

for holding these layers together. Whether a similar result will be obtained with niobium is yet to be determined.

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The Crystal Structure of RhBe_{6.6}*

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The crystal structure of a compound in the beryllium-rich portion of the Rh-Be system has been determined. The final structure corresponds to the composition RhBe_{6.6}. The crystals are hexagonal, with probable space group *P6m2*. The structure is closely related to the *D2a* type. The non-integer formula is a result of partial occupancy of two sites. Identical powder patterns are observed in the Fe-Be, the Co-Be and the Ir-Be systems. Cell constants for these compounds are as follows:

	<i>a</i>	<i>c</i>	<i>c/a</i>
FeBe _x	4·137 ± 0·002 Å	10·720 ± 0·005 Å	2·591
CoBe _x	4·114 ± 0·006	10·66 ± 0·01	2·591
RhBe _{6.6}	4·191 ± 0·001	10·886 ± 0·003	2·597
IrBe _x	4·197 ± 0·001	10·842 ± 0·003	2·583

Compositions for the Fe-, Co- and Ir-Be compounds were not determined. In the case of FeBe_x, this unit cell and structure account for the powder pattern of 'ζ-FeBe₁₁' (*J. Metals*, **1**, 285). This suggests that a considerable compositional variation might be expected.

Introduction

The most beryllium-rich structure observed in binary compounds between the Group VIII elements and beryllium is of the type ThMn₁₂ (Florio, Rundle & Snow, 1952), so far reported for Fe, Co, Pd, and Pt with Be

(Batchelder & Raeuchle, 1957, 1958). This type of structure has not yet been found in the Ni, Os, Ru, Ir and Rh-Be systems, although size considerations alone would not appear to rule it out. A previous publication dealt with the currently most beryllium-rich phase found in the Os- and Ru-Be systems (Sands, Johnson, Krikorian & Kromholtz, 1962). This work covers the most beryllium-rich phase so far identified in the Rh- and Ir-Be systems.

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Experimental

Samples were prepared from mixed powders of the elements, either by inductively heating specimens in BeO crucibles or by arc melting. In both cases, the melting was done under an argon atmosphere. Various atomic ratios were melted together, ranging from AB₅ to AB₂₀. The resultant samples were crushed and inspected for suitable single crystals. Satisfactory crystals were obtained from an Rh-Be preparation, but suitable crystals could not be obtained for the other compounds.

Oscillation, Weissenberg, and precession photographs of crystals from the Rh-Be preparations indicated that the structure of the most beryllium-rich compound is hexagonal. The powder patterns obtained from samples containing Co, Fe, or Ir in place of Rh indicated isostructural phases. Values for cell constants were obtained from powder patterns taken with Cr K α radiation ($\lambda K\alpha_1 = 2.2896 \text{ \AA}$). A least-squares fit gave the values:

	<i>a</i>	<i>c</i>	<i>c/a</i>	<i>Q_x</i>
FeBe _x	4.137 ± 0.002 Å	10.720 ± 0.005 Å	2.591	2.805 g.cm ⁻³
CoBe _x	4.114 ± 0.006	10.66 ± 0.01	2.591	2.929
RhBe ₆₋₆	4.191 ± 0.001	10.886 ± 0.003	2.597	3.792
IrBe _x	4.197 ± 0.001	10.842 ± 0.003	2.583	5.887

The observed Laue symmetry $6/mmm$ and lack of any systematic extinctions are consistent with the space groups $P6/mmm$, $P6_322$, $P6mm$, $P\bar{6}m2$ and $P\bar{6}2m$. We chose the centrosymmetric space group in order to proceed with the structure determination. Intensities for 140 reflections recorded at less than 40° in 2θ were measured with a single-crystal orienter, using the stationary crystal-stationary counter technique (Furnas, 1957), Zr-filtered Mo K α radiation, and pulse-height discrimination. The crystal was an irregularly shaped fragment with a maximum dimension of 0.06 mm. No absorption correction was applied to the data.

