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The Rhodium–Germanium System. I. The Crystal Structures of Rh_2Ge, Rh_5Ge_3 and RhGe

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X-ray data obtained from crystals of Rh_2Ge, Rh_5Ge_3 and RhGe have led to a determination of the structures of these intermetallic compounds. RhGe has a distorted NiAs-type structure and is isostructural with MnP ($B31$ type). Rh_2Ge has a distorted Ni_2In-type structure. The relation of the Rh_5Ge_3 structure to the Ni_2In structure is indicated. The relation of the Rh_2Ge to the Rh_2B and Ni_2Si structures is also described.

Interatomic distances for all compounds are given and the coordination of the atoms is described.

Introduction

The study of the rhodium–germanium system was undertaken as part of a program of investigation of superconductivity in intermetallic systems (Matthias, 1952, 1953, 1954). This system is particularly interesting because it contains a superconductor, Rh_5Ge_3.* It was found by Matthias (1953) that IrGe with MnP ($B31$) type structure (Pfisterer & Schubert, 1950) was superconducting, whereas RhGe, with the same type structure, is not superconducting above 1·0° K.†

The intermetallic compounds discussed in this paper were first made by B. T. Matthias and E. Corenzwit. The region 25·0–66·7 atomic % germanium was studied. Mixtures of rhodium and germanium of very high purity were put into graphite crucibles and heated by induction in helium atmosphere to about 1600±200° C. for a few minutes. Heating was discontinued and the crucible and contents allowed to cool in the helium atmosphere. After heating was discontinued, about 2·5 min. elapsed before the crucible turned black.

Four distinct intermetallic phases were found in the region studied, three of which will be discussed in this paper. These have the stoichiometric formulae Rh_2Ge, Rh_5Ge_3 and RhGe. Powder diffraction photographs of these intermetallic compounds indicated that all had orthorhombic or lower symmetry.

Each of the crushed alloys was examined carefully with a binocular microscope until suitable specimens for single-crystal photography were found. Crystals were aligned by application of the Hendershot (1937) method. Weissenberg photographs were taken using Zr-filtered Mo $K\alpha$ radiation. Three films interleaved with 0·001 in. copper foil were used for each exposure (Hughes, 1941). Precession photographs were also taken with Zr-filtered Mo $K\alpha$ radiation. All intensities were estimated visually by comparison with an intensity scale.

Determination of the structures

1. *The structure of* Rh_2Ge

The crystal used in this determination was a tiny irregular fragment. Its largest cross-sectional dimension was 0·12 and its smallest 0·06 mm. As will be shown, this crystal was adequate for determination of its structure.

The diffraction symmetry of the single-crystal photographs is D_{2h}–mmm. It was possible to index the powder photograph, accounting for every line. Thus it was shown that the crystal was representative of the whole sample. The powder photograph, as well as Weissenberg layer photographs about the c axis (which was the rotation axis of the crystal described above), indicated that reflections of the types $(h0l)$, h odd, and $(0kl)$, $k+l$ odd, are absent. Thus the probable space groups are either D_{2h}^{16}–$Pnam$ or C_{2v}^{9}–Pna. The cell dimensions (all ±0·02 Å), number of Rh_2Ge per unit cell, X-ray and pycnometrically measured densities are given in Table 1.

Table 1. *The rhodium–germanium system*

Compound	Space group	a (Å)	b (Å)	c (Å)	Vol. (Å^3)	N	Density (g.cm.$^{-3}$) X-ray	Density (g.cm.$^{-3}$) Pycnometric
Rh_2Ge	*Pnam*	5·44	7·57	4·00	164·7	4	11·2	11·4*
Rh_5Ge_3	*Pbam*	5·42	10·32	3·96	221·5	2	11·0	10·6†
RhGe	*Pnam*	5·70	6·48	3·25	120·0	4	9·7	9·7

* Probably high because of presence of minute amount of elemental rhodium.

† This is actually the density of material with 40 atomic % Ge, i.e. it contains a very small amount of RhGe.

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* In Matthias (1953) the formula Rh_3Ge_2 should be changed to read Rh_5Ge_3.

† Private communication from B. T. Matthias.

The short c axis of the unit cell rules out the possibility that eight rhodium atoms are in $8(d)$ of *Pnam* (see *International Tables for X-ray Crystallography*); also positions $4(a)$ and $4(b)$ are ruled out for the same reason.

It was noted that the Weissenberg photographs taken about the c axis have the property that odd-numbered layer photographs are similar, as are the even-numbered ones. For example, the relative intensities of the $(hk1)$ reflections appear to be very nearly the same as the $(hk3)$, and the relative $(hk0)$ intensities very nearly the same as the relative $(hk2)$ intensities, and so on. From this observation, one may conclude that all of the atoms lie in planes separated by $\frac{1}{2}c$. This conclusion leads to the choice of *Pnam* as the most probable space group, with two sets of four rhodium and one set of four germanium atoms occupying positions $4(c)$.

