0	79	83	2	14	43	46	3	9	-	10	2	6	116	126
4	4	164	164	2	5	230	231	10	0	82	86	3	14	12	13	4	9	86	83	3	6	-	27
6	4	26	24	3	5	126	125	11	0	56	62	4	14	32	30	5	9	-	8	4	6	26	22
8	4	103	101	4	5	23	21	0	2	182	195	5	14	-	12	6	9	34	31	5	6	21	24
10	4	18	20	5	5	95	101	1	2	213	227	6	14	39	38	7	9	-	6	6	6	92	95
12	4	57	57	6	5	146	155	2	2	92	86	0	16	-	18	8	9	60	60	7	6	-	22
0	6	218	216	7	5	88	80	3	2	196	188	1	16	26	29	0	11	127	116	8	6	-	18
2	6	15	21	8	5	-	10	4	2	145	133	2	16	45	44	1	11	24	19	9	6	-	19
4	6	170	174	9	5	68	62	5	2	146	144	3	16	30	27	2	11	-	23	10	6	56	60
6	6	15	17	10	5	99	93	6	2	61	54	4	16	19	17	3	11	-	17	0	8	147	148
8	6	112	113	0	7	130	144	7	2	106	110	5	16	27	25	4	11	110	103	1	8	89	88
10	6	-	15	1	7	110	117	8	2	84	80	6	16	40	36	5	11	-	15	2	8	-	19
12	6	64	64	2	7	36	31	9	2	73	83	0	18	34	33	6	11	-	20	3	8	88	82
0	8	32	40	3	7	109	106	10	2	43	33	1	18	42	38	7	11	-	12	4	8	120	129
2	8	181	185	4	7	114	120	11	2	58	61	2	18	-	14	8	11	72	73	5	8	70	71
4	8	38	34	5	7	87	90	12	2	42	47	3	18	40	36	0	13	22	24	6	8	-	14
6	8	134	139	6	7	19	23	13	2	34	43	4	18	33	30	1	13	22	15	7	8	57	59
8	8	27	23	7	7	72	73	14	2	25	18	5	18	37	32	2	13	109	98	8	8	92	91
10	8	87	88	8	7	80	82	0	4	75	78	6	18	-	12	3	13	-	14	9	8	41	47
12	8	18	14	9	7	50	57	1	4	23	20	7	18	26	28	4	13	24	21	0	10	30	23
0	10	195	195	10	7	-	16	2	4	147	144	0	20	-	6	5	13	-	13	1	10	52	47
2	10	68	67	11	7	40	42	3	4	19	17	1	20	22	20	6	13	79	79	2	10	147	125
4	10	171	171	12	7	50	48	4	4	67	60	2	20	24	27	7	13	-	11	3	10	47	44
6	10	41	50	13	7	33	30	5	4	17	14	3	20	22	19	8	13	-	16	4	10	25	19
8	10	122	119	0	9	51	55	6	4	104	97					9	13	-	8	5	10	40	40
10	10	33	29	1	9	-	12	7	4	-	12	k = 3				10	13	51	52	6	10	92	99
12	10	64	69	2	9	79	82	8	4	45	40	h	l			0	15	99	92	7	10	39	34
0	12	-	8	3	9	-	12	9	4	-	12	0	1	233	238	1	15	21	15	8	10	-	12
2	12	97	92	4	9	51	48	10	4	56	59	1	1	38	38	2	15	29	25	9	10	30	27
4	12	-	7	5	9	-	12	11	4	-	12	2	1	-	17	3	15	22	14	10	10	57	64
6	12	71	74	6	9	66	64	12	4	28	25	3	1	29	32	4	15	83	82	0	12	71	79
8	12	-	6	7	9	-	12	0	6	42	52	4	1	195	178	5	15	-	13	1	12	50	43
10	12	53	50	8	9	37	35	1	6	54	55	5	1	21	25	6	15	25	19	2	12	-	12
0	14	52	52	9	9	-	11	2	6	135	130	6	1	-	16	7	15	-	11	3	12	44	41
2	14	33	33	10	9	41	42	3	6	51	50	7	1	26	19	8	15	52	60	4	12	77	71
4	14	48	48	0	11	-	21	4	6	44	43	8	1	106	110	0	17	-	9	5	12	40	36
6	14	30	28	1	11	38	36	5	6	38	42	9	1	23	13	1	17	-	4	6	12	-	9
8	14	38	36	2	11	87	92	6	6	101	94	10	1	-	17	2	17	47	42	7	12	35	31
0	16	74	72	3	11	37	34	7	6	36	35	11	1	-	9	3	17	-	4	8	12	49	52
2	16	20	20	4	11	20	20	8	6	35	31	12	1	59	62	4	17	-	9	9	12	26	25
4	16	70	65	5	11	22	31	9	6	31	28	0	3	40	39	5	17	-	3	0	14	35	36
6	16	17	17	6	11	76	73	10	6	62	58	1	3	38	41	6	17	31	35	1	14	-	16
0	18	16	16	7	11	-	27	0	8	107	104	2	3	236	242					2	14	30	36
2	18	57	56	8	11	-	17	1	8	143	136	3	3	37	35	k = 4				3	14	-	15
4	18	-	14	9	11	-	22	2	8	49	46	4	3	28	29	h	l			4	14	30	32
6	18	40	46	10	11	41	47	3	8	134	126	5	3	31	28	0	0	68	57	5	14	-	14
0	20	50	46	11	11	24	18	4	8	94	90	6	3	167	161	1	0	101	97	6	14	19	30
2	20	14	11	0	13	88	84	5	8	107	108	7	3	25	22	2	0	250	251	0	16	-	12
4	20	36	42	1	13	81	73	6	8	42	36	8	3	-	18	3	0	94	85	1	16	-	18
				2	13	-	13	7	8	85	89	9	3	-	16	4	0	44	43	2	16	46	49
k = 1				3	13	72	68	8	8	64	64	10	3	100	99	5	0	78	70	3	16	-	17
h	l			4	13	71	76	9	8	63	69	11	3	-	12	6	0	171	171	4	16	-	11
0	1	87	82	5	13	67	61	10	8	27	24	12	3	-	12	7	0	54	56	5	16	-	16
1	1	43	42	6	13	-	11	11	8	46	52	13	3	-	8	8	0	31	24	6	16	50	40
2	1	219	222	7	13	52	51	12	8	37	38	14	3	48	53	9	0	41	44	0	18	44	45
3	1	37	36	8	13	48	55	13	8	30	37	0	5	290	293	10	0	100	103	1	18	23	26
4	1	60	56	9	13	41	41	0	10	-	13	1	5	58	56	0	2	213	216	2	18	-	9
5	1	29	27	10	13	-	8	1	10	100	90	2	5	107	99	1	2	115	124	3	18	32	24
6	1	127	124	11	13	26	31	2	10	114	106	3	5	53	50	2	2	20	16	4	18	39	41
7	1	22	21	12	13	29	33	3	10	87	84	4	5	240	240	3	2	121	111	5	18	28	22
8	1	30	34	0	15	-	6	4	10	-	12	5	5	41	42	4	2	180	173	6	18	-	7
9	1	-	18	1	15	45	40	5	10	75	74	6	5	70	68	5	2	98	92				
10	1	76	71	2	15	74	69	6	10	82	83	7	5	31	33	6	2	-	7				
11	1	-	16	3	15	44	38	7	10	55	62	8	5	156	157	7	2	72	73				
12	1	29	22	4	15	-	5	8	10	-	10	9	5	27	25	8	2	101	112				