Determination of structure

The unit-cell constants for this phase suggested a relation to the $D2_d$ (CaZn₅) structure; the c/a ratio for a three-layered CaZn₅-like structure is $3\sqrt{3}/2 = 2.598$, almost exactly equal to the observed ratio for the Rh-Be compound (2.597). A trial model was therefore considered in which three CaZn₅-like unit cells were stacked one on top of the other, followed by replacement of one rhodium atom with a pair of beryllium atoms aligned along the c axis. Florio, Baenziger & Rundle (1956) have shown how this approach works in accounting for the $D2_d$ -like structures Th₂Ni₁₇ and ThMn₁₂. A difference Fourier calculation based on this model established that the $\pm \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ site, which had been thought to be beryllium occupied, had more electrons than beryllium but less than rhodium. In addition, changes of some of the beryllium atom sites were necessary. Correction of the beryllium positions and refinement of the occupancy of a rhodium atom at the $\pm \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ site resulted in an R value of 7.9%.

At this point, calculation of an $N(z)$ distribution function (Howells, Phillips & Rogers, 1950) indicated that the space group might be noncentric. A satisfactory fit of the above model was found in space group $P\bar{6}m2$. For this space group the $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ site is a onefold position, but the earlier calculations had shown that only one-third of a rhodium atom is accommodated here; therefore, this site was again treated as partially occupied and with a temperature factor fixed at 0.5. A difference Fourier calculation based on the refined positional parameters of the rhodium atoms was used to locate all beryllium atoms. The temperature factor of Be(6) at $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ refined to a high value in the subse-

Table 1. Final parameters

	Wyckoff notation	E.s.d.'s in parentheses.			<i>B</i> (Å ²)	Occupancy (%)
		10 ⁴ <i>x</i>	10 ⁴ <i>y</i>	10 ⁴ <i>z</i>		
Rh(1)	2(<i>g</i>)	0	0	1931 (2)	0.43 (0.04)	100
Rh(2)	1(<i>d</i>)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{2}$	(0.5)	36 (3)
Be(1)	2(<i>h</i>)	$\frac{1}{3}$	$\frac{2}{3}$	1233 (39)	0.47 (0.66)	100
Be(2)	2(<i>i</i>)	$\frac{1}{3}$	$\frac{2}{3}$	1592 (62)	1.31 (0.67)	100
Be(3)	2(<i>g</i>)	0	0	4018 (24)	0.64 (0.40)	100
Be(4)	6(<i>n</i>)	4998 (63)	-4998	3170 (14)	1.16 (0.30)	100
Be(5)	3(<i>j</i>)	8378 (65)	6757	0	1.16 (0.42)	100
Be(6)*	1(<i>f</i>)	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	(1.0)	34 (48)

* The presence of this atom cannot be established with certainty, see text.

quent least-squares refinement; it was set equal to 1.0 and the occupancy parameter of Be(6) was refined instead. For these calculations, atomic scattering factors were those for the neutral atoms listed in *International Tables for X-ray Crystallography* (1962), corrected for anomalous dispersion (Dauben & Templeton, 1955). The quantity minimized in the least-squares program is $\sum w(|F_o| - (1/k)|F_c|)^2$ where k is the scale factor relating $|F_o|$ and $|F_c|$ and the w 's are given by the following weighting scheme: $w = F_o^{1/4}$, $F_o < A$; $w = A^{5/4}F_o^{-1}$, $F_o > A$, with $A = 17$. Final R value for these refinements is 5.3%. The final parameters are given in Table 1.

