

tassium hydrogen chloromaleate is 2.41 Å long (Ellison & Levy, 1965) and in acetamide hemihydrochloride, 2.40 Å (Takei & Hughes, 1955). Hydrogen bonds similar to those in nitrilotriacetic acid are found in cytosine-5-acetic acid, where the hydrogen-bonded O...O distance is observed to be 2.506 Å (Marsh, Bierstedt & Eichhorn, 1962). The high density of nitrilotriacetic acid (1.66 g.cm<sup>-3</sup>) is probably a manifestation of the strong hydrogen bonding.

Fig. 9 shows half of the molecules in the structure which form a hydrogen-bonded network of interconnected right- and left-handed helices with axes approximately normal to the *xy* plane. The molecules which are not shown form a similar network that is interleaved with the one in Fig. 9, the molecules in it being parallel to and equidistant from the molecules shown. The vectors  $\mathbf{a}' = \mathbf{a}$ ,  $\mathbf{b}' = \mathbf{b}$ , and  $\mathbf{c}' = \mathbf{a} + 2\mathbf{c}$  form a nearly orthogonal cell with twice the volume of the chosen cell and with a unique angle  $\beta'$  of 89.7°. In terms of this nearly orthogonal cell the molecules shown on top of each other in Fig. 9 are related by multiples of the translation vector  $\mathbf{c}'$ , while those not shown are generated by odd multiples of  $\frac{1}{2}\mathbf{c}'$ . There is no hydrogen bonding between the two networks.

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## A New Structure Type with Octahedron Pairs for Rh<sub>2</sub>S<sub>3</sub>, Rh<sub>2</sub>Se<sub>3</sub> and Ir<sub>2</sub>S<sub>3</sub>

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The structure of Rh<sub>2</sub>S<sub>3</sub> has been determined, using single-crystal data. The space group is *Pbcn* (*D*<sub>2h</sub><sup>14</sup>) and the lattice constants are  $a = 8.462$ ,  $b = 5.985$ ,  $c = 6.138$  Å. The expected octahedral coordination of the rhodium atoms is confirmed. Every octahedron shares a common face with one other octahedron to form octahedron pairs. These octahedron pairs may be imagined to be arranged in layers which show the stacking sequence *ABABA*... Four rhodium atoms surround each sulfur atom at the vertices of a distorted tetrahedron. Isotypic compounds are Ir<sub>2</sub>S<sub>3</sub> and Rh<sub>2</sub>Se<sub>3</sub>. From intensity calculations for Rh<sub>2</sub>(S<sub>1-x</sub>Se<sub>x</sub>)<sub>3</sub> it is inferred that a complete range of solid solubility exists between Rh<sub>2</sub>S<sub>3</sub> and Rh<sub>2</sub>Se<sub>3</sub>.

### Introduction

Disagreement exists in the literature concerning the structure and composition of the phases in the system Rh-S. In particular, earlier experiments by one of us

showed that all attempts to prepare the reported Rh<sub>2</sub>S<sub>3</sub> led to a two-phase mixture containing elementary S and a homogeneous rhodium sulfide phase which was identified to be Rh<sub>2</sub>S<sub>3</sub> (Hulliger, 1964). This compound was found to be a diamagnetic semiconductor which

indicates an ionic formula  $\text{Rh}_2^3+\text{S}_3^{2-}$  with six  $4d$  electrons left to the rhodium atoms. A diamagnetic  $d^6$  configuration suggests the occurrence of  $[\text{RhS}_6]$  octahedra in the structure. It was of interest to us to see if the actual structural features agree with our assumptions.

### Experimental

Powder samples of  $\text{Rh}_2\text{S}_3$ ,  $\text{Rh}_2\text{Se}_3$ , and  $\text{Ir}_2\text{S}_3$  were prepared by sintering pressed stoichiometric mixtures of the constituent powdered elements in evacuated and sealed quartz tubes. To avoid explosion due to the sulfur pressure before the reaction took place, the temperature was raised slowly to reach  $900^\circ\text{C}$  within one to three days, and the samples were kept at this temperature at least one day. In the case of the compounds  $\text{Rh}_2\text{S}_2\text{Se}$  and  $\text{Rh}_2\text{SSe}_2$  the reaction product was re-ground and annealed at  $700^\circ\text{C}$  for one week.