There was reason to believe that since the RhGe structure (to be described later) has a distorted NiAs-type arrangement, Rh_2Ge might have a distorted Ni_2In structure. If this were so, one could readily obtain the six required trial parameters.

The Ni_2In structure (Laves & Wallbaum, 1942) belongs to the space group D_{6h}^4–$P6_3/mmc$. The structure is as follows:

$$\begin{aligned} &2\,\mathrm{Ni}\ \text{in}\ 2(a)\colon\ 0, 0, 0;\ 0, 0, \tfrac{1}{2}\\ &2\,\mathrm{Ni}\ \text{in}\ 2(d)\colon\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{3}{4};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{4}\\ &2\,\mathrm{In}\ \text{in}\ 2(c)\colon\ \tfrac{1}{3}, \tfrac{2}{3}, \tfrac{1}{4};\ \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{3}{4} \end{aligned}$$

If an orthorhombic cell is chosen, as shown in Fig. 2(*b*), the new cell would have twice the volume of the hexagonal cell. Atoms could be put into the positions $4(c)$ of *Pnam* as follows:

$$\begin{array}{llll} \mathrm{Ni_I} & x = 0{\cdot}00, & y = 0{\cdot}25, & z = \tfrac{1}{4}\\ \mathrm{Ni_{II}} & x = 0{\cdot}25, & y = 0{\cdot}583, & z = \tfrac{1}{4}\\ \mathrm{In} & x = 0{\cdot}75, & y = 0{\cdot}583, & z = \tfrac{1}{4} \end{array}$$

There is another orientation which would interchange the Ni_{II} and In positions. But it turns out that the correct one for Rh_2Ge is that shown.

The structure of Rh_2B was published by Mooney & Welch (1954) at the time this study was under way. The similarity in lattice constants between the two compounds is striking. When the structure of Rh_2B was examined, it was found that it does have a distorted Ni_2In structure. This made the choice of trial parameters for Rh_2Ge even simpler than anticipated. The Rh_2B parameters were adjusted to fit more closely to the Rh_2Ge data. The trial parameters were refined by Fourier projection on (001). The Fourier computations were carried out on IBM machines. The final correction grid, which involved very few terms with small F value, was computed rapidly with Beevers & Lipson strips (1936; Beevers, 1952).

The final parameters are shown in Table 2. No series-termination correction was made. It is felt, however, that such correction, if any, would be small, since reflections from far out in the reciprocal lattice have been used. Satisfactory convergence was indicated by absence of sizable spurious peaks.

Table 2. *Atomic coordinates in* Rh_2Ge

Atom	x	y	z
$\mathrm{Rhodium_I}$	0·029	0·207	$\frac{1}{4}$
$\mathrm{Rhodium_{II}}$	0·163	0·571	$\frac{1}{4}$
Germanium	0·713	0·605	$\frac{1}{4}$

The comparison of observed and calculated $(hk0)$ reflections is shown in Table 3.* Values of atomic scattering factors were taken from the *Internationale Tabellen* (vol. II). A temperature factor $\exp\,[-0{\cdot}35\times10^{-16}\,(\sin\theta/\lambda)^2]$ was applied to the calculated structure factor values. No correction was made for absorption. The value of the discrepancy factor R for the $(hk0)$ reflection amplitudes is 11·8%, excluding those for which intensities were too weak to be observed.

2. *The structure of* Rh_5Ge_3

The Rh_5Ge_3 crystal used in this investigation was obtained from a melt containing 40 atomic% germanium.† The cross-sectional dimensions of the crystal are $0{\cdot}05\times0{\cdot}05$ mm. The crystal was aligned on the Weissenberg goniometer so that the c axis of the orthorhombic unit cell was the rotation axis. Weissenberg photographs were taken about this axis, and precession photographs were taken with the b and c axes as precession axes.

The symmetry of the X-ray photographs is that of D_{2h}–mmm. Reflections of the types $(h0l)$, h odd, and $(0kl)$, k odd, are absent. Thus the probable space groups are either D_{2h}^9–$Pbam$ or C_{2v}^{8c}–Pba. The cell dimensions (all ±0·02 Å), number of Rh_5Ge_3 per unit cell, X-ray and pycnometrically measured densities are shown in Table 1.