Table 2. *Observed and calculated structure factors*

H	K	L	F_o	$ F_c $	H	K	L	F_o	$ F_c $	H	K	L	F_o	$ F_c $	H	K	L	F_o	$ F_c $
0	0	1	9	9	0	2	4	5	6	0	5	1	6	6	1	3	3	14	14
0	0	2	25	25	0	2	5	26	25	0	5	2	11	11	1	3	4	2	2
0	0	3	35	33	0	2	6	12	12	0	5	3	11	11	1	3	5	21	22
0	0	4	10	9	0	2	7	12	12	1	1	0	39	41	1	3	6	6	6
0	0	5	25	24	0	2	8	29	27	1	1	1	5	5	1	3	7	8	9
0	0	6	30	28	0	2	9	1	1	1	1	2	16	17	1	3	8	15	16
0	0	7	17	16	0	2	10	18	18	1	1	3	33	36	1	3	9	0	1
0	0	8	21	20	0	2	11	10	10	1	1	4	5	5	1	3	10	12	13
0	0	9	5	3	0	2	12	8	8	1	1	5	20	22	1	4	0	20	20
0	0	10	29	27	0	2	13	13	12	1	1	6	16	17	1	4	1	3	3
0	0	11	8	7	0	2	14	9	8	1	1	7	17	17	1	4	2	9	8
0	0	12	3	2	0	3	0	30	30	1	1	8	14	15	1	4	3	18	18
0	0	13	18	17	0	3	1	5	4	1	1	9	8	8	1	4	4	2	3
0	0	14	4	3	0	3	2	13	12	1	1	10	20	20	1	4	5	12	12
0	0	15	11	10	0	3	3	28	27	1	1	11	8	8	1	4	6	10	9
0	1	0	32	33	0	3	4	4	4	1	1	12	4	4	2	2	0	32	33
0	1	1	17	16	0	3	5	18	17	1	1	13	19	19	2	2	1	4	4
0	1	2	29	28	0	3	6	14	13	1	1	14	1	2	2	2	2	11	12
0	1	3	28	27	0	3	7	13	14	1	2	0	21	22	2	2	3	17	18
0	1	4	4	4	0	3	8	12	12	1	2	1	11	11	2	2	4	4	5
0	1	5	36	37	0	3	9	6	6	1	2	2	19	20	2	2	5	12	14
0	1	6	10	10	0	3	10	17	17	1	2	3	15	19	2	2	6	15	16
0	1	7	15	14	0	3	11	7	7	1	2	4	2	3	2	2	7	9	10
0	1	8	26	25	0	3	12	4	4	1	2	5	26	27	2	2	8	12	12
0	1	9	2	2	0	4	0	19	18	1	2	6	7	8	2	2	9	1	2
0	1	10	20	18	0	4	1	5	5	1	2	7	10	11	2	2	10	17	18
0	1	11	19	16	0	4	2	18	17	1	2	8	18	20	2	2	11	4	5
0	1	12	9	8	0	4	3	11	11	1	2	9	2	2	2	3	0	14	14
0	1	13	17	15	0	4	4	3	3	1	2	10	14	15	2	3	1	7	7
0	1	14	6	6	0	4	5	16	17	1	2	11	13	13	2	3	2	12	13
0	1	15	14	13	0	4	6	9	8	1	2	12	7	7	2	3	3	11	12
0	2	0	31	31	0	4	7	8	8	1	2	13	13	13	2	3	4	2	2
0	2	1	8	8	0	4	8	19	18	1	3	0	18	18	2	3	5	17	19
0	2	2	30	29	0	4	9	0	0	1	3	1	9	8	2	3	6	5	5
0	2	3	19	17	0	5	0	13	12	1	3	2	15	15	2	3	7	7	7

It is necessary to say a few words about Be(6). Because of the extremely large correlation between Be(6) and Rh(2) (the correlation coefficient relating the two occupancy factors is -0.94), it cannot be established with certainty whether or not Be(6) is present. Note that the occupancy differs by less than 1.0σ from zero. There are two arguments in favor of the presence of this atom. First, there is a hole big enough to accommodate a beryllium atom. Secondly, this atom was clearly present on the rhodium atom difference map. The first argument can be countered by noting that a large empty hole exists in the structure of Os_3Be_{17} (Sands, Johnson, Krikorian & Kromholtz, 1962). The second argument is probably not very strong either, as it is not unreasonable to expect an artifact at this site on the difference Fourier synthesis in view of the large correlation between the sites. Since the data do not suffice to settle this question of occupancy, the last row of Table 1 must be taken as tentative. For the sake of establishing a label for this structure type, Be(6) and Rh(2) were assumed to be present one-third of the time. The structure then corresponds to the composition $RhBe_{6.6}$. A final difference Fourier calculation showed two peaks of about $1.4 \text{ e.}\text{\AA}^{-3}$ which were associated with Rh(1). The next largest peak was $0.7 \text{ e.}\text{\AA}^{-3}$. Observed and calculated structure factors are listed in Table 2. Interatomic distances are given in Table 3.