Single crystals of  $\text{Rh}_2\text{S}_3$  were prepared by chemical transport reaction.  $\text{Rh}_2\text{S}_3$  powder was used as a starting material, and bromine as a transport agent in a concentration of  $5 \text{ mg.cm}^{-3}$ . The  $\text{Rh}_2\text{S}_3$  powder was placed at the hot end of a quartz tube and held at  $1100^\circ\text{C}$  while small  $\text{Rh}_2\text{S}_3$  crystals formed at the cool end which was kept at  $1020^\circ\text{C}$ .

Powder and single-crystal diffraction techniques were employed in this structure study, using  $\text{Cu } K\alpha$  ( $\lambda \text{ Cu } K\alpha = 1.54051 \text{ \AA}$ ) and  $\text{Cr } K\alpha$  ( $\lambda \text{ Cr } K\alpha = 2.28962 \text{ \AA}$ ) for the first and  $\text{Mo } K\alpha$  ( $\lambda \text{ Mo } K\alpha = 0.7107 \text{ \AA}$ ) for the latter technique.

The cylindrical  $\text{Rh}_2\text{S}_3$  single crystal used for this investigation had a slightly irregular cross-section of  $0.0083 \text{ cm}$  diameter and a length of  $0.025 \text{ cm}$ . It was rotated around the cylinder axis corresponding to the  $[100]$  direction. The diffracted intensities were recorded photographically on a Nonius integrating Weissenberg camera using the multiple film technique and were visually estimated by comparison with a calibrated film strip. Precession photographs of the  $h0l$  zone were taken to provide the data for the cross-correlation of Weissenberg layers. A total of 1329 independent reflections within the range of the zero and the first three upper Weissenberg levels were examined. Of these 659 were of measurable intensity. Relative  $|F_{hkl}|$  values were obtained by applying Lorentz-polarization and absorption corrections to the visually estimated intensities. Pronounced primary extinction of the nine reflections with highest intensity became apparent during the initial stages of refinement. These reflections, namely 400, 020, 420, 211, 231, 022, 402, 113 and 213 were given zero weight in the subsequent structure refinement. No other corrections for extinctions were made. Table 5.3.5B of the *International Tables for X-ray Crystallography* (1959) was used for the absorption correction for a cylindrical specimen with  $\mu R = 0.5$ ; the  $L_p$  correction, using Table 5.2.5F of *International Tables*, was applied in the usual manner. The atomic scattering factors for this investigation were taken from *International Tables for X-ray Crystallography* (1962).

### Structure determination

Weissenberg and precession photographs of a  $\text{Rh}_2\text{S}_3$  single crystal could be indexed with an orthorhombic unit cell. The lattice parameters, subsequently refined from powder diffractometer data using the least-squares program by Mueller, Heaton & Miller (1960) and Gvildys (1965), are

$$a = 8.462 \pm 0.003 \text{ \AA}$$

$$b = 5.985 \pm 0.002$$

$$c = 6.138 \pm 0.002$$

Systematic absences among the observed reflections on the Weissenberg photographs are:  $hkl$ , no extinctions,  $hk0$  with  $h+k=2n+1$ ,  $h0l$  with  $l=2n+1$  and  $0kl$  with  $k=2n+1$ . These extinctions are consistent with the uniquely determinable space group  $Pbcn$  ( $D_{2h}^{14}$ ). Assuming four formula units of  $\text{Rh}_2\text{S}_3$  per unit cell the X-ray density was calculated to be  $6.46 \text{ g.cm}^{-3}$ , which agrees well with the measured density at  $25^\circ\text{C}$  of  $6.40 \text{ g.cm}^{-3}$  as determined by Juza, Huelsmann, Meisel & Biltz (1935).

