

## The crystal structure of pyrite-related $\text{Rh}_3\text{Se}_8$

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### Auszug

$\text{Rh}_3\text{Se}_8$  kristallisiert rhomboedrisch mit  $a = 5,9648 \text{ \AA}$  und  $\alpha = 90^\circ 44'$ . In der Elementarzelle der Raumgruppe  $R\bar{3}-C_{3i}^2$  befinden sich drei Rh-Atome in der Punktlage  $3e$ , zwei Se in  $2c$  mit  $x = 0,3816$  und sechs Se in  $6f$  mit  $x = 0,8877$ ,  $y = 0,1166$  und  $z = 0,6204$ . Die Struktur des  $\text{Rh}_3\text{Se}_8$  ist das erste Beispiel für eine dem Pyrit verwandte Struktur mit geordneten Fehlstellen in den Metallatom-Positionen.

### Abstract

$\text{Rh}_3\text{Se}_8$  crystallizes rhombohedrally with  $a = 5.9648 \text{ \AA}$  and  $\alpha = 90^\circ 44'$ . With space group  $R\bar{3}-C_{3i}^2$ , three Rh atoms are in  $3e$ , two Se in  $2c$  with  $x = 0.3816$  and six Se in  $6f$  with  $x = 0.8877$ ,  $y = 0.1166$  and  $z = 0.6204$ . The structure of  $\text{Rh}_3\text{Se}_8$  is the first example of a pyrite-related structure with ordered metal defects.

### Introduction

The system rhodium–selenium was the object of a recent survey and investigation by RUMMERY and HEYDING (1967). The phase relationships in this system are not completely solved; in particular there is some disagreement on the homogeneity ranges of the different phases. The structure types and the approximate (averaged) compositions are as follows:

$\text{Rh}_3\text{Se}_4$	$B8$ superstructure, possibly with orthorhombic distortion and defects
$\text{Rh}_2\text{Se}_3$	$\text{Rh}_2\text{S}_3$ -type structure
$\text{RhSe}_2$	$\text{IrSe}_2$ -type structure up to $843^\circ\text{C}$
$\text{RhSe}_{\sim 2.0}$ to $\text{RhSe}_{\sim 2.6}$	pyrite-type structure at higher temperatures
$\text{Rh}_3\text{Se}_8$	x-ray diffraction pattern similar to rhombohedrally deformed pyrite-type structure up to $825^\circ\text{C}$ .

Except for Rh<sub>2</sub>Se<sub>3</sub> all literature references are compiled in the paper by RUMMERY and HEYDING (1967) while the data for the Rh<sub>2</sub>S<sub>3</sub> structure type have only recently been obtained by us (PARTHÉ, HOHNKE and HULLIGER, 1967). In continuation of this investigation we found it of interest to determine the accurate crystal structure of Rh<sub>3</sub>Se<sub>8</sub>. For a compound of approximate composition RhSe<sub>2.9</sub> HULLIGER (1964) reported a rhombohedral unit cell with  $a = 5.962 \pm 0.002$  Å and  $\alpha = 90^\circ 44' \pm 2'$ ; RUMMERY and HEYDING (1967) found the lattice parameters  $a = 5.964 \pm 0.002$  Å and  $\alpha = 90^\circ 46' \pm 1'$  for a composition RhSe<sub>2.67</sub> (= Rh<sub>3</sub>Se<sub>8</sub>). It was observed by both authors that the x-ray diffraction pattern had similarity to a pyrite-type structure diffraction pattern, however a structure determination has not been made.

#### Sample preparation and identification

Powder mixtures of the elements (Rh 99.9%, Se 99.0%) were sealed in evacuated quartz tubes and heated to 900°C. After 24 hours the reactions were complete and the ampules were slowly cooled to 400°C and there held for 4 days. The ultimate equilibrium product was a fine dark grey powder which was completely stable on air. To obtain high resolution of the diffraction lines the material was ground to 400 mesh and re-annealed at 400°C for 24 hours.

The evaluation of powder diffractometer data using the least-squares program for lattice constants by MUELLER, HEATON and MILLER (1960) gave the rhombohedral-lattice parameters of

$$a = 5.9648 \pm 0.0006 \text{ \AA}$$

$$\alpha = 90^\circ 44.4' \pm 0.6'$$

or, for a hexagonal setting of the unit-cell axes,

$$a = 8.5444 \pm 0.0008 \text{ \AA}$$

$$c = 10.1971 \pm 0.0010 \text{ \AA}$$

in good agreement with the previous data.