Discussion

As stated above, the occupancies of Rh(2) and Be(6) are considered to be one-third. It is recognized that these particular values may not necessarily apply to the compounds in the Co-, Fe-, and Ir-Be systems. Likewise, the Rh-Be phase discussed here may have an extended range of composition.

In the case of the Rh- and Ir-Be systems, the $RhBe_{6.6}$ structure type represents the first compound reported

Table 3. *Interatomic distances in RhBe_{6.6}*

	Ligancy	Distance	E.s.d.		Ligancy	Distance	E.s.d.
Rh(1)	1 Be(3)	2.274	0.026	Be(3)	1 Be(3)	2.141	0.052
	3 Be(5)	2.411	0.009		1 Rh(1)	2.274	0.026
	3 Be(2)	2.448	0.010		6 Be(4)	2.290	0.024
	6 Be(4)	2.493	0.021		$3 \times \frac{1}{3}$ Rh(2)	2.646	0.011
	3 Be(1)	2.537	0.013		$3 \times \frac{1}{3}$ Be(6)	2.646	0.011
Rh(2)	6 Be(4)	2.332	0.017	Be(4)	4 Be(4)	2.093	0.040
	$3 \times \frac{1}{3}$ Be(6)	2.420	0.001		1 Be(2)	2.103	0.058
	6 Be(3)	2.646	0.011		2 Be(3)	2.290	0.024
Be(1)	3 Be(4)	2.432	0.040		$1 \times \frac{1}{3}$ Rh(2)	2.332	0.017
	3 Be(2)	2.452	0.013		$1 \times \frac{1}{3}$ Be(6)	2.332	0.017
	6 Be(5)	2.490	0.026		1 Be(1)	2.432	0.040
	3 Rh(1)	2.537	0.013		2 Rh(1)	2.493	0.021
	1 Be(1)	2.688	0.084	Be(5)	2 Be(5)	2.039	0.022
Be(2)	3 Be(4)	2.103	0.058		2 Be(2)	2.134	0.056
	3 Be(5)	2.134	0.056		2 Be(5)	2.152	0.022
	3 Rh(1)	2.448	0.010		2 Rh(1)	2.411	0.009
	3 Be(1)	2.452	0.013	Be(6)	4 Be(1)	2.490	0.026
					6 Be(4)	2.333	0.017
					$3 \times \frac{1}{3}$ Rh(2)	2.420	0.001
					6 Be(3)	2.646	0.011

for which a structure has been determined. In the case of the Co- and Fe-Be systems other structures have been reported, including some more rich in beryllium, *i.e.* CoBe_{12} and FeBe_{12} with the ThMn_{12} structure (Batchelder & Raechle, 1957), and ' ζ - FeBe_{11} ' (Teitel & Cohen, 1949; Rooksby, 1962; le Hazif, Donze, Dupouy & Adda, 1964). We have been unable to confirm the existence of the ThMn_{12} structure type in either the Fe- or Co-Be systems.