The short c axis of the unit cell immediately ruled out the possibility that eight rhodium atoms occupied positions $8(i)$ of *Pbam*. Thus, unless the structure were disordered, the rhodium atoms would have to occupy two sets of fourfold and one set of twofold positions, and the germanium atoms one set of fourfold and one set of twofold positions. As in the case of Rh_2Ge, the even (odd) numbered Weissenberg photographs taken about the c axis were strikingly similar, again indicating that the atoms all lie in planes separated by $\frac{1}{2}c$. Thus the most probable space group is *Pbam*. The precession photographs also showed the $(00l)$ reflections for l odd to be very weak, thus

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* *Editorial note.* Tables 3, 5, 6, 7 and 8 have been deposited as Document No. 4417 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $1·25 for photoprints, or $1·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

† The powder photograph of this melt showed some extra lines at low angles due to presence of very small amount of RhGe (see also Table 1).

indicating that very nearly half the atoms must lie in each of the planes $z = 0$ and $z = \frac{1}{2}$. The closest one can come to equality in the planes is to put two germanium and six rhodium atoms in one plane and four each of rhodium and germanium atoms in the other.

The intensities of the $(hk0)$ reflections on the Weissenberg photographs and those of the $(h0l)$ and $(0kl)$ reflections on precession photographs were estimated visually. The Waser (1951, 1952) chart was used to convert intensities on the precession photographs to $|F_{hkl}|^2$ values.

The trial parameters were obtained from Patterson syntheses and were refined by Fourier projection on (001). The Fourier projection indicated satisfactory convergence by absence of spurious peaks. The final parameters are listed in Table 4.

Table 4. *Atomic coordinates in* Rh_5Ge_3

Atom	Position	x	y	z
Ge_I	2(a)	0	0	0
Rh_I	2(c)	0	$\frac{1}{2}$	0
Rh_{II}	4(g)	0·152	0·220	0
Ge_{II}	4(h)	0·388	0·152	$\frac{1}{2}$
Rh_{III}	4(h)	0·330	0·393	$\frac{1}{2}$

The comparison of observed and calculated $(hk0)$ reflection amplitudes is shown in Table 5.* The values of the atomic scattering factors used to calculate the structure factors were taken from *Internationale Tabellen.* A temperature factor $\exp[-10^{-16}(\sin\theta/\lambda)^2]$ was applied to calculated structure factor values. The value of the linear absorption coefficient for Rh_5Ge_3 (Mo $K\alpha$ radiation) is 403 cm.$^{-1}$. Absorption corrections were applied to the $|F_o|$ values, assuming the crystal to have a radius equal to half the diagonal of the cross-section (0·004 cm.); i.e. the effective μR was assumed to be equal to 1·6. The value for the discrepancy factor R for the $(hk0)$ amplitudes is 11·6%, excluding those for which intensities were too weak to be observed.

The comparison of observed and calculated $(0kl)$ and $(h0l)$ amplitudes (from precession camera photographs) is shown in Table 6.* The $(0k0)$ and $(h00)$ values are the same (except for the (200) which was not observed on the precession photographs) as those listed in Table 2. It will be seen that there are several very high values among the $0kl$ reflections and these seem to be very much affected by secondary extinction, particularly in the case of the (002) reflection. The lower valued F's agree very well for both $(0kl)$ and $(h0l)$ reflections.

3. *The structure of* RhGe

A cylindrical crystal, with a diameter of 0·04 mm., was found in a crushed sample of RhGe. A rational direction was found to be along the cylinder axis. This direction turned out to be along the diagonal of the (010) pinacoid of an orthorhombic unit cell. Weissenberg photographs were taken with this direction as rotation axis. The zero-level photograph recorded the (hkl) reflections with $|h| = |l|$.

The crystal was moved 30° in the (010) plane so as to make the a axis the rotation axis. Precession photographs were taken with the b and c axes as precession axes.

The symmetry of the X-ray photographs is that of D_{2h}–mmm. Reflections of the types $(h0l)$, h odd, and $(0kl)$, $k+l$ odd, are absent. Thus the probable space groups are either D_{2h}^{16}–$Pnam$* or C_{2v}^{9}–Pna. The cell dimensions ($\pm 0{\cdot}03$ Å), number of RhGe per unit cell, X-ray and pycnometrically measured densities are given in Table 1.

Parameters were determined by trial and error, first using the $(hk0)$ data. The parameters were refined by Fourier projection on (001). It was necessary to apply a convergence factor $\exp[-10^{-16}(\sin\theta/\lambda)^2]$ to the data. Very little change from trial parameters occurred. Calculations were made with Beevers–Lipson strips.

