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The Crystal Structure of $ReBe_{22}$*

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$ReBe_{22}$ is face-centered cubic with $a = 11{\cdot}561$ Å; there are eight formula units per unit cell and the space group is $Fd3m$. Each Re atom has 16 Be neighbors at 2·50 to 2·53 Å. There are 4 types of Be atoms: Be_1 has 2 Re neighbors at 2·50 Å and 12 Be neighbors at 2·46 Å; Be_2 and Be_3 each have 12 Be neighbors at 2·05 to 2·29 Å; Be_4 has 1 Re neighbor at 2·53 Å and 11 Be neighbors at 2·13 to 2·46 Å.

Introduction

Beryllides of Mo, W, and Re containing more than 95 at.% Be, and unit cell data for these compounds, were reported by Paine & Carrabine (1960). These mutually isomorphous phases are face-centered cubic; the space groups consistent with the systematic extinctions observed on powder diffraction patterns are $Fd3$ and $Fd3m$. We have confirmed these results in our work in the Re–Be system and, in addition, have carried out a structural determination by single crystal studies.‡

Experimental

In order to prepare single crystals of $ReBe_{22}$, a mixture of Re plus Be powders, with Be well in excess of the composition $ReBe_{22}$, was heated in a BeO crucible to 1650 °C. for about 5 min. under ½-atmosphere argon. Approximately 200-mesh powders of 99·9% Re and 99% Be purity were used. The sample was heated in a high-temperature, high-vacuum induction furnace with a tantalum heater. Visual examination of the reacted sample showed that it had melted. The sample was crushed and single crystals were selected for X-ray examination.

Weissenberg photographs of a single crystal taken with Cu $K\alpha$ radiation show diffraction symmetry and systematic extinctions characteristic of space group $Fd3m$–O_h^7. This space group was ultimately confirmed by the structure.

The lattice constant, determined from back-reflection measurements on a powder pattern taken with Cu $K\alpha$ radiation ($\lambda K\alpha_1 = 1{\cdot}54050$, $\lambda K\alpha_2 = 1{\cdot}54434$ Å), is

$$a = 11{\cdot}561 \pm 0{\cdot}003 \text{ Å} .$$

The volume of the unit cell is 1545 Å^3; the sum of the atomic volumes, obtained from the elemental metals, of 8 Re (14·705 Å^3/atom) and 176 Be (8·106 Å^3/atom) is 1544 Å^3, indicating that the formula of the phase is $ReBe_{22}$. The reliability of this addition of elemental volumes has been established for other metallic beryllides (Zalkin, Sands & Krikorian, 1959). The composition $ReBe_{22}$ has been independently deduced by Paine & Carrabine (private communication).

The intensities from an irregularly shaped single crystal of approximate dimensions $0{\cdot}08 \times 0{\cdot}02 \times 0{\cdot}02$ mm. were measured with Mo $K\alpha$ radiation on a General Electric XRD-5 X-ray spectrometer equipped with a single crystal orienter and a scintillation counter. The stationary crystal-stationary counter technique was used, and 40-second counts were taken at the calculated settings for all reflections with $2\theta \leq 60°$. Background corrections were obtained from a plot of intensity versus θ made with the crystal out of reflecting position. The intensities of 136 reflections, of which 11 were not observable above background, were recorded. No absorption corrections were made.

Determination of the structure

The eight rhenium atoms are required to occupy the $Fd3m$ positions $8a$: $\pm(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$+face-centering (*International Tables for X-ray Crystallography*, 1952). Signs based on the rhenium atom contributions were used in a 3-dimensional Fourier computation from which the positions of all beryllium atoms were obtained; ambiguities due to spurious peaks and diffraction ripple were resolved by consideration of interatomic distances.

The beryllium parameters, before refinement, were

16 Be_1 in $16(c)$:

$(0, 0, 0;\ 0, \frac{1}{4}, \frac{1}{4};\ \frac{1}{4}, 0, \frac{1}{4};\ \frac{1}{4}, \frac{1}{4}, 0)$+face-centering,

16 Be_2 in $16(d)$:

$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, \frac{1}{4}, \frac{1}{4};\ \frac{1}{4}, \frac{1}{2}, \frac{1}{4};\ \frac{1}{4}, \frac{1}{4}, \frac{1}{2})$+face-centering,

48 Be_3 in $48(f)$:

$\pm(x, \frac{1}{8}, \frac{1}{8};\ \frac{1}{8}, x, \frac{1}{8};\ \frac{1}{8}, \frac{1}{8}, x;\ \frac{1}{4}-x, \frac{1}{8}, \frac{1}{8};\ \frac{1}{8}, \frac{1}{4}-x, \frac{1}{8};\ \frac{1}{8}, \frac{1}{8}, \frac{1}{4}-x)$+face-centering with $x = 0{\cdot}50$,

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‡ *Note added, January* 3, 1962: $ZrZn_{22}$ (Samson, 1961) is isostructural with $ReBe_{22}$.