#### Structure determination

No systematic extinctions were observed in the diffractometer pattern of Rh<sub>3</sub>Se<sub>8</sub>. Therefore the possible space groups are  $R\bar{3}$ ,  $R\bar{3}2$ ,  $R\bar{3}m$  and  $R\bar{3}m$ .

Since an atomic arrangement similar to the pyrite-type structure was to be expected from the similarity of the diffraction patterns we searched for those rhombohedral space groups which permit an atomic arrangement as in pyrite. There are only two, namely  $R\bar{3}$  and  $R\bar{3}$ . In Table 1 the two settings for pyrite are presented, one in the conventional cubic space group  $Pa\bar{3}-T_h^6$ , the other in the trigonal space group  $R\bar{3}-C_{3i}^2$ .

Table 1. Description of the pyrite-type structure with space groups  $Pa\bar{3}$  and  $R\bar{3}$

$Pa\bar{3}$	
cubic unit cell	
4 Fe in 4a:	$0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0 \quad \bar{Q}$
8S in 8c:	$\pm (x, x, x; \frac{1}{2} + x, \frac{1}{2} - x, \bar{x} \quad \bar{Q}) \quad x \sim 0.38$
$R\bar{3}$	
rhombohedral unit cell, $\alpha = 90^\circ$	
1 Fe in 1a:	$0, 0, 0$
3 Fe in 3e:	$\frac{1}{2}, \frac{1}{2}, 0 \quad \bar{Q}$
2S in 2c:	$\pm (x, x, x) \quad x \sim 0.38$
6S in 6f:	$\pm (x, y, z \quad \bar{Q}) \quad x \sim \frac{1}{2} + 0.38 = 0.88$ $y \sim \frac{1}{2} - 0.38 = 0.12$ $z \sim 1 - 0.38 = 0.62$

For the composition  $Rh_3Se_8$  three different kinds of atomic arrangements can be considered:

(a) Defects on the metal sites. With a formula unit of  $Rh_{0.75}Se_2$  the calculated density is  $7.39 \text{ g/cm}^3$ .

(b) Some non-metal atoms occupy metal sites. With formula unit  $Rh_{0.82}Se_{0.18}Se_2$  a calculated density of  $8.06 \text{ g/cm}^3$  is obtained.

(c) Some of the non-metal atoms occupy interstitial sites. The calculated density for  $RhSe_{2+0.66}$  is  $9.85 \text{ g/cm}^3$ .

The last alternative is not possible for geometrical reasons and because of the disagreement between observed and calculated densities. With the experimental density of  $7.27 \text{ g/cm}^3$  as measured by RUMERY and HEYDING (1967) the defect structure model (a) is the only one acceptable.

A cursory examination of various possible defect models in the context of the experimental diffraction observations immediately rules out a random distribution of the defects on the four metal sites. For this case the  $a$ -glide extinctions found with cubic pyrite would as well occur in the rhombohedral pattern. However in Rh<sub>3</sub>Se<sub>8</sub> the 100 and 110 reflections are observed. The powder diffraction intensities of other defect models were calculated, using the atomic parameters for pyrite-type RhSe<sub>2</sub> from GELLER and CETLIN (1955) in the computer program by JEITSCHKO and PARTHÉ (1966). Agreement between observed and calculated intensities was not good except for the case of complete ordering of the defects at the origin of the rhombohedral unit cell. The good agreement for this last structure proposal indicated that the structure model was essentially correct, but that a refinement of the atomic position coordinates was desirable.

### Structure refinement

For the refinement of the structure of Rh<sub>3</sub>Se<sub>8</sub> the integrated intensities from a powder-diffractometer recording were used. Due to the low-symmetry Laue group of space group  $R\bar{3}$  only the intensities of 26  $hkl$ ,  $hkk$  and  $hhh$  reflections were available for the calculation of observed structure factors. The relative  $|F_{hkl}|$  values were obtained by applying multiplicity factors and Lorentz-polarization corrections [International tables for x-ray crystallography, Vol. 2 (1959), Table 5.2.5B] in the usual manner. The atomic scattering factors for the refinement

Table 2. *Calculated and observed structure factors for Rh<sub>3</sub>Se<sub>8</sub>*