It was not, as in the cases of the compounds described above, quite as obvious that the atoms in the RhGe structure all lie in planes separated by $\frac{1}{2}c$ along the c-axis direction, because the crystal was not photographed about this direction as rotation axis on the Weissenberg goniometer. Therefore, in order to find whether the choice of z parameters was correct, the intensities of the zero-layer Weissenberg photograph mentioned above were estimated. The F_{hkl} for $h = l$ were calculated using the parameters obtained from the $(hk0)$ data and assuming the rhodium and germanium atoms to occupy two sets of positions 4(c), $\pm(x, y, \frac{1}{4}; \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{4})$ of space group D_{2h}^{16}–$Pnam$. The agreement between calculated and observed reflection amplitudes confirmed the validity of this assumption. The parameters are

$$x_{Rh} = 0{\cdot}007,\ y_{Rh} = 0{\cdot}202;$$
$$x_{Ge} = 0{\cdot}191,\ y_{Ge} = 0{\cdot}564\,.$$

The comparison of observed and calculated $(hk0)$ reflection amplitudes is shown in Table 7,† that of the (hkl) for $h = l$ reflection amplitudes in Table 8.† A temperature factor $\exp[-0{\cdot}5\times10^{-16}(\sin\theta/\lambda)^2]$ was applied to calculated structure factor values. The value of the linear absorption coefficient for RhGe (Mo $K\alpha$ radiation) is 398 cm.$^{-1}$. For the crystal used in this investigation, $\mu R = 0{\cdot}8$. Proper corrections were made on the $|F_o|$ for absorption. However, no attempt was made to correct for extinction, which is apparently quite important in some cases, particularly for (220).

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* See footnote on p. 16.

* It will be noticed that this author's choice of axes differs from that of the *Strukturbericht* (1937) and of Pfisterer & Schubert (1950). The present choice is in keeping with the conventional method of choosing axes, i.e. whenever possible to choose axes such that $c < a < b$.

† See footnote on p. 16.

Discrepancy factors were calculated (excluding reflections too weak to be observed). These are 14% for the (*hk*0) reflections and 12% for the (*hkl*), $h = l$ reflections. (The value is 12% for the (*hk*0) reflections if the (220) reflection amplitude is omitted.)

Discussion of the structures

The relationship that exists among the three structures may be given most clearly by discussing the RhGe structure first, followed by the Rh_2Ge and finally the Rh_5Ge_3 structures. All three structures are related to the NiAs (*B*8) structure to a greater or lesser degree. It will be shown subsequently that the relation of the Rh_5Ge_3 to the NiAs structure is remote, but it does exist.

The RhGe *structure*

The RhGe has a distorted NiAs or the MnP (*B*31) type structure (Fylking, 1934; *Strukturbericht*, 1937*; Pfisterer & Schubert, 1950*). Details of the comparison of the RhGe with the NiAs structure are illustrated in Fig. 1(*a*) and (*b*). The interatomic distances in RhGe are shown in Table 9.

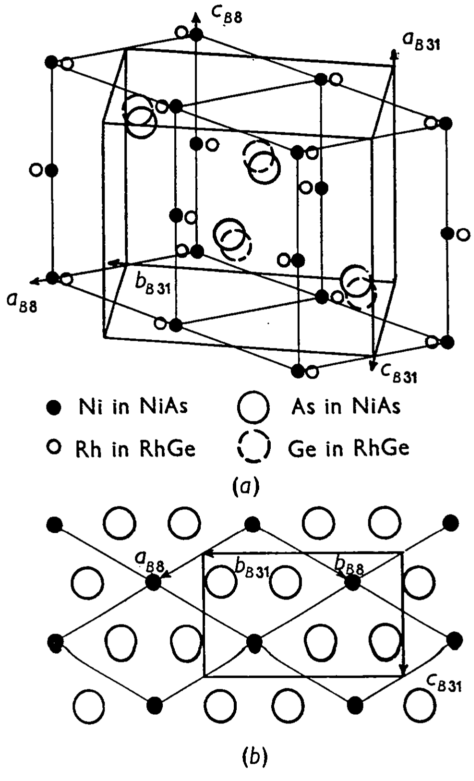

Fig. 1. (*a*) Relationship between NiAs (*B*8) and RhGe (*B*31) structures. (*b*) The (00.1) projection of the *B*8-type structure indicating axis positions of the *B*31-type structure.

Table 9. *Interatomic distances in* RhGe

(All distances in Ångström units)

Rh:	6 Ge	at	2·49, 2·49(2), 2·53(2), 2·57
	4 Rh	at	2·92(2), 3·08(2)
Ge:	6 Rh	at	2·49, 2·49(2), 2·53(2), 2·57
	2 Ge	at	2·84

In the NiAs structure each Ni atom is coordinated to six As atoms at the corners of a regular octahedron, and to two Ni atoms, one immediately above, the other immediately below it. Each As atom is coordinated to six Ni atoms at the corners of a right trigonal prism. In the RhGe structure the octahedron of Ge atoms coordinated to the Rh atom becomes somewhat distorted and four Rh atoms are tetrahedrally distributed about each Rh atom, but the Rh–Rh distances are all longer than they would be if the RhGe structure did crystallize in the NiAs type. That is, the probable expected average for the NiAs type should be the sum of the elemental radii (see Table 11).