To obtain a trial structure for the placement of the 8 Rh and 12 S atoms in the orthorhombic unit cell we made use of our observation on the Weissenberg and precession photographs that all reflections with  $k+l=2n+1$  are systematically weaker than reflections with  $k+l=2n$ . If all reflections with  $k+l=2n+1$  were totally absent, the structure would be based on an  $A$ -centered orthorhombic Bravais lattice. Tentatively we assumed that the heavy Rh atoms have an atomic arrangement approximately based on an  $A$ -centered lattice. This restricts the possible values of the adjustable parameters. Assuming that the Rh atoms occupy the eight-fold position  $8(d)$  one finds that an  $A$ -centered pattern of repetition can be constructed only if  $y = \frac{1}{4}$  and  $x = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ , or  $z = 0, \frac{1}{4}, \frac{1}{2}, \frac{3}{4}$ . The twelve S atoms were tentatively placed on equipoints  $8(d)$  and  $4(c)$ . To find the values of the adjustable parameters we made use of the observation that five reflections had practically zero intensity: 006, 102, 202, 206 and 504. The five non-linear structure factor equations could be solved for the adjustable parameters by the use of a variation method. A small computer program was written which permitted the calculation of the structure factors of the five reflections for different parameters, rejecting all those solutions which did not result in zero for all five  $F$  values. Of the results obtained only one set of parameters gave a trial structure which was acceptable from geometrical considerations. Using this set of parameters the intensities of a powder diffraction pattern were calculated (program by Jeitschko & Parthé, 1966) and compared with an experimentally obtained Debye-Scherrer pattern. The good agreement indicated that the structure proposal was essentially correct, but that a refinement of the parameters was needed.

The refinement proceeded along two independent methods: electron density projections and least-squares

calculation. The  $x$  and  $y$  parameters were refined by reiterative electron density projections  $\rho(x, y)$ . The final electron density projection is shown in Fig. 1 with the  $z$  values written next to each atom.

For the least-square calculations the full-matrix computer program by Gantzel, Sparks & Trueblood (1961) as modified by Okaya (1962) was used. The function minimized was  $\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$ . In this calculation amplitudes of reflections which were actually observed were given unit weight; those of reflections too weak to be observed were given zero weight. After excluding those reflections from the refinement for which primary extinction was present, the convergence was rapid.

A total of eleven parameters were refined for this structure, seven positional coordinates, three isotropic temperature factors and one scale factor. At the end of the refinement all parameter shifts were less than  $10^{-4}$  of the estimated standard deviation computed from the inverse matrix. Considering all observed reflections, except those nine with pronounced extinction, a final  $R$  value of 0.069 is obtained, where  $R = \sum ||F_c| - |F_o|| / \sum |F_o|$ . If the upper limits for all unobserved reflections are taken as  $\frac{1}{2}|F_{\text{min}}|$  (corresponding to the smallest structure factor which can be observed near that part of reciprocal space), the discrepancy index for all allowed reflections becomes  $R = 0.145$ . The considerable increase from  $R = 0.069$  for observed reflections only to  $R = 0.145$  for all reflections allowed is due to the fact that 670 of 1329 reflections are in the un-

observed category. Table 2 contains the values for  $F_{\text{calc}}$  and  $F_{\text{obs}}$  from the final least-squares cycle. The final positional parameters, isotropic temperature factors and their estimated standard deviations, obtained from the refinement for all possible reflections, are given in Table 1.

### Discussion of the structure

The projection of the Rh<sub>2</sub>S<sub>3</sub> structure along the  $c$  axis is shown in Fig. 1. A close study reveals that the structure of Rh<sub>2</sub>S<sub>3</sub> is characterized by distorted [RhS<sub>6</sub>] octahedra and distorted [SRh<sub>4</sub>] tetrahedra. The maximum deviation of the octahedron angles from 90° amounts to almost 19°; the deviations of the tetrahedron angles from 109° are as high as  $\pm 20^\circ$ . The [RhS<sub>6</sub>] octahedra occur in pairs having one face in common. The octahedron pairs are three-dimensionally connected; however, one may for descriptive purposes consider the arrangement of the octahedron pairs in a layer parallel to the (010) plane. The arrangement of such a single layer perpendicular to the  $b$  axis is shown in Fig. 2. There are two layers per unit cell, one being the mirror image of the other. In this way one may describe the Rh<sub>2</sub>S<sub>3</sub> structure as a stacking sequence  $ABAB$  of octahedron-pair layers along [010] where  $A$  and  $B$  are related by a  $b$ -glide reflection.