Least-squares refinements assuming the lower symmetrical space groups $CmC2_1$ and $Ama2$ were then carried out, and the resulting R-factors obtained were 0.0603 and 0.0595, respectively. The final parameters referring to the three possible space groups and the estimated standard deviations are listed in Table 2. Refinements assuming palladium atoms in the eight-fold position 8(*c*) in the space groups $Ama2$ was also tried, but a satisfactory solution was not obtained. In this space group the palladium atoms had to be distributed in three four-fold positions.

The relative probability of the correctness of the three space groups has been examined using the significance test on the crystallographic R-factor suggested by Hamilton:[5] If the reliability factors * found by the refinements according to the space groups $Ama2$, $Cmc2_1$, and $Cmcm$ are denoted R_c, R_b and R_a, respectively, one find the following ratios:

$$R_a/R_b = 1.060;\ R_a/R_c = 1.074 \text{ and } R_b/R_c = 1.013.$$

The corresponding significance ratios at the 0.005 level are interpolated as 1.021, 1.019, and 1.011, respectively. According to Hamilton [5] this means that the space group $Ama2$ is the correct one even at a significance level better than 0.005.

The interatomic distances and the estimated standard deviations corresponding to the three different solutions of the structure are calculated and listed in Table 3. The numbers of the atoms correspond to those in Fig. 1.