$hkl$	$ F_{\text{obs}} $	$F_{\text{calc}}$	$hkl$	$ F_{\text{obs}} $	$F_{\text{calc}}$
100	38.0	-39.7	33 $\bar{1}$	31.5	33.1
110	39.8	-40.2	331	46.2	43.1
111	33.1	29.1	33 $\bar{2}$	109.4	-101.1
200	130.9	134.5	332	49.1	46.9
211	62.4	63.3	$\bar{4}22$	76.7	73.7
211	137.5	-138.3	422	74.3	72.6
220	97.1	100.7	500	31.7	-30.2
221	20.3	-24.1	511	131.9	127.2
$\bar{3}11$	153.2	154.2	333	114.4	112.6
311	150.9	152.9	440	189.5	192.4
222	84.0	80.6	611	27.6	38.6
400	72.5	-75.7	$\bar{5}33$	97.5	94.8
$\bar{3}22$	39.8	-38.7	$\bar{6}22$	61.1	61.5

Table 3. Powder intensity calculation for  $Rh_3Sc_6$   
CuK $\alpha_1$  radiation [ $\lambda(\text{CuK}\alpha_1) = 1.54051 \text{ \AA}$ ]

h	k	l	$\sin^2\theta_c$	$\sin^2\theta_o$	$I_c$	$I_o$	h	k	l	$\sin^2\theta_c$	$\sin^2\theta_o$	$I_c$	$I_o$	h	k	l	$\sin^2\theta_c$	$\sin^2\theta_o$	$I_c$	$I_o$
1	0	0	0.0167	0.0165	275	254	-5	1	1	0.4465	0.4466	92	136	-5	3	3	0.7081	0.7081	40	44
-1	1	0	329	327	131	128	-3	3	3	42	42	180	180	5	4	1	7132	7132	<1	<1
1	1	0	338	336	136	136	5	-1	1	4500	4502	85	85	5	1	4	7134	7134	81	81
-1	1	1	496	494	22	24	5	1	-1	4552	4554	72	79	5	-3	3	7134	7134	38	38
1	1	1	514	512	16	20	5	3	3	4621	4629	19	20	6	0	2	7253	7252	18	18
2	0	0	668	665	728	700	3	3	3	4777	4777	4	85	6	-2	2	7322	7321	13	30
-2	0	1	825	823	45	1005	-4	3	2	4777	4777	77	77	6	2	-2	7322	7321	13	30
2	1	0	843	841	357	413	-5	2	0	4794	4794	3	3	5	3	3	7343	7346	43	45
2	0	1	987	985	104	104	-5	0	2	4794	4794	3	3	-5	4	2	7411	7412	23	23
-2	-1	1	996	994	522	615	4	2	-3	4794	4794	33	33	5	-4	2	7428	7428	4	4
2	1	-1	1022	1021	106	106	4	3	-2	4829	4830	1	27	5	2	-4	7432	7432	2	26
2	1	0	1022	1021	476	472	4	-2	3	4829	4830	25	25	-6	3	0	7428	7428	2	2
-2	2	0	1317	1314	196	194	5	2	0	4881	4882	36	42	-6	0	3	7462	7462	2	2
2	2	0	1352	1350	182	174	5	0	2	4881	4882	36	42	6	2	2	7462	7462	-	**
-2	2	1	1484	1481	4	45	-5	2	1	4948	4948	23	23	5	4	-2	7515	7514	29	27
2	2	1	1484	1481	39	39	-5	1	2	4948	4948	13	97	5	-2	4	7515	7514	1	1
5	0	0	1501	1499	10	40	4	3	2	4950	4950	64	64	-6	3	1	7582	7582	2	2
2	2	1	1536	1534	9	6	5	-2	1	4974	4974	19	66	6	3	0	7584	7584	34	150
3	-1	0	1655	1655	15	29	5	1	-2	4974	4974	40	66	6	0	3	7584	7584	4	4
3	0	-1	1681	1680	8	27	5	2	-1	5017	5019	5	42	6	-3	1	7608	7608	19	19
3	0	1	1681	1680	20	27	5	-1	2	5017	5019	39	15	6	1	-3	7608	7608	39	39
-3	1	1	1813	1812	300	304	5	1	2	5078	5079	12	15	5	2	4	7672	7671	9	10
3	-1	1	1831	1829	276	573	-4	4	0	5269	5268	150	150	6	3	-1	7713	7717	1	10
3	1	-1	1865	1864	285	285	-5	2	2	5407	5411	150	149	6	-1	3	7713	7717	9	10
-2	2	2	1984	1983	102	100	-4	4	1	5435	5436	6	6	6	3	1	7791	7795	26	32
2	2	2	2054	2054	25	24	-4	1	4	5435	5436	6	6	-4	4	4	7937	7938	10	9
-3	2	0	2143	2140	10	297	5	-2	3	5487	5487	<1	<5	-6	3	2	8069	8070	<1	16