The observed interatomic distances and angles are listed in Table 3 and Fig. 3. The average Rh-S distance

Table 1. Atomic coordinates and temperature factors

	$x$	$\sigma_x$	$y$	$\sigma_y$	$z$	$\sigma_z$	$B$	$\sigma_B$
8 Rh in 8( $d$ )	0.10645	0.00008	0.2517	0.0003	0.0338	0.0002	0.186	0.008
8 S in 8( $d$ )	0.1518	0.0003	0.3906	0.0005	0.3930	0.0010	0.169	0.030
4 S in 4( $c$ )	0		0.9525	0.0007	0.25		0.149	0.042

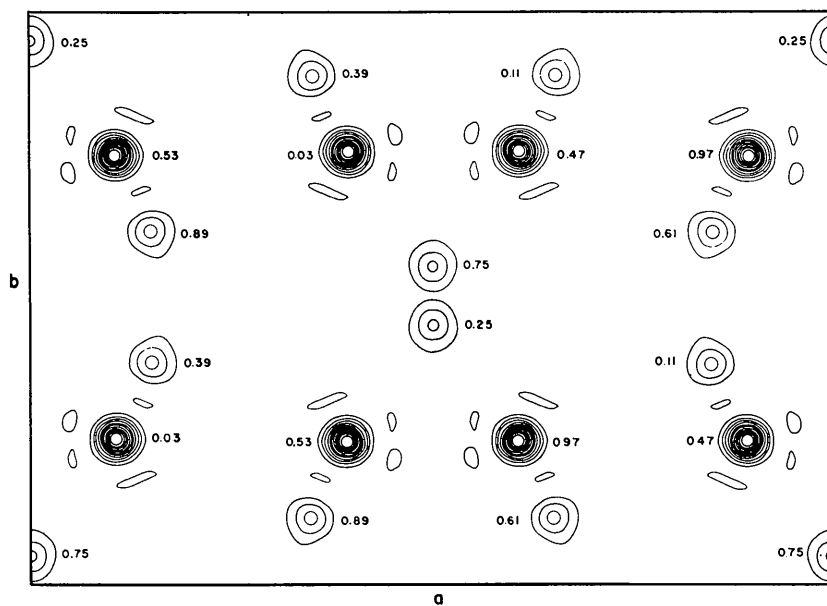


Fig. 1. Electron density projection  $\rho(x, y)$  for Rh<sub>2</sub>S<sub>3</sub>. The contours are at equally spaced intervals on an arbitrary scale; the numbers indicate the atomic  $z$  parameters.

Table 2. Calculated and observed structure factors of Rh<sub>2</sub>S<sub>3</sub>

Reading from left to right, the columns contain the values of h, |F<sub>obs</sub>|, and F<sub>calc</sub>.

Table with multiple columns containing calculated and observed structure factors for Rh2S3. The table is organized into groups of columns, each representing a different set of hkl indices. Each group contains columns for h, |F\_obs|, and F\_calc. The data is presented in a grid-like format with varying column widths and some missing values indicated by dashes.

is 2.36 Å, which corresponds precisely to the sum of Pauling's covalent Rh radius for coordination 6, namely 1.32 Å, plus the tetrahedral S radius of 1.04 Å.

Table 3. *Interatomic distances and octahedron angles in  $\text{Rh}_2\text{S}_3$*

The interatomic distances have an error of  $<0.003$  Å, the octahedral angles an error of  $<0.3^\circ$ .

[RhS <sub>6</sub> ] octahedra			
Rh...S(1)	2.387 Å	S(1)...Rh...S(2)	79.0°
Rh...S(2)	2.404	S(1)...Rh...S(3)	81.5
Rh...S(3)	2.378	S(1)...Rh...S(4)	108.8
Rh...S(4)	2.378	S(1)...Rh...S(5)	89.8
Rh...S(5)	2.340	S(2)...Rh...S(3)	79.2
Rh...S(6)	2.311	S(2)...Rh...S(4)	104.8
		S(2)...Rh...S(6)	82.9
		S(3)...Rh...S(5)	84.3
Rh...Rh distance in octahedron pairs:	3.208 Å	S(3)...Rh...S(6)	88.2
		S(4)...Rh...S(5)	93.0
Average Rh...S distance in an octahedron:	2.365 Å	S(4)...Rh...S(6)	97.4
		S(5)...Rh...S(6)	105.6