The direct application of Pauling's (1949) resonating-valence-bond theory to the RhGe structure leads to somewhat unsatisfactory results. If the valences of the atoms are computed by assigning bond numbers to each of the bonds by use of the equation

$$D_n = D_1 - 0{\cdot}600 \log n \,,$$

in which D_n is the observed interatomic distance, D_1 the sum of the single radii (as in Pauling's paper), and n the bond number, one obtains for the valence of Rh, 5·76 and for Ge, 5·64. The value for Rh is fairly close to the expected value of 6·0 but the value for Ge is much too high.

The Rh_2Ge *structure*

The relation between the Ni_2In and the NiAs structures has already been described. It was shown also that the Rh_2Ge structure is a distorted Ni_2In structure. This is illustrated in Fig. 2(*a*) and (*b*) (see also Fig. 3).

In the Ni_2In structure each $\mathrm{Ni_I}$ is coordinated to 6 $\mathrm{Ni_{II}}$ atoms and 6 In atoms arranged in two interpenetrating octahedra. These twelve atoms also form a right regular hexagonal prism with alternating $\mathrm{Ni_{II}}$ and In atoms. There are also two $\mathrm{Ni_I}$ atoms coordinated to each $\mathrm{Ni_I}$ atom, one immediately above, the other below it. Each $\mathrm{Ni_{II}}$ atom is coordinated to 6 $\mathrm{Ni_I}$ atoms at the corners of a right trigonal prism and 5 In atoms at the corners of a trigonal bipyramid. Each In atom is coordinated to 6 $\mathrm{Ni_I}$ atoms at the corners of a right trigonal prism and 5 $\mathrm{Ni_{II}}$ atoms at the corners of a trigonal bipyramid.

The interatomic distances in Rh_2Ge are listed in Table 10. By comparison with the Ni_2In type, it can be seen that the $\mathrm{Rh_{II}}$ atom octahedron coordinated to the $\mathrm{Rh_I}$ atom is distorted. The Ge atom octahedron surrounding the $\mathrm{Rh_I}$ atom is even more distorted, so much so perhaps that it can now hardly be said to exist. This is so because the 3·33 Å distance cannot really

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* It should be pointed out that the $2f''$ distances given in Pfisterer & Schubert's paper for MnP, FeP, CoP and FeAs are incorrect. These values are also incorrect in the *Strukturbericht*.

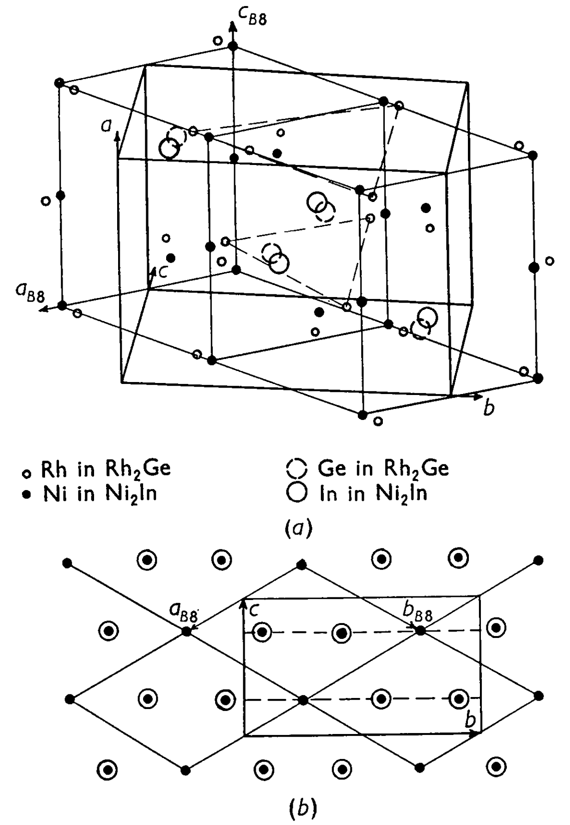

Fig. 2. (a) Relationship between the Rh_2Ge and Ni_2In ('filled in' B8) structures. (b) The (00.1) projection of the Ni_2In structure indicating axis positions of the Rh_2Ge structure.

be said to be a contact. The trigonal bipyramid of Ge atoms about the Rh_{II} atom also appears to be changed appreciably from what would obtain in the Ni_2In type structure.

It is interesting at this point to compare this structure with that of Rh_2B (Mooney & Welch, 1954) which, as has been pointed out, is isostructural with Rh_2Ge. The Rh–Rh distances in the two compounds are very similar. Also the Rh–Ge and Rh–B distances are similar. If one uses as the single-bond radius for boron, 0·90 Å and for rhodium, 1·25 Å (Pauling, 1949), the sum is 2·15 Å, which is considerably shorter than any of the distances in Rh_2B. This could mean that 0·90 Å is short for the B radius in this compound, i.e. boron may have a 'metallic' radius which is, say about 0·30 Å longer than the single covalent bond radius. The justification for this statement is as follows. The Rh–Rh contacts in the Rh_2B and in Rh_2Ge are all long; on the average (see Table 11) 0·14 Å longer than the metallic diameter. It would appear that the Rh_2B cell could be appreciably smaller because of expectedly closer Rh–Rh contacts. This should certainly be feasible with the smaller boron atoms.