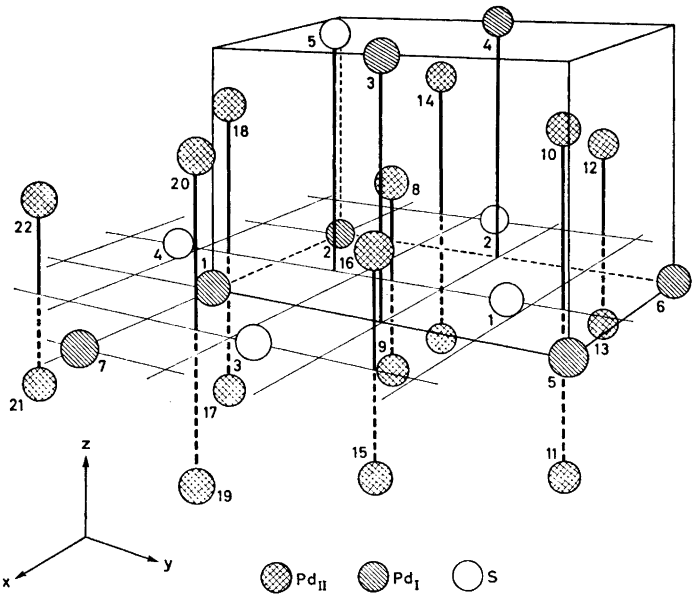

Fig. 1. A perspective view of the crystal structure of Pd_3S. The parallelepiped is a quarter of the unit cell: $a/2$, b, $c/2$.

* In the present work the R-factor is taken as $\sum||F_o|-|F_c||/\sum|F_o|$.

The significance of the differences between corresponding distances are tested using Cruickshank's [6] method. According to Cruickshank the difference is significant if $\delta l/\sigma > 2.3$ and highly significant if $\delta l/\sigma > 3.1$, ($\sigma = (\sigma_A^2 + \sigma_B^2)^{\frac{1}{2}}$). The $\delta l/\sigma$ ratios listed in Table 3 show that some of the differences between corresponding interatomic distances in the three solutions of the crystal structure are highly significant. Thus, the distance from $Pd_{II}(8)$ to $Pd_{II}(10)$ and (18) are identical according to the space groups *Cmcm* and $Cmc2_1$ but in *Ama*2 they are split up into two different distances, 2.751 and 2.859 Å, respectively. The difference between the two distances is highly significant, $\delta l/\sigma$ being 9.5. Further, the lack of a mirror plane in (*hk*0) in space group *Ama*2 leads to a splitting of a number of interatomic distances that are equivalent in the other space groups. As examples may be mentioned that the distances from S(1) to $Pd_{II}(8)$ and (9) are 2.283 and 2.351 Å and the distances from S(1) to $Pd_{II}(10)$ and (11) are 2.405 and 2.461 Å, respectively.

The distance S(1)—Pd(6) of 2.246 Å (space group $Cmc2_1$) is rather short but a corresponding short distance is also found in PdS [7] (2.26 Å). The shortest Pd—Pd distance in the present structure is 2.751 Å ($Pd_{II}(8)$—$Pd_{II}(10)$, space group *Ama*2). This distance corresponds approximately to that found in metallic palladium. Short distances between palladium atoms are also found in several palladium-rich compounds: 2.70 and 2.72 Å in Pd_5B_2 and Pd_3B, respectively,[8] 2.741 Å in $Pd_{4.8}P$,[9] and 2.76 Å in Pd_4Se.[10]

Concerning the interatomic distances, the structures referring to the space groups *Ama*2, $Cmc2_1$, and *Cmcm* are all acceptable but according to the significance test referred above *Ama*2 is regarded as being the correct one. Table 4 shows the observed and calculated structure factors based on this space group.

A perspective view of the crystal structure of Pd_3S is given in Fig. 1. The parallelepiped outlined in the figure is a quarter of the unit cell: $a/2$, b, $c/2$ and the nearest surroundings of the atoms $Pd_I(1)$, $Pd_{II}(8)$, and S(1) can be seen. Referring to the space group *Ama*2 the palladium atoms in position (I) are coordinated to two sulfur atoms at 2.284 Å and to ten palladium atoms at distances ranging from 2.811 to 3.044 Å. Palladium atoms in the (II) position are surrounded by two sulfur atoms at 2.283 and 2.461 Å and by seven palladium atoms in the range 2.751 to 2.921 Å. Closest to the sulfur atoms are six palladium atoms at distances from 2.283 to 2.461 Å. There is no contact between sulfur atoms. The coordination polyhedra surrounding the atoms are distorted and irregular.

As far as coordination number and interatomic distances are concerned Pd_3S is comparable to Pd_4S. According to Grønvold and Røst [10] irregular surroundings of the atoms also exist in Pd_4S. In this compound the palladium atoms are coordinated to ten palladium atoms at distances between 2.78 and 3.10 Å and to two sulfur atoms at 2.34 and 2.48 Å.

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