#### [SRh<sub>4</sub>] tetrahedra

S (8d)...Rh:	2.378, 2.378, 2.340, 2.387 Å	$\bar{d}=2.371$ Å
S (4c)...Rh:	2.311, 2.311, 2.404, 2.404	$\bar{d}=2.357$ Å

Our expectation of an octahedral coordination of Rh thus has been substantiated. Two features are, however, surprising, namely the strong distortion of the coordination polyhedra and the formation of octahedron pairs by sharing a face. In terms of the ligand field theory the diamagnetic  $d^6$  configuration requires no distortion of the octahedral symmetry in order to obtain the energetically most stable arrangement. In view of the predominantly covalent bonding in  $\text{Rh}_2\text{S}_3$ , additional information about the reasons for such distortion must take into account the energy states of the electrons as obtained from MO-LCAO calculations. The separation of the Rh atoms within the octahedron pairs (3.21 Å) is large enough to assure that no Rh-Rh bonds occur. A distance of 2.72 Å would result if the Rh atoms of a double-octahedron were at the centers of regular octahedra with all Rh-S distances set equal to their average value in this structure 2.365 Å.

#### Isotypic compounds

Powder patterns of the chalcogenides  $\text{Rh}_2\text{S}_2\text{Se}$ ,  $\text{Rh}_2\text{SSe}_2$ ,  $\text{Rh}_2\text{Se}_3$  and  $\text{Ir}_2\text{S}_3$  could be indexed in a manner similar to that of the  $\text{Rh}_2\text{S}_3$  powder pattern in Table 4. The lattice constants of these compounds and the measured magnetic susceptibilities at liquid nitrogen and room temperatures are assembled in Table 5.  $\text{Rh}_2\text{Se}_3$  and  $\text{Ir}_2\text{S}_3$  show also the (nearly) temperature-independent diamagnetism like  $\text{Rh}_2\text{S}_3$  and will thus have a bonding mechanism similar to  $\text{Rh}_2\text{S}_3$ .

Integrated intensities of the  $\text{Rh}_2\text{SSe}_2$  powder diffraction peaks, obtained from a diffractometer recording, were used to investigate the two alternatives of ordered or disordered substitution of sulfur atoms in positions 8(d) and 4(c) in space group *Pbcn*. Comparison in

Table 6 of the observed intensities with intensities calculated for an ordered and a disordered arrangement (atom coordinates from  $\text{Rh}_2\text{S}_3$ ) shows conclusively that sulfur is randomly substituted by Se. Similarly, an intensity comparison for  $\text{Rh}_2\text{S}_2\text{Se}$  demonstrates that this compound is a disordered compound and thus a complete range of solid solubility presumably extends from  $\text{Rh}_2\text{S}_3$  to  $\text{Rh}_2\text{Se}_3$  with  $8(\text{S}_{1-x}\text{Se}_x)$  in 8(d) and  $4(\text{S}_{1-x}\text{Se}_x)$  in 4(c). Fig. 4 shows the linear change of unit cell volume with increasing substitution of S by Se.

Attempts to prepare the isoelectronic compounds  $\text{Rh}_2\text{Te}_3$ ,  $\text{Ir}_2\text{Se}_3$ ,  $\text{Rh}_2\text{S}_2\text{Te}$ ,  $\text{Rh}_2\text{Se}_2\text{Te}$  and also  $\text{CoRhS}_3$ ,  $\text{GaRhS}_3$ ,  $\text{YRhS}_3$ ,  $\text{RhPdPS}_2$ ,  $\text{RhIrSe}_3$  and  $\text{RuPdS}_3$  were not successful.