Table 10. *Interatomic distances in* Rh_2Ge

(All distances in Ångström units)

Rh_I:	8 Rh	2 Rh_I at	2·80(2)
		6 Rh_{II} at	2·75, 2·81(2), 2·81(2), 2·85
	6 Ge	at	2·49(2), 2·57, 2·83(2), 3·33
RH_{II}	8 Rh	2 Rh_{II} at	2·88(2)
		6 Rh_I at	2·75, 2·81(2), 2·81(2), 2·85
	5 Ge	at	2·46, 2·47, 2·50(2), 3·00
Ge:	11 Rh	6 Rh_I at	2·49(2), 2·57, 2·83(2), 3·33
		5 Rh_{II} at	2·46, 2·47, 2·50(2), 3·00
	4 Ge	at	3·45(2), 3·50(2)

Table 11. *Average interatomic distances in* Rh–Ge *compounds* and in* Rh_2B

Compound	Rh–Rh	Rh–Ge or Rh–B
Rh_2Ge	2·82 Å	2·57 Å
Rh_5Ge_3	2·84	2·54
RhGe	2·92	2·52
Sum of elemental radii	2·68	2·56
Rh_2B	2·82	2·56

* Only distances for which bond number $\geq 0{\cdot}2$ were included. Bond number calculated from Pauling's (1949) formula $D_n = D_1 - 0{\cdot}600 \log n$.

Another observation is worth noting here. One may ask what happens to the average distances in the Rh_2Ge-type of structure as compared with the Ni_2In-type. There is a possibility of predicting this from an examination of the Ni_2Si structure (Toman, 1952). Toman found two forms of Ni_2Si, which it turns out are the Ni_2In and distorted Ni_2In types.* To see this more clearly, it will be necessary to rename the axes and also the space group of δ-Ni_2Si to correspond with those of Rh_2Ge. If this is done, the parameters as obtained by Toman are as shown in Table 12 (cf. Table 2).

Table 12. *Atomic coordinates in* Ni_2Si

Atom	*x*	*y*	*z*
Ni_I	0·042	0·203	¼
Ni_{II}	0·175	0·563	¼
Si	0·714*	0·614	¼

* This number is not the one which is derived from Toman's parameters. Toman has for his cell designation $y_{Si} = 0{\cdot}236$, which would give in the designation of this paper $x_{Si} = 0{\cdot}764$. However, if this parameter is used the Ni–Si distances are not only in complete disagreement with those given by Toman, but one is 2·09 Å, which is unreasonably short. Since 0·714 is much closer to the parameters in Rh_2Ge and Rh_2B, it was felt that perhaps a typographical error was made in the 0·236 figure replacing an 8 by a 3. When 0·286 was used, the interatomic distances obtained were much closer to those given by Toman.

In θ-Ni_2Si, which is the high temperature form, the average Ni–Ni distance is 2·50 Å and for Ni–Si, 2·42 Å. In δ-Ni_2Si, the average Ni–Ni distance is 2·64 Å and the average Ni–Si distance is 2·42 Å. Thus

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* The writer has also looked into the Co_2Si structure. It appears that the structure reported by Borén, Ståhl & Westgren (1935) is incorrect. This phase is isostructural with Rh_2Ge. Details will be published at a future date.

in the transition from the θ to the δ structure no change occurs in the average Ni–Si distance, but the average Ni–Ni distance changes by 0·14 Å. If this result is applied in reverse to the Rh_2Ge and Rh_2B structures, it seems that it should be possible to predict the lattice constants of a possible Ni_2In-type phase for each. These should be $a = 4{\cdot}0$ Å, $c = 5{\cdot}2$ Å for Rh_2Ge and very nearly the same for Rh_2B.

The average Ni–Ni and Ni–Si distances in θ-Ni_2Si are equal respectively to the sum of the elemental radii of Ni–Ni and Ni–Si. In the δ-form, the average Ni–Ni distance has increased by 0·14 Å over the elemental Ni diameter but the Ni–Si average is unchanged. Referring to Table 11, it is seen that the Rh–Rh distance is 0·14 Å, larger than the rhodium diameter, but the average Rh–Ge distance is within experimental error equal to the sum of the elemental radii.