-3	0	2	2195	2194	119	120	4	4	-1	5539	5539	<1	<5	-6	2	3	8122	8122	<1	<5
3	0	2	2195	2194	119	120	-4	3	3	5607	5607	6	6	6	2	-3	8122	8122	<1	<5
-3	2	1	2305	2303	59	13	-5	3	3	5607	5607	3	20	7	0	0	8174	8174	5	14
3	-2	1	2314	2312	46	211	5	2	2	5609	5609	2	20	6	-2	3	8216	8216	<1	<5
3	1	-2	2314	2312	86	1	4	4	1	5609	5609	86	1	4	4	4	8232	8232	-	<5
3	2	-1	2340	2339	164	237	4	-3	3	5633	5634	<1	<5	-5	0	3	8240	8240	-	<5
3	-1	2	2340	2339	80	237	4	3	-3	5633	5634	<1	<5	-5	4	3	8267	8267	<1	14
3	2	1	2383	2383	137	149	5	3	0	5737	5737	<1	<5	-5	3	4	8267	8267	<1	14
3	1	2	2669	2669	45	42	-5	3	1	5765	5765	<1	<5	5	5	-4	8310	8310	11	11
-3	2	2	2801	2800	11	12	-5	1	1	5782	5782	<1	<5	5	-3	-3	8310	8310	6	6
-4	1	0	2818	2818	6	39	5	-3	1	5782	5782	<1	<5	-7	1	0	8310	8310	2	16
3	-2	2	2818	2818	14	1	4	3	3	5815	5815	<1	<5	-7	0	1	8310	8310	2	16
3	2	-2	2818	2818	14	1	-4	3	3	5815	5815	<1	<5	-7	0	1	8310	8310	2	16
4	0	1	2853	2854	<1	8	-4	4	2	5869	5869	<1	<5	6	2	3	8330	8330	10	14
3	2	2	2905	2905	3	5*	-4	4	2	5936	5936	28	28	7	1	0	8371	8374	5	7
-3	3	0	2968	2962	6	6	-4	2	4	5936	5936	21	55	7	0	1	8371	8374	1	7
-4	1	1	2972	2972	1	<5	5	3	1	5938	5938	1	55	-5	5	1	8399	8399	<1	<5
4	-1	1	2998	2998	13	18	6	0	0	6005	6007	3	35	-5	5	0	8449	8454	2	6
4	1	-1	2998	2998	2	18	4	4	-2	6005	6007	30	35	-7	1	1	8451	8454	2	6
3	3	0	3042	3043	5	21	4	4	2	6144	6144	18	31	7	-1	1	8503	8504	9	17
-3	3	1	3130	3129	13	26	-6	0	1	6144	6144	12	31	7	1	-1	8503	8504	17	17
3	3	-1	3182	3182	7	7	6	1	0	6198	6201	42	45	5	3	4	8545	8545	2	6
3	3	1	3234	3233	12	13	6	0	1	6198	6201	1	45	-6	4	0	8570	8570	58	58
-4	0	2	3301	3301	19	45	-5	3	2	6257	6258	17	15	-6	0	4	8573	8571	6	117
4	0	2	3371	3373	26	62	-6	0	2	6257	6258	21	15	5	5	-1	8573	8571	6	117
-4	2	1	3460	3459	82	86	5	-3	2	6291	6292	50	84	5	5	1	8660	8660	<1	<5
4	2	1	3460	3459	82	86	5	2	-3	6291	6292	12	84	-6	4	1	8728	8729	32	52
4	-2	1	3477	3477	35	39	6	-1	1	6335	6335	8	70	-6	1	4	8745	8745	1	10
4	1	-2	3512	3512	4	27	6	1	1	6394	6394	6	5	6	4	0	8778	8778	47	47
4	-1	2	3512	3512	3	27	6	1	1	6394	6394	6	5	6	0	4	8778	8778	34	145
4	1	2	3564	3567	99	98	5	2	-3	6480	6481	13	29	-7	2	0	8780	8780	1	1
-3	3	2	3631	3631	8	60	-6	2	0	6620	6620	13	25	-6	3	3	8890	8890	8	8
3	3	-2	3657	3657	56	66	6	2	0	6725	6729	10	30	-5	5	2	8899	8899	5	5
-3	3	2	3761	3762	12	13	-5	4	0	6752	6752	17	30	-5	2	0	8902	8904	4	192
-4	2	2	3951	3952	28	30	-5	0	4	6752	6752	<1	<5	7	2	0	8902	8904	59	59
4	-2	2	3986	3987	29	54	-6	2	1	6770	6770	8	8	6	-1	4	8902	8902	4	4
4	2	-2	4090	4092	26	28	-6	1	2	6770	6770	<1	<5	-7	2	1	8925	8927	72	86
4	2	2	4118	4116	14	19	-4	4	3	6770	6770	<1	<5	-7	1	2	8925	8927	17	17
-4	0	3	4170	4172	4	5	-6	3	4	6804	6803	<1	<5	7	-2	1	8969	8969	<1	<5
4	3	0	4222	4225	<1	4	6	1	-2	6804	6803	<1	<5	6	-3	3	8969	8969	28	84