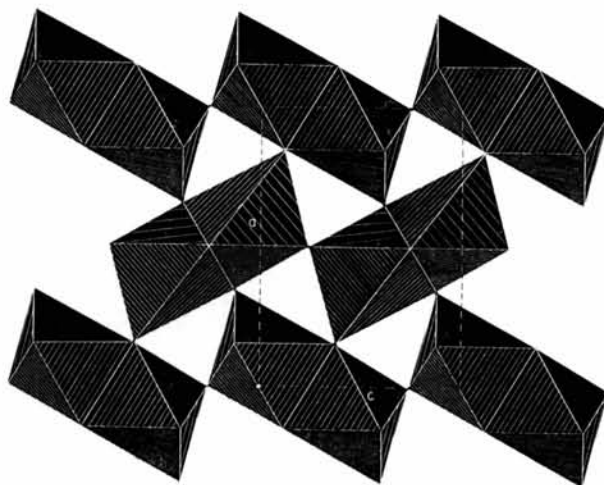


Fig. 2. The arrangement of the [RhS<sub>6</sub>] double octahedra in a layer parallel to the (010) plane. There are two such layers per unit cell, one being the mirror image of the other.

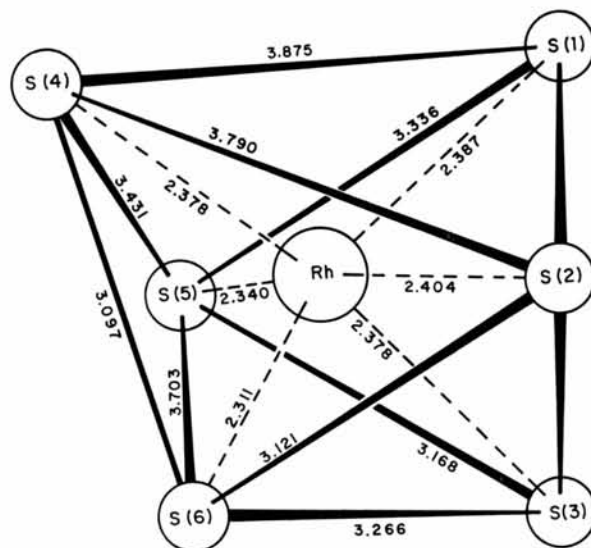


Fig. 3. Bond distances in the [RhS<sub>6</sub>] octahedron.

Table 4. Powder intensity calculation for  $Rh_2S_3$ 

Cr $K\alpha$ radiation ( $\lambda$ Cr $K\alpha=2.28962 \text{ \AA}$ )									
$hkl$	$10^3 \cdot \sin^2 \theta_c$	$10^3 \cdot \sin^2 \theta_o$	$I_c$	$I_o$	$hkl$	$10^3 \cdot \sin^2 \theta_c$	$10^3 \cdot \sin^2 \theta_o$	$I_c$	$I_o$
110	54.9	—	<1	—	512	633.3	—	4	—
200	73.2	73.2	77	w	141	638.5	—	2	—
111	89.7	89.7	102	mw	521	638.7	—	10	—
002	139.1	139.1	277	ms	413	642.5	643.0	22	vw
211	144.6	144.6	942	vvs	431	656.9	—	20	—
020	146.4	146.6	240	ms	240	658.6	—	15	—
102	157.5	—	<1	—	600	658.9	659.8	3	vw
021	181.1	181.5	42	vw	133	660.7	—	9	—
112	194.0	194.0	36	vw	214	666.4	—	2	—
121	199.4	—	34	—	241	693.4	—	3	—
310	201.3	200.7	67	w	024	702.9	703.5	38	vw
202	212.4	—	<1	—	233	715.6	716.2	107	mw
220	219.6	—	6	—	124	721.2	722.5	50	—
311	236.1	235.9	43	vw	304	721.3	—	44	mw
212	248.9	249.6	28	vw	042	724.5	724.4	68	w
221	254.4	—	<1	—	611	730.3	730.8	100	mw
022	285.5	286.0	274	ms	142	742.8	743.3	49	—
400	292.8	292.9	118	mw	522	743.1	—	4	vw
122	303.8	—	40	—	423	752.3	752.1	20	vw
302	303.9	304.6	20	w	314	757.9	—	<1	vvs
312	340.5	—	3	—	432	761.3	—	2	—
321	345.9	—	1	—	224	776.1	—	<1	—
130	347.6	—	8	—	341	784.9	—	1	—
222	358.7	359.1	42	vw	530	786.9	—	1	—
411	364.2	364.9	103	mw	242	797.8	797.9	8	—
113	368.0	368.5	128	mw	602	798.0	—	55	w
131	382.4	—	12	—	620	805.2	—	82	—
213	422.9	422.7	211	m	333	807.1	806.6	5	m
402	432.0	432.8	147	mw	513	807.2	—	67	—
231	437.3	—	359	—	531	821.6	—	3	—
420	439.2	438.2	130	s	612	834.6	—	3	—
322	450.2	450.7	38	vw	621	840.0	—	15	—
023	459.4	—	5	—	404	849.4	—	10	—
412	468.6	—	5	—	324	867.7	867.9	140	m
421	474.0	—	1	—	440	878.2	878.5	62	w
123	477.7	—	2	—	414	886.0	—	2	—
132	486.7	—	1	—	342	889.3	889.5	63	w
330	494.0	—	<1	—	043	898.5	—	<1	—
510	494.2	—	2	—	134	904.2	—	<1	—
313	514.4	514.5	32	vw	441	913.0	—	4	—
331	528.8	—	7	—	143	916.8	—	<1	—
511	528.9	528.6	13	vw	523	917.0	—	5	—
223	532.6	—	6	—	115	924.5	924.8	157	m
232	541.6	—	3	—	532	926.0	—	5	—
004	556.6	557.6	18	vw	150	933.0	—	4	—
104	574.9	—	12	—	710	933.4	—	1	—
422	578.3	579.4	100	mw	433	935.2	935.6	80	mw
040	585.4	585.6	32	vw	622	944.4	944.3	109	mw
502	596.7	—	4	—	234	959.1	—	2	—
114	611.5	—	12	—	151	967.8	—	<1	—
041	620.2	—	4	—	711	968.2	—	2	—
323	624.2	—	<1	—	243	971.7	—	20	—
204	629.8	—	15	—	215	979.5	979.4	354	s
332	633.2	—	4	—	424	995.8	995.8	1000	vvs

