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The Crystal Structure of Ru_3Be_{17}*

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Ru_3Be_{17} is body-centered cubic with $a = 11{\cdot}337$ Å; there are eight formula units in the unit cell and the space group is $Im3$. A feature of the structure which is unusual for an intermetallic beryllide is the occurrence of a hole of radius 2·81 Å around the origin of the unit cell. Powder patterns show a corresponding isostructural osmium beryllide with $a = 11{\cdot}342$ Å.

Introduction

Powder diffraction patterns of Ru–Be preparations showed a body-centered cubic phase of approximate composition $RuBe_6$. Single crystals of this phase were subsequently made. The determination of its crystal structure established its correct stoichiometry as Ru_3Be_{17}.

Experimental

Samples of Ru_3Be_{17} were prepared from −50 mesh 99·9% pure Ru powder and −200 mesh 99% pure Be powder. The main impurity in the Be was oxygen. The powders were mixed in an atomic ratio of one Ru to six Be to make up 1 g. of sample. This mixture was reacted in a dense BeO crucible at 1480 °C. for 15 min. under ½ atmosphere argon. An inductively heated Ta crucible was used as the furnace. The sample showed evidence of reaction, but not of melting. Two higher heatings were made in attempts to melt the sample. Melting was not indicated at 1530 °C., but did occur at 1635 °C. The resultant sample was crushed and single crystals were selected for the structural study.

Powder diffraction patterns taken with Cu $K\alpha$ radiation ($\lambda\ K\alpha_1 = 1{\cdot}54050$ Å, $\lambda\ K\alpha_2 = 1{\cdot}54434$ Å) show that the material is body-centered cubic with

$$a = 11{\cdot}337 \pm 0{\cdot}005 \text{ Å} .$$

The first 17 lines of this pattern are listed in Table 1. Powder patterns show a corresponding isostructural osmium beryllide with $a = 11{\cdot}342$ Å. Oscillation and Weissenberg photographs of a single crystal of Ru_3Be_{17} showed Laue symmetry $Im3$. The possible space groups, consistent with the diffraction effects, are $I23$, $I2_13$, and $Im3$. The choice of the centrosymmetric space group, $Im3$, was ultimately confirmed by the structure determination.

Table 1. *Powder pattern of* Ru_3Be_{17}

Photographed with Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å.
Intensities estimated visually

d	*hkl*	*I*	*d*	*hkl*	*I*
8·1 Å	110	10	2·525 Å	420	25
5·64	200	30	2·408	332	25
4·60	211	15	2·308	422	10
3·99	220	45	2·219	510 431	30
3·56	310	100	2·062	521	50
3·25	222	65	1·937	530 433	100
3·01	321	100	1·883	442 600	45
2·82	411 330	25	1·832	611 532	100

The intensities from an irregularly shaped single crystal of approximate dimensions 0·04 × 0·06 × 0·08 mm. were measured with Mo $K\alpha$ radiation on a General Electric XRD-5 X-ray spectrometer equipped with a single crystal orienter. The stationary crystal-stationary counter technique was used, and 40-sec. counts were taken at the calculated settings of 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 506 reflections, of which 13 were not observable above background, were measured.

Structure determination

Preparations of intermetallic beryllides are generally microcrystalline. Establishing their stoichiometries by chemical analysis is complicated by the necessity for proving that the material is single phase and by the possibility that some of these compounds have extended homogeneity ranges. The solution of the stoichiometry problem is usually based upon a combination of the structure determination and the assumption of the additivity of elemental volumes (e.g., Zalkin, Sands & Krikorian, 1959). In the present case, the volume of the unit cell is 1457 Å³, and the volume of 24 Ru atoms plus 140 Be atoms obtained from the elements (13·57 Å³/Ru, 8·105 Å³/Be) is 1460

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Table 2. *Observed and calculated structure factors, F_o and F_c, respectively*