were taken from Table 3.3.1B of the International tables for x-ray crystallography, Vol. 3, 1962. No corrections for absorption or anomalous scattering were made.

For the least-square refinement the full-matrix computer program by GANTZEL, SPARKS and TRUEBLOOD (1961) was employed. The function minimized was  $\Sigma(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$ . After four refinement cycles the final value  $R = \frac{\Sigma||F_{\text{c}}| - |F_{\text{o}}||}{\Sigma|F_{\text{o}}|}$  for 26 reflections was 0.035. Because of the limited number of reflections in the refinement a fixed overall temperature factor of  $B = 0.3 \cdot 10^{-16} \text{ cm}^2$  was assumed, similar to values obtained from the structure refinement of Rh<sub>2</sub>S<sub>3</sub>. Table 2 contains the values for  $F_{\text{calc}}$  and  $|F_{\text{obs}}|$  from the last least-square cycle. The final positional parameters of Rh<sub>3</sub>Se<sub>8</sub> and their estimated standard deviations are as follows:

$$\begin{aligned} &3 \text{ Rh in } 3e \\ &2 \text{ Se in } 2c \quad x = 0.3816 \pm 0.0045 \\ &6 \text{ Se in } 6f \quad x = 0.8877 \pm 0.0023 \\ &\quad \quad \quad y = 0.1166 \pm 0.0019 \\ &\quad \quad \quad z = 0.6204 \pm 0.0015. \end{aligned}$$

Observed intensities and intensities calculated for all allowed reflections in a powder diffraction pattern are listed in Table 3.

### Discussion

The characteristic coordination figure of transition-metal chalcogenides with 50 or more percent chalcogen is the metal-centered chalcogen octahedron. This is found for example in the pyrite type (BRAGG, 1914), the marcasite type (BUERGER, 1931) and the NiAs type. For the latter type a large number of ordered defect structures are known (JELLINEK, 1959; KJEKSHUS and PEARSON, 1964; CHEVRETON, BERTAUT and BRUNIE, 1964). The structure of Rh<sub>3</sub>Se<sub>8</sub> is the first example of a pyrite-related structure with ordered defects. A projection of the Rh<sub>3</sub>Se<sub>8</sub> structure on the *ab* plane demonstrating the arrangement of the empty and Rh-filled [Se<sub>6</sub>] octahedra is shown in Fig. 1. The distances in the filled octahedra are insignificantly different from those found in pyrite-type RhSe<sub>2</sub> while the Se atoms in the empty octahedron move slightly towards the center of the octahedron. The

shift is, however, large enough to make the octahedral hole too small for a Rh atom. In comparison to the Se—Se-pair distances of 2.50 Å in RhSe<sub>2</sub> we find Se—Se dumbbells with 2.41 Å separation in Rh<sub>3</sub>Se<sub>8</sub>. A list of the interatomic distances and the octahedral angles is given in Table 4.