Table 5. Lattice constants of Rh and Ir chalcogenides with  $Rh_2S_3$  structure type and their measured magnetic susceptibilities

Compound	$a$ ( $\text{\AA}$ )	$b$ ( $\text{\AA}$ )	$c$ ( $\text{\AA}$ )	$10^6 \cdot \chi_M$ (Room temperature)	$10^6 \cdot \chi_M$ (Liquid nitrogen)
$Rh_2S_3$	$8.462 \pm 0.003$	$5.985 \pm 0.002$	$6.138 \pm 0.002$	—21	—20
$Rh_2S_2Se$	$8.646 \pm 0.004$	$6.090 \pm 0.003$	$6.220 \pm 0.003$	—	—
$Rh_2SSe_2$	$8.782 \pm 0.005$	$6.181 \pm 0.006$	$6.310 \pm 0.005$	—	—
$Rh_2Se_3$	$8.888 \pm 0.002$	$6.294 \pm 0.002$	$6.423 \pm 0.002$	—14*	—6*
$Ir_2S_3$	$8.465 \pm 0.002$	$6.011 \pm 0.002$	$6.149 \pm 0.002$	—35	—27

\* Because of ferromagnetic impurities the given values correspond to an upper limit of the susceptibility.

Table 6. Intensity calculation for ordered and disordered Rh<sub>2</sub>SSe<sub>2</sub>

Cu K $\alpha$  radiation  
( $\lambda_{\text{Cu K}\alpha} = 1.54051 \text{ \AA}$ )