Asterisks denote unobserved reflection

H	K	L	FO	FC
0	0	2	89	-81
0	0	4	182	175
0	0	6	290	295
0	0	8	87	-71
0	0	10	286	287
0	0	12	66	48
0	0	14	60	50
0	0	16	149	154
0	1	1	24	-22
0	1	3	141	-136
0	1	5	33	31
0	1	7	38	-39
0	1	9	83	-79
0	1	11	27	25
0	1	13	68	-66
0	1	15	20	-25
0	1	17	17	26
0	2	2	150	-144
0	2	4	115	-115
0	2	6	44	-44
0	2	8	126	-124
0	2	10	76	-74
0	2	12	20	-17
0	2	14	107	-111
0	2	16	9	-10
0	3	1	212	206
0	3	3	116	-110
0	3	5	342	373
0	3	7	42	-40
0	3	9	74	70
0	3	11	175	168
0	3	13	63	-66
0	3	15	162	157
0	4	2	52	-49
0	4	4	45	37
0	4	6	67	66
0	4	6	67	-69
0	4	10	117	110
0	4	12	18	15
0	4	14	37	-40
0	4	16	80	80
0	5	1	117	-112
0	5	3	163	-161
0	5	5	121	-119
0	5	7	60	-61
0	5	9	154	-146
0	5	11	45	-46
0	5	13	83	-80
0	5	15	107	-106
0	6	2	131	-125
0	6	4	77	73
0	6	6	145	139
0	6	8	122	-122
0	6	10	175	171
0	6	12	18	-12
0	6	14	13	-16
0	6	16	103	104
0	7	1	113	114
0	7	3	49	-48
0	7	5	220	223
0	7	7	*7	4
0	7	9	23	23
0	7	11	129	124
0	7	13	29	-33
0	7	15	91	90
0	8	2	80	-83
0	8	4	111	-109
0	8	6	48	-51
0	8	8	87	-88
0	8	10	84	-84
0	8	12	9	1
0	8	14	106	-105
0	9	1	26	24
0	9	3	128	-129
0	9	5	110	105
0	9	7	90	-89
0	9	9	31	-20
0	9	11	52	54
0	9	13	99	-100
0	10	2	25	-17
0	10	4	101	101
0	10	6	165	165
0	10	8	26	-28
0	10	10	174	181
0	10	12	40	36
0	11	1	25	-24
0	11	3	50	-51
0	11	5	19	-14
0	11	7	14	8
0	11	9	74	-71
0	11	11	*9	2
0	11	13	26	-24
0	12	2	119	-120
0	12	4	47	-47
0	12	6	8	5
0	12	8	129	-124
0	12	10	9	7
0	12	12	46	-35
0	13	1	106	112
0	13	3	68	-71
0	13	5	197	199
0	13	7	12	-13
0	13	9	26	30
0	13	11	120	120
0	14	2	8	7
0	14	4	9	10
0	14	6	34	35
0	14	8	9	-10
0	15	1	54	-57
0	15	3	100	-101
0	15	5	29	-27
0	15	7	72	-69
0	16	2	70	-68
0	16	4	38	44
0	16	6	74	78
0	17	1	49	53
1	1	2	33	-34
1	1	4	15	2
1	1	6	31	-32
1	1	8	14	-10
1	1	10	15	-6
1	1	12	28	-26
1	1	14	12	10
1	1	16	23	-19
1	2	3	86	-82
1	2	5	20	18
1	2	7	83	-83
1	2	9	13	10
1	2	11	32	-31
1	2	13	54	-52
1	2	15	20	20
1	2	17	48	-48
1	3	2	183	172
1	3	4	17	13
1	3	6	43	-41
1	3	8	148	150
1	3	10	69	-73
1	3	12	71	68
1	3	14	27	26
1	3	16	23	-24
1	4	3	52	46
1	4	5	35	-32
1	4	7	26	24
1	4	9	27	20
1	4	11	20	-19
1	4	13	42	39
1	4	15	9	-8
1	5	2	126	-122
1	5	4	18	-14
1	5	6	33	-32
1	5	8	83	-84