From ligand-field theory one would expect to find an octahedral coordination for Rh if the latter has a  $d^6$  configuration corresponding to a Rh<sup>3+</sup> ion. If it is assumed that the Se—Se pairs complete their valence shell, they must accept two electrons corresponding to (Se<sub>2</sub>)<sup>2-</sup>

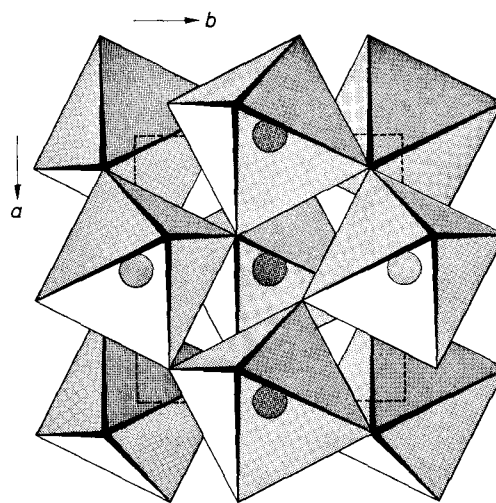


Fig. 1. The arrangement of [Se<sub>6</sub>] octahedra in Rh<sub>3</sub>Se<sub>8</sub>

According to HULLIGER (1964) this rhodium selenide is a diamagnetic semiconductor which indicates that there are no unpaired electrons and no conduction electrons. On this basis HULLIGER assumed that the ideal composition of the compound was RhSe<sub>3</sub> or Rh<sub>2/3</sub><sup>3+</sup>(Se<sub>2</sub>)<sup>2-</sup>. The actual composition is however Rh<sub>3</sub>Se<sub>8</sub>. If again the presence of Rh<sup>3+</sup> and (Se<sub>2</sub>)<sup>2-</sup> ions is assumed and consequently a formula unit Rh<sub>3/4</sub><sup>3+</sup>(Se<sub>2</sub>)<sup>2-</sup>, one electron per unit cell cannot be accommodated within this bonding scheme.

The structure type of Rh<sub>3</sub>Se<sub>8</sub> is also observed with Ir<sub>3</sub>S<sub>8</sub> but with a rhombohedral angle very close to 90°. Rh<sub>3</sub>S<sub>8</sub> and Ir<sub>3</sub>Se<sub>8</sub> are not isotopic but have Rh<sub>3</sub>Se<sub>8</sub>-related structures. The results of these continuing investigations will be published at a later time.

Table 4. *Interatomic distances and octahedron angles in Rh<sub>3</sub>Se<sub>8</sub>*

[RhSe <sub>6</sub> ] octahedra centered at the 3e equivalent positions (estimated standard deviations in brackets)			
Rh—Se (1)	2.500 (9) Å	Se (1)—Rh—Se (3)	93.7° (5)
Rh—Se (2)	2.500 (9)	Se (1)—Rh—Se (4)	95.6° (7)
Rh—Se (3)	2.492 (11)	Se (1)—Rh—Se (5)	86.3° (5)
Rh—Se (4)	2.500 (13)	Se (1)—Rh—Se (6)	84.4° (7)
Rh—Se (5)	2.492 (11)	Se (2)—Rh—Se (3)	86.3° (5)
Rh—Se (6)	2.500 (13)	Se (2)—Rh—Se (4)	84.4° (7)
		Se (2)—Rh—Se (5)	93.7° (5)
		Se (2)—Rh—Se (6)	95.6° (7)
		Se (3)—Rh—Se (6)	93.2° (2)
		Se (3)—Rh—Se (4)	93.2° (2)
		Se (5)—Rh—Se (4)	86.8° (3)
		Se (5)—Rh—Se (6)	86.8° (3)
[Se <sub>6</sub> ] defect octahedra centered at the origin			
□—6 Se	2.464 (9) Å	6 Se—□—Se	95.6° (4)
		6 Se—□—Se	84.4° (4)
Tetrahedra			
[Se—SeRh <sub>2</sub> □] centered at the 6f equivalent positions		[Se—SeRh <sub>3</sub> ] centered at the 2c equivalent positions	
Se—Se	2.416 (16)	Se—Se	2.415 (65) Å
Se—Rh	2.500 (13)	Se—Rh	2.500 (9)
Se—Rh	2.492 (11)	Se—Rh	2.500 (9)
Se—□	2.464 (9)	Se—Rh	2.500 (9)

□ indicates a metal defect at the origin of the unit cell

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