<i>hkl</i>	<i>I<sub>c</sub><sup>ord</sup></i>	<i>I<sub>c</sub><sup>disord</sup></i>	<i>I<sub>o</sub></i>	<i>hkl</i>	<i>I<sub>c</sub><sup>ord</sup></i>	<i>I<sub>c</sub><sup>disord</sup></i>	<i>I<sub>o</sub></i>
110	130	1	—	214	16	9	—
200	34	150	150	241	2	10	—
111	377	186	190	024	47	26	26
002	607	355	350	233	69	70	60
211	918	1000	1240	611	65	66	195
020	347	235		304	34	32	
102	127	50	60	042	48	40	
021	270	233	216	124	54	46	
112	102	197	190	522	8	6	—
121	354	202	600	142	123	81	143
310	404	388		423	70	58	
202	<1	13	—	432	10	6	—
220	15	<1	—	314	19	1	—
311	219	182	175	224	<1	2	—
212	306	175	180	530	1	3	—
221	4	2	—	341	1	1	—
022	489	544	774	602	29	44	156
400	403	231		242	9	4	
302	15	18	—	620	67	73	
122	107	84	85	513	43	32	
312	<1	17	—	333	7	<1	—
321	13	7	—	531	2	<1	—
130	38	44	45	612	12	7	—
222	82	129	455	621	33	30	32
411	310	237		404	<1	<1	—
113	365	316	300	324	72	63	59
131	2	25	20	440	8	8	—
213	469	385	710	414	5	3	—
402	313	336		342	43	33	32
420	209	243	1050	043	<1	1	—
231	1000	768		134	1	<1	—
322	75	64	70	441	<1	4	—
023	80	29	58	523	10	6	—
412	53	30		143	<1	<1	—
421	28	4	—	532	2	5	—
123	22	12	—	710	9	1	—
132	<1	5	—	115	50	39	85
510	2	11	—	150	9	5	
330	15	2	—	433	36	28	
313	145	81	78	622	33	17	
511	18	23	130	711	6	2	—
331	56	60		234	3	2	—
223	33	36		151	1	4	—
232	35	20		243	6	13	91
004	3	15	—	215	106	77	
422	139	84	89	424	79	88	136
104	4	6	—	613	60	51	
040	10	21	20	504	3	1	—
502	56	30	32	442	64	69	280
114	46	59	65	631	118	94	
041	10	17	—	251	152	126	
323	2	1	—	025	<1	1	
512	5	18	130	702	28	20	20
332	10	17		125	39	22	20
204	34	44		514	4	9	—
521	83	47		334	17	17	20
141	9	5	—	343	<1	<1	—
413	17	17	20	712	8	14	12
600	1	1	—	721	7	4	—
431	4	8	—	152	<1	<1	—
240	33	30	32	541	4	2	—
133	<1	<1	—	315	14	16	20





type is observed (Hohnke & Parthé, 1967). This structure type is also found with Ir<sub>3</sub>S<sub>8</sub> and most probably with RhS<sub>~3</sub> and IrSe<sub>~3</sub>.

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## Structures Cristallines des Composés DyAl et CeAl et des Autres Composés Equiatomiques de l'Aluminium avec les Métaux des Terres Rares\*

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The crystalline structures of the compounds TAl, where T is a rare earth element, are of two types. The first type, DyAl, crystallizes in space group *Pbcm*; the compounds of praseodymium to thulium, except europium, are isomorphous with DyAl. The second type, CeAl, crystallizes in space group *Cmcm*; LaAl is isomorphous with this type of structure. The compound PrAl can have either of these two structures, depending upon the thermal treatment. Both structures are formed from the same motifs, viz. chains of aluminum, trigonal prisms which present an analogy with a half-cell of CsCl. Only the arrangement of these motifs differs. The structure CeAl can be formed from the structure DyAl by sliding the atomic layers in a direction parallel to the *a* axis of DyAl.

### Introduction

L'étude des alliages avec les métaux des terres rares a été longtemps retardée en raison des difficultés de préparation; il est en effet difficile de les fondre dans des creusets d'oxydes réfractaires sans les contaminer. Runnals & Lorimer (1965), en préparant un monocristal de samarium métallique dans un creuset d'alumine recristallisée, ont observé des cristaux en forme d'aiguilles sur la paroi du creuset; leur composition

étudiée à la sonde électronique était SmAl. Après analyse aux rayons X, ils ont attribué à ce composé une structure du type CsCl. Van Vucht (1957), Buschow (1965a,b), Buschow & van Vucht (1965, 1966) ont montré que les alliages de composition équiatomique avec l'aluminium cristallisent avec deux mailles orthorhombiques; l'une pour les composés avec le lanthane, le cérium et le praséodyme, l'autre pour les composés avec les éléments allant du praséodyme à l'erbium. Ils ont déterminé les paramètres de la maille et laissé le choix pour ces structures entre plusieurs groupes spatiaux. Avant d'entreprendre l'étude magnétique de ces composés, nous avons cherché à élucider leurs structures cristallines.

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