We can support the so-called ' ζ - FeBe_{11} ' phase to the extent that our powder patterns and unit-cell constants for the $\text{RhBe}_{6.6}$ structure type occurring in the Fe-Be system agree with those reported for ' ζ - FeBe_{11} '. There is, however, a conspicuous disparity between the composition reported for these two materials. We were unsuccessful in attempts to prepare single crystals of either the Co- or Fe-Be compounds. We have, on the other hand, measured the approximate density of the same single crystal of $\text{RhBe}_{6.6}$ that was used in the intensity measurements. This was accomplished by carefully dissolving away the glue which held the crystal to the fiber and immersing the crystal in a thallos formate-malonate salt solution which had a density of 3.71 g.cm^{-3} . The crystal slowly sank in this solution establishing a lower density limit of 3.71 g.cm^{-3} in keeping with the calculated density of 3.79 g.cm^{-3} . Thus, volume requirements can independently rule out the AB_{11} composition for the material used in this investigation.

The structure of $\text{RhBe}_{6.6}$ is viewed in projection in Fig. 1. The resemblance to the $D2_a$ structure type is

apparent in this Figure. One significant deviation is that Be(5) is in a site not found in the $D2_a$ structure type. Coordination polyhedra are shown in Fig. 2. These polyhedra which are commonly encountered in complex intermetallic compounds, are of the following kinds: Rh(1) and Be(1) Friauf polyhedra; Rh(2) and Be(6) μ -phase polyhedra; Be(2), Be(4), and Be(5) icosahedra; Be(3) hexagonal antiprism with two atoms at extended poles. The coordination for Be(5) could also be presented as a 17-fold polyhedron about two Be(5) atoms. The exact arrangement of polyhedra incorporating Rh(2) or Be(6) is of course open to conjecture, since these atoms are present only one-third of the time.

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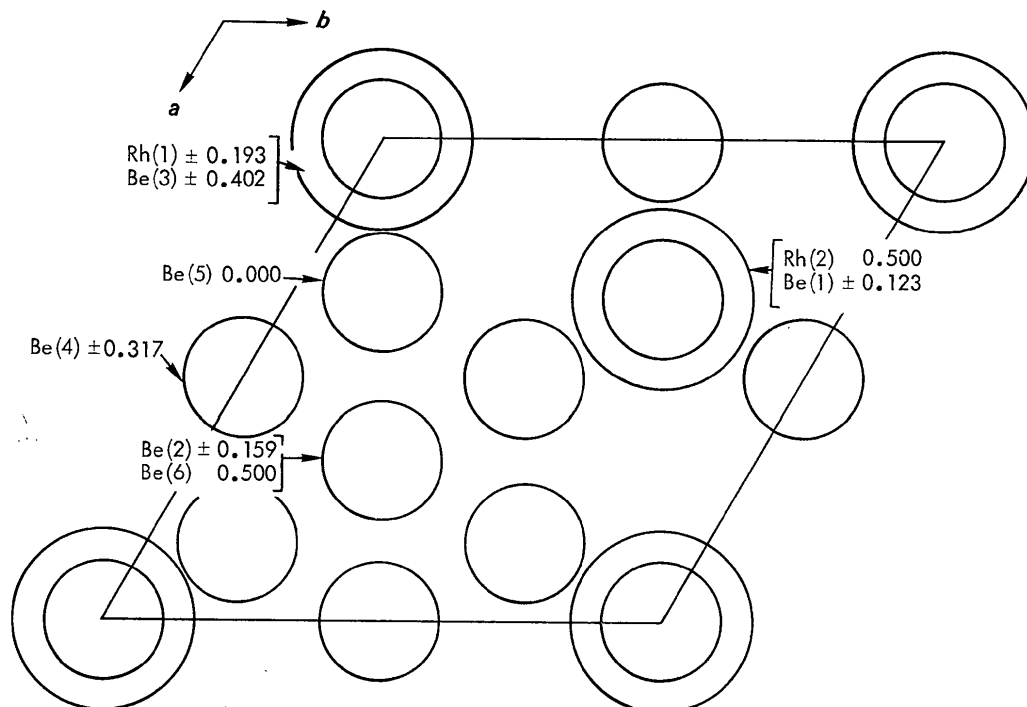


Fig. 1. Projection of the $\text{RhBe}_{6.6}$ crystal structure. The z parameter is given after the name of the atom.