96 Be_4 in 96(g):

$\pm(x, x, z;\ z, x, x;\ x, z, x;\ x, \frac{1}{4}-x, \frac{1}{4}-z;\ z, \frac{1}{4}-x, \frac{1}{4}-x;$
$x, \frac{1}{4}-z, \frac{1}{4}-x;\ \frac{1}{4}-x, x, \frac{1}{4}-z;\ \frac{1}{4}-z, x, \frac{1}{4}-x;$
$\frac{1}{4}-x, z, \frac{1}{4}-x;\ \frac{1}{4}-x, \frac{1}{4}-x, z;\ \frac{1}{4}-z, \frac{1}{4}-x, x;$
$\frac{1}{4}-x, \frac{1}{4}-z, x)$ + face-centering with $x=0{\cdot}08$, $z=0{\cdot}33$.

These parameters were refined by the least-squares method, using the IBM 704 program of Busing & Levy (1959). Individual isotropic temperature factors for each atom were included in the refinements. The atomic scattering factors used were those of Thomas & Umeda (1957) for Re and Ibers (1957) for Be. The final reliability factor,

$$R=\Sigma|F_o-F_c|/\Sigma|F_o|\ ,$$

was 0·036; the standard error of fit,

$$[\Sigma(F_o-F_c)^2/(m-n)]^{\frac{1}{2}},$$

was 2·6 ($m=136$ was the number of observations, $n=9$ was the number of parameters being refined).

Table 1. *Observed and calculated structure factors,* FO *and* FC, *respectively*

Asterisks denote unobserved reflections

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	0	0	111	-121	2	2	2	*3	1	11	11	3	36	38
8	0	0	90	94	4	2	2	113	114	4	4	4	77	-75
12	0	0	68	-70	6	2	2	27	27	6	4	4	*5	3
16	0	0	83	83	8	2	2	103	-107	8	4	4	93	93
2	2	0	130	-131	10	2	2	15	17	10	4	4	15	13
6	2	0	122	123	12	2	2	63	66	12	4	4	53	-53
10	2	0	90	-94	14	2	2	*7	0	14	4	4	*7	-0
14	2	0	71	72	16	2	2	53	-53	6	6	4	95	91
4	4	0	119	122	4	4	2	12	-11	8	6	4	5	-3
8	4	0	86	-85	6	4	2	98	-96	10	6	4	72	-71
12	4	0	81	79	8	4	2	*5	4	12	6	4	9	-1
6	6	0	108	-106	10	4	2	72	72	14	6	4	57	59
10	6	0	79	76	12	4	2	*6	5	8	8	4	75	-72
14	6	0	66	-64	14	4	2	60	-64	10	8	4	6	-2
8	8	0	125	124	6	6	2	*5	-1	12	8	4	66	66
12	8	0	65	-64	8	6	2	86	87	10	10	4	57	59
10	10	0	62	-60	10	6	2	*6	1	12	10	4	*7	-6
1	1	1	94	-90	12	6	2	70	-71	5	5	5	81	78
3	1	1	90	-92	14	6	2	7	12	7	5	5	73	69
5	1	1	76	78	8	8	2	6	1	9	5	5	67	-67
7	1	1	56	56	10	8	2	65	-66	11	5	5	62	-61
9	1	1	59	-61	12	8	2	*7	-2	13	5	5	46	45
11	1	1	53	-54	14	8	2	60	62	7	7	5	54	-52
13	1	1	46	48	10	10	2	7	4	9	7	5	52	-51
15	1	1	44	45	12	10	2	56	59	11	7	5	52	51
3	3	1	86	83	3	3	3	79	78	13	7	5	36	36
5	3	1	97	94	5	3	3	98	-99	9	9	5	49	49
7	3	1	67	-68	7	3	3	76	-77	11	9	5	32	49
9	3	1	63	-63	9	3	3	70	72	6	6	6	27	21
11	3	1	62	63	11	3	3	75	75	8	6	6	86	-85
13	3	1	42	42	13	3	3	48	-48	10	6	6	18	15
15	3	1	39	-41	15	3	3	41	-42	12	6	6	59	61
5	5	1	64	-62	5	5	3	73	-70	8	8	6	*6	-1
7	5	1	63	-63	7	5	3	61	59	10	8	6	74	72
9	5	1	61	59	9	5	3	54	54	12	8	6	7	2
11	5	1	50	51	11	5	3	50	-50	10	10	6	10	10
13	5	1	55	-54	13	5	3	52	-52	7	7	7	34	-33
15	5	1	39	-41	15	5	3	36	44	9	7	7	41	40
7	7	1	64	63	7	7	3	58	57	11	7	7	43	43
9	7	1	53	52	9	7	3	55	-54	9	9	7	45	44
11	7	1	52	-50	11	7	3	48	-49	11	9	7	43	-41
13	7	1	40	-41	13	7	3	45	48	8	8	8	64	66
9	9	1	44	-44	9	9	3	50	-52	10	8	8	7	-1
11	9	1	48	-49	11	9	3	48	47	10	10	8	60	-61
13	9	1	38	40	13	9	3	45	47	9	9	9	46	-46
11	11	1	42	43										