1	5	10	16	15
1	5	12	79	-76
1	5	14	*9	4
1	5	16	27	-25
1	6	3	83	81
1	6	5	131	-84
1	6	7	68	68
1	6	9	14	-7
1	6	11	48	-47
1	6	13	73	71
1	6	15	46	-50
1	7	2	104	101
1	7	4	24	21
1	7	6	13	2
1	7	8	108	104
1	7	10	40	-36
1	7	12	53	52
1	7	14	32	32
1	8	3	92	-93
1	8	5	32	32
1	8	7	98	-98
1	8	9	17	12
1	8	11	20	-16
1	8	13	66	-64
1	8	15	34	31
1	9	2	33	34
1	9	4	20	-15
1	9	6	56	-54
1	9	8	42	39
1	9	10	46	-50
1	9	12	*9	8
1	9	14	*10	3
1	10	3	132	132
1	10	5	54	-53
1	10	7	82	81
1	10	9	29	30
1	10	11	18	-13
1	10	13	85	83
1	11	2	64	-67
1	11	4	13	13
1	11	6	14	-10
1	11	8	52	-49
1	11	10	31	29
1	11	12	59	-58
1	12	3	17	-13
1	12	5	36	-38
1	12	7	22	-20
1	12	9	9	-7
1	12	11	36	-33
1	13	2	106	110
1	13	4	14	7
1	13	6	19	-19
1	13	8	108	108
1	13	10	50	-51
1	14	3	23	-25
1	14	5	28	32
1	14	7	28	-29
1	14	9	19	19
1	15	2	36	-39
1	15	4	9	-13
1	15	6	27	-28
1	15	8	26	-25
1	16	3	76	79
1	16	5	69	-71
1	17	2	10	9
2	2	2	228	235
2	2	4	44	42
2	2	6	30	-29
2	2	8	199	203
2	2	10	74	-74
2	2	12	84	83
2	2	14	67	66
2	2	16	28	-35
2	3	3	81	-78
2	3	5	49	-44
2	3	7	106	-103
2	3	9	11	-0
2	3	11	80	-80
2	3	13	52	-47
2	3	15	9	-1
2	4	4	34	-31
2	4	6	84	-83
2	4	8	56	54
2	4	10	70	-69
2	4	12	8	-7
2	4	14	25	23
2	4	16	67	-66
2	5	3	299	314
2	5	5	100	-98
2	5	7	177	178
2	5	9	100	94
2	5	11	22	-20
2	5	13	174	171
2	5	15	25	-28
2	6	4	*6	9
2	6	6	58	-56
2	6	8	12	-3
2	6	10	11	-4
2	6	12	60	-60
2	6	14	36	31
2	7	3	14	-6
2	7	5	88	-90
2	7	7	46	-45
2	7	9	10	-7
2	7	11	92	-89
2	7	13	13	-9
2	7	15	30	-30
2	8	4	30	30
2	8	6	42	-40
2	8	8	193	191
2	8	10	70	-70
2	8	12	94	92
2	8	14	55	56
2	9	3	45	45
2	9	5	20	-18
2	9	7	26	26
2	9	9	44	36
2	9	11	32	-29
2	9	13	49	51
2	10	4	47	-45
2	10	6	82	-82
2	10	8	44	-46
2	10	10	46	-46
2	10	12	83	-81
2	11	3	145	150
2	11	5	112	-110
2	11	7	105	106
2	11	9	24	23
2	11	11	66	-60
2	11	13	117	115
2	12	4	36	33
2	12	6	8	-5
2	12	8	97	94
2	12	10	9	-8
2	12	12	32	31
2	13	3	38	-45
2	13	5	41	-43
2	13	7	77	-78
2	13	9	13	-2
2	13	11	59	-61
2	14	4	23	-23
2	14	6	62	-60
2	14	8	79	76
2	15	3	128	130
2	15	5	16	-19
2	15	7	85	88
2	16	4	*10	3
3	3	4	137	-136
3	3	6	40	-43
3	3	8	84	-82
3	3	10	107	-111
3	3	12	*8	15
3	3	14	105	-104
3	3	16	32	-32
3	4	5	72	68
3	4	7	61	-61
3	4	9	49	-51