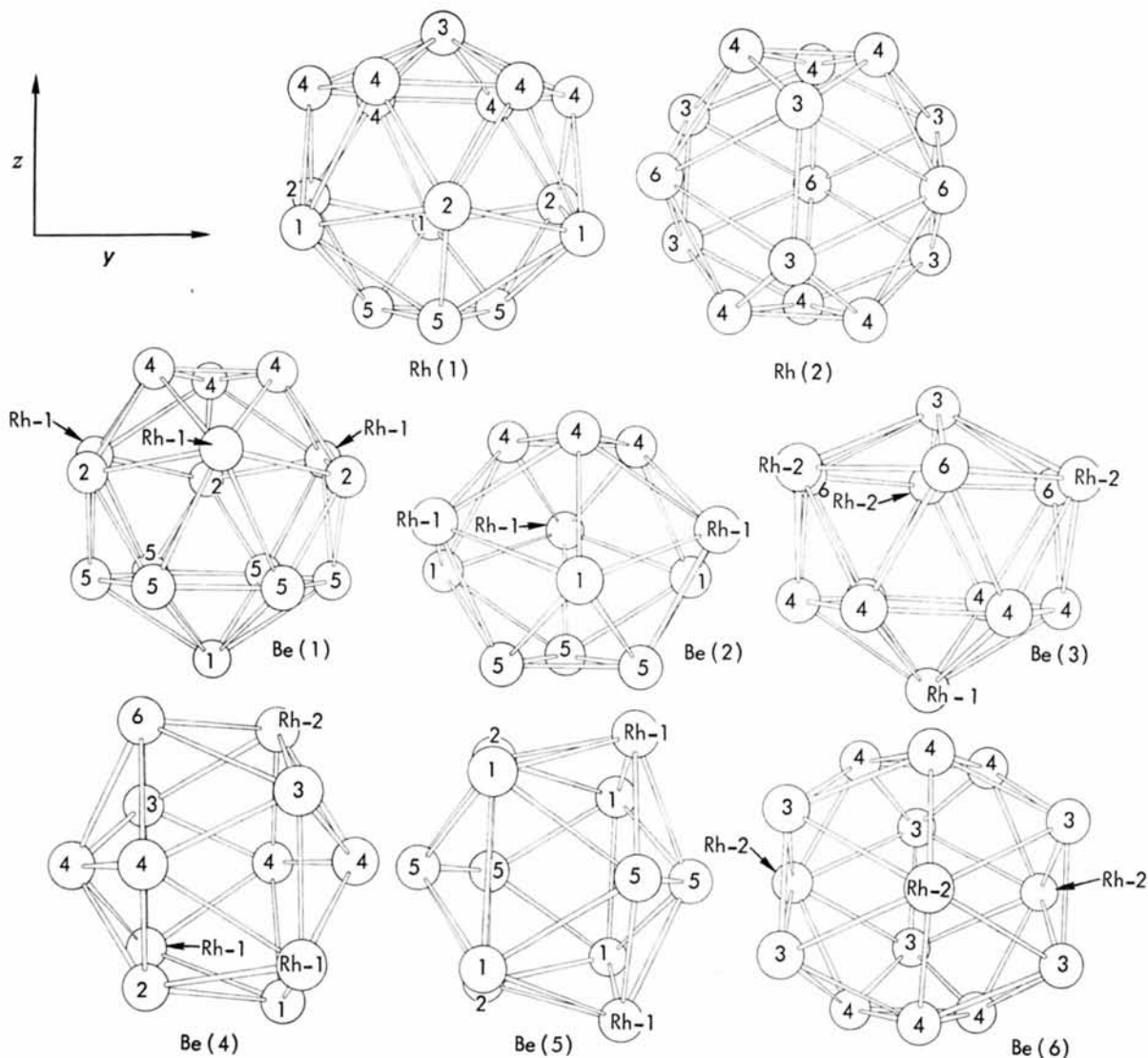


Fig.2. Coordination polyhedra of atoms in the RhBe_6 crystal structure. The central atom has been omitted for the sake of clarity.

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