The observed and calculated structure factors are compared in Table 1. The atomic parameters and temperature factors are listed in Table 2. The standard errors on the parameters were computed by Busing & Levy's program.

Discussion

The interatomic distances of $ReBe_{22}$ are given in Table 3. The standard deviations of the distances were calculated by the method of Cruickshank & Robertson (1953).

Table 3. *Interatomic distances in* $ReBe_{22}$

Re – 4 Be_1	2·503 ± 0·001 Å
–12 Be_4	2·530 ± 0·011
Be_1– 2 Re	2·503 ± 0·001
–12 Be_4	2·457 ± 0·006
Be_2– 6 Be_3	2·047 ± 0·001
– 6 Be_4	2·263 ± 0·011
Be_3– 2 Be_2	2·047 ± 0·001
– 4 Be_3	2·216 ± 0·023
– 4 Be_4	2·290 ± 0·007
– 2 Be_4	2·194 ± 0·018
Be_4– 1 Re	2·530 ± 0·011
– 2 Be_1	2·457 ± 0·006
– 1 Be_2	2·263 ± 0·011
– 2 Be_3	2·290 ± 0·007
– 1 Be_3	2·194 ± 0·018
– 2 Be_4	2·356 ± 0·021
– 2 Be_4	2·179 ± 0·018
– 1 Be_4	2·132 ± 0·021

The point symmetry at each rhenium atom is T_d–$\bar{4}3m$. The 12 Be_4 neighbors of a rhenium atom, at 2·530 Å, occupy the vertices of a truncated tetrahedron, of which the 4 equilateral triangle faces have 2·179 Å edges and the 4 hexagonal faces have alternately 2·179 Å and 2·132 Å edges. The rhenium atom also has four Be neighbors at a distance of 2·503 Å along lines normal to the hexagonal faces of the Be_4 polyhedron. This configuration (Fig. 1) also occurs in $NbBe_2$ and in $NbBe_3$ (Sands, Zalkin & Krikorian, 1959), except that four Nb atoms replace the four Be_1 atoms observed here.

The point symmetry at each Be_1 atom is D_{3d}–$\bar{3}m$. These atoms are sandwiched between two planar, nearly regular hexagons of Be_4 atoms. The beryllium environment of Be_1 therefore resembles hexagonal close-packing with local symmetry nearly D_{3h}–$\bar{6}m2$, except that the Be_1–Be_4 distance is 2·457 Å. The two rhenium neighbors of Be_1 are at 2·503 Å along the axis of the Be_4 hexagons.

The point symmetry at each Be_2 atom is also D_{3d}–$\bar{3}m$. The 12 nearest neighbors of Be_2 consist

Table 2. *Atomic parameters of* $ReBe_{22}$

Atom	Position	x	y	z	B
Re	8(a)	1/8	1/8	1/8	0·4 Å²
Be_1	16(c)	0	0	0	1·0
Be_2	16(d)	1/2	1/2	1/2	0·6
Be_3	48(f)	0·4894 ± 0·0014	1/8	1/8	1·0
Be_4	96(g)	0·0598 ± 0·0007	0·0598 ± 0·007	0·3235 ± 0·0009	0·9

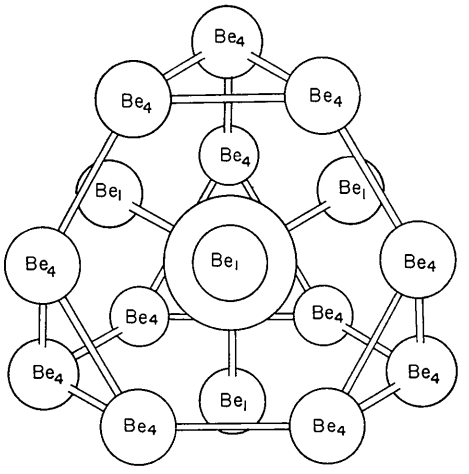

Fig. 1. The Be configuration about a Re atom.