It seems somewhat strange that the stable form of Rh_2B appears to be such a loose structure. (Rh_2B, incidentally, was checked by B. T. Matthias for superconductivity and found not to be superconducting.*)

The direct application of Pauling's (see above) resonating-valence-bond theory to the Rh_2Ge structure leads to somewhat unsatisfactory results: one obtains for the valence of Rh_I, 5·6; for Rh_{II}, 6·3; and for Ge, 7·0. The values for Rh are close to the expected value of 6·0; that for Ge is extremely high, as in the RhGe case.

The Rh_5Ge_3 *structure*

The structure of Rh_5Ge_3 is actually the one of greatest interest to us, because Rh_5Ge_3 is a superconductor (Matthias, 1953). There does not appear to be any other reported compound which is isostructural with Rh_5Ge_3. This compound can be described as a distortion of part of the Ni_2In structure which repeats itself by a twofold axis to give the whole cell. This is illustrated in Fig. 3, in which this unit is outlined on a (110) projection of the Ni_2In-type structure. If this unit is compared with the (001) projection of Rh_5Ge_3 (Fig. 4) it is possible to see how the Rh_5Ge_3 cell may be built out of the (distorted) unit described above.

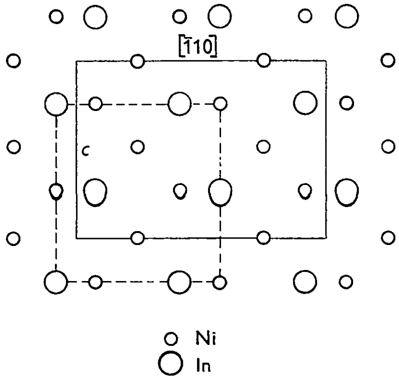

Fig. 3. Ni_2In projection along [11.0]. Solid lines indicate axis positions of the Rh_2Ge structure. Broken lines indicate ideal repeating unit for Rh_5Ge_3 (see text).

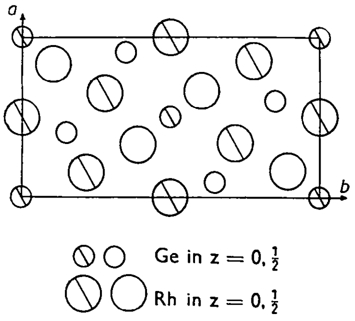

Fig. 4. The structure of Rh_5Ge_3 projected on (001).

Table 13. *Interatomic distances in* Rh_5Ge_3

(All distances in Ångström units)

Ge_I:	8 Rh:	2 Rh_I at 2·71; 2 Rh_{II} at 2·41 4 Rh_{III} at 2·45
	4 Ge_{II}	at 3·29
Ge_{II}:	10 Rh:	2 Rh_I at 2·60; 4 Rh_{II} at 2·46(2), 2·78(2) 4 Rh_{III} at 2·44(2), 2·51, 2·92
	3 Ge:	2 Ge_I at 3·29, 1 Ge_{II} at 3·36
Rh_I:	8 Rh:	4 Rh_{II} at 2·95(2), 3·00(2); 4 Rh_{III} at 2·89
	6 Ge:	2 Ge_I at 2·71; 4 Ge_{II} at 2·60
Rh_{II}:	10 Rh:	2 Rh_I at 2·95, 3·00; 2 Rh_{II} at 2·78 6 Rh_{III} at 2·72(2), 2·89(2), 3·52(2)
	6 Ge:	2 Ge_I at 2·41, 3·46; 4 Ge_{II} at 2·46(2), 2·78(2)
Rh_{III}:	7 Rh:	2 Rh_I at 2·89; 4 Rh_{II} at 2·72(2), 2·89(2) 1 Rh_{III} at 2·87
	6 Ge:	2 Ge_I at 2·45, 4 Ge_{II} at 2·44(2), 2·51, 2·92

The interatomic distances in the Rh_5Ge_3 structure are shown in Table 13. It will be seen that there are some very short Rh–Ge distances in this structure (cf. Tables 9 and 10). Yet if the weighted average of the Rh–Ge distances is taken (excluding those with bond number $< 0{\cdot}2$) the average Rh–Ge distance does not differ by much (possibly not at all, considering experimental error) from the sum of the elemental radii or from the average Rh–Ge distance in Rh_2Ge and RhGe (see Table 11). The average Rh–Rh distance is very nearly the same as in Rh_2Ge, and is 0·16 Å greater than the elemental rhodium diameter.

In the Rh_5Ge_3 structure (see Figs. 4 and 5) each Ge atom in position 2(a), i.e. Ge_I, is coordinated to eight Rh atoms at distances 2·41–2·71 Å. Six of the Rh atoms are at the corners of a distorted octahedron, and the remaining two are immediately above and below the Ge atom along the a axis (2·71 Å). (The eight atoms may also be said to be at the corners of a slightly distorted parallelopiped.) No Ge atom can really be said to be coordinated to another, the shortest Ge–Ge distance being 3·29 Å. Each Ge atom

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* Private communication from B. T. Matthias.

in position $4(h)$ is coordinated to nine Rh atoms (the distance 2·92, being quite long, is excluded) at distances 2·44–2·78 Å. Six of these (the Rh$_{\mathrm{I}}$ and Rh$_{\mathrm{II}}$ atoms) are at the corners of a right trigonal prism. The other three lie in the same plane ($z = \frac{1}{2}$) as the Ge atom. The coordination of this Ge atom is very similar to that of the Ge atom in $\mathrm{Rh_2Ge}$.