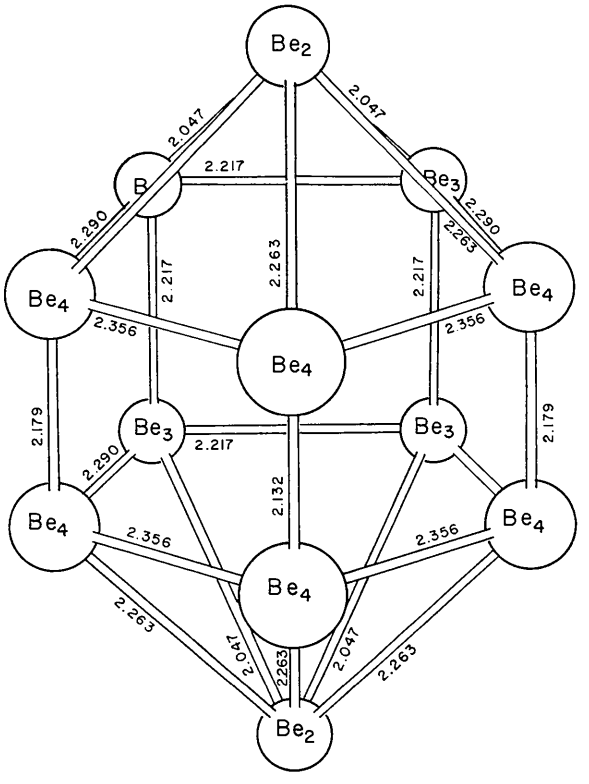

Fig. 2. The environment of a Be_3 atom.

entirely of beryllium atoms, arranged at the vertices of a compressed icosahedron. The six Be_3 neighbors form two equilateral triangles with Be_3–Be_3 = 2·216 Å (Be_2–Be_3 = 2·047 Å). The six Be_4 neighbors form a puckered hexagon with Be_4–Be_4 = 2·356 Å (Be_2–Be_4 = 2·263 Å).

The point symmetry at each Be_3 atom is C_{2v}–$mm2$.

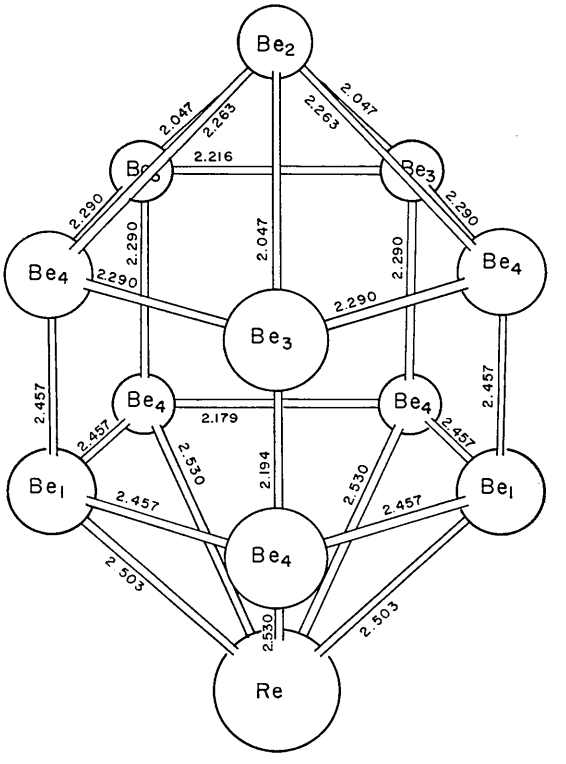

Fig. 3. The environment of a Be_4 atom.

The four Be_3 neighbors form a perfect square of edge 2·217 Å; these four Be_3 neighbors and the six Be_4 neighbors occupy the vertices of a distorted pentagonal prism, the ends of which are pyramidally terminated by the two Be_2 neighbors (Fig. 2).

The point symmetry at each Be_4 atom is C_s–m. The coordination polyhedron is like that of Be_3 except that a Re atom replaces one of the end berylliums (Fig. 3).

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