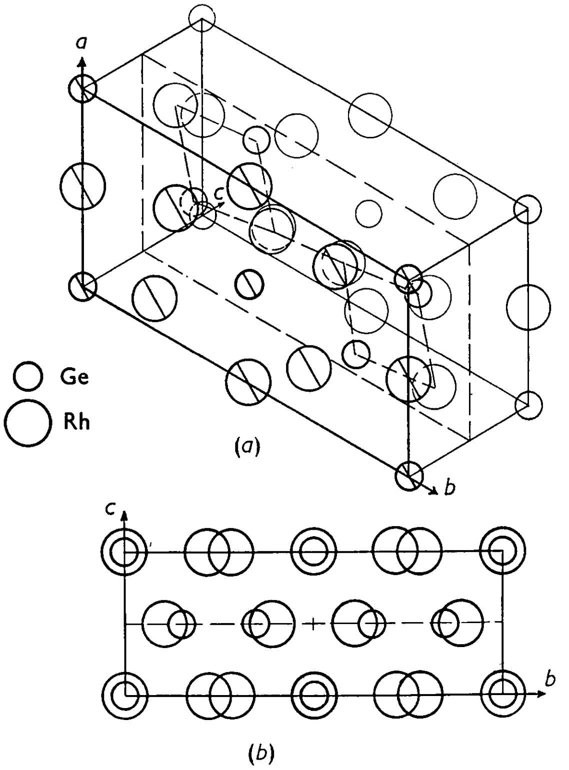

Fig. 5. (a) The $\mathrm{Rh_5Ge_3}$ structure. Broken lines join atoms in the plane $z = \frac{1}{2}$. Circles with lines through them indicate atoms in $z = 0$. (b) The (001) projection of the $\mathrm{Rh_5Ge_3}$ structure.

Each Rh atom in position $2(c)$ is coordinated to eight Rh atoms at distances 2·89–3·00 Å and six Ge atoms at distances 2·60–2·71 Å. The four Rh$_{\mathrm{III}}$ atoms form a distorted octahedron with each of two pairs of Rh$_{\mathrm{II}}$ atoms (just as in the Ge$_{\mathrm{I}}$ case). The Ge atoms are also at the corners of a distorted octahedron. Each Rh atom in position $4(g)$ is coordinated to eight Rh atoms at distances 2·72–3·00 Å and five Ge atoms at distances 2·41–2·78 Å. The four Rh$_{\mathrm{III}}$ atoms form distorted octahedra with either a pair of Rh$_{\mathrm{I}}$ or a pair of Rh$_{\mathrm{II}}$ atoms. The five Ge atoms are at the corners of a pyramid with a rectangular base. (If the Ge atom at distance 3·46 Å is included, the six Ge atoms are then at the corners of a distorted octahedron.) Each Rh atom in position $4(h)$ is coordinated to seven Rh atoms at distances 2·72–2·89 Å and to five Ge at distances 2·44–2·51 Å. The 2 Rh$_{\mathrm{I}}$ and 4 Rh$_{\mathrm{II}}$ atoms are at corners of a right trigonal prism, while the Rh$_{\mathrm{III}}$ atom lies in the plane of the Rh$_{\mathrm{III}}$ atom being discussed. The five Ge atoms are at the corners of a highly distorted trigonal bipyramid.

The valences of the atoms were calculated by direct application of Pauling's expression, as for RhGe and $\mathrm{Rh_2Ge}$. The distances $\leqslant$ 2·46 Å gave bond numbers greater than one. However, in computing the valences, no bond number was taken greater than one (see, for example, Tunell & Pauling, 1952). The results are as follows:

6·8 for Ge$_{\mathrm{I}}$, 7·2 for Ge$_{\mathrm{II}}$, 4·9 for Rh$_{\mathrm{I}}$, 6·0 for Rh$_{\mathrm{II}}$ and 6·9 for Rh$_{\mathrm{III}}$.

These values indicate the inadequacy of applying the expression directly. This has been pointed out by Pauling (1949) himself.

It is again interesting to note (Table 11) that the average Rh–Rh distance in $\mathrm{Rh_5Ge_3}$ is appreciably longer than the elemental Rh diameter and that the average Rh–Ge distance is very nearly equal to the sum of the elemental radii of Rh and Ge.

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