3	4	11	42	42
3	4	13	82	-79
3	4	15	18	11
3	5	4	111	107
3	5	6	187	185
3	5	8	54	-55
3	5	10	215	212
3	5	12	22	19
3	5	14	35	34
3	5	16	122	120
3	6	5	26	-24
3	6	7	13	-3
3	6	9	67	-65
3	6	11	8	1
3	6	13	39	-39
3	6	15	29	-31
3	7	4	73	-75
3	7	6	35	-31
3	7	8	103	-108
3	7	10	37	-38
3	7	12	35	-31
3	7	14	81	-82
3	8	5	262	267
3	8	7	22	-17
3	8	9	48	47
3	8	11	150	145
3	8	13	49	-47
3	9	4	12	-3
3	9	6	48	41
3	9	8	28	-25
3	9	10	39	39
3	9	12	37	38
3	9	14	35	-35
3	10	5	62	-65
3	10	7	52	-52
3	10	9	107	-104
3	10	11	35	-32
3	10	13	75	-74
3	11	4	45	46
3	11	6	85	84
3	11	8	91	-92
3	11	10	132	129
3	11	12	30	-26
3	12	5	124	123
3	12	7	24	21
3	12	9	27	32
3	12	11	89	90
3	13	4	76	-81
3	13	6	42	-47
3	13	8	62	-59
3	13	10	62	-67
3	14	5	91	93
3	14	7	63	-62
3	14	9	20	-19
3	15	4	46	53
3	15	6	104	105
3	16	5	26	-29
4	4	4	*5	3
4	4	6	24	20
4	4	8	43	-43
4	4	10	34	30
4	4	12	12	-6
4	4	14	18	-14
4	4	16	17	21
4	5	5	75	-77
4	5	7	50	51
4	5	9	33	-32
4	5	11	8	-4
4	5	13	39	38
4	5	15	58	-52
4	6	6	34	31
4	6	8	83	-85
4	6	10	64	65
4	6	12	48	-50
4	6	14	18	-10
4	7	5	61	61
4	7	7	45	-43
4	7	9	8	7
4	7	11	32	32
4	7	13	56	-52
4	7	15	37	35
4	8	6	17	-15
4	8	8	39	41
4	8	10	60	-63
4	8	12	48	46
4	8	14	25	-28
4	9	5	37	37
4	9	7	24	-28
4	9	9	16	-11
4	9	11	33	29
4	9	13	30	-31
4	10	6	65	65
4	10	8	69	-70
4	10	10	73	69
4	10	12	30	-28
4	11	5	55	-56
4	11	7	55	52
4	11	9	28	-27
4	11	11	9	-10
4	12	6	12	12
4	12	8	9	-13
4	12	10	13	10
4	13	5	81	79
4	13	7	58	-58
4	13	9	19	13
4	14	6	13	-5
4	14	8	*10	13
4	15	5	13	-12
4	15	7	20	15
5	5	6	127	-130
5	5	8	64	-66
5	5	10	51	-55
5	5	12	116	-114
5	5	14	9	-3
5	6	7	137	136
5	6	9	26	25
5	6	11	73	-68
5	6	13	137	131
5	6	15	51	-49
5	7	6	7	2
5	7	8	167	172
5	7	10	30	-32
5	7	12	74	73
5	7	14	86	85
5	8	7	98	-101
5	8	9	11	-8
5	8	11	90	-85
5	8	13	53	-54
5	9	6	80	-84
5	9	8	96	95
5	9	10	92	-90
5	9	12	18	18
5	10	7	126	130
5	10	9	85	80
5	10	11	16	-17
5	10	13	136	134
5	11	6	50	-50
5	11	8	9	-6
5	11	10	9	-8
5	11	12	58	-59
5	12	7	9	-11
5	12	9	26	-23
5	12	11	87	-90
5	13	6	24	-19
5	13	8	165	166
5	13	10	40	-41
5	14	7	*10	10
5	15	6	84	-87
6	6	6	70	71
6	6	8	64	-66
6	6	10	97	97
6	6	12	15	-16
6	6	14	*10	-0
6	7	7	18	16
6	7	9	28	27
6	7	11	73	73
6	7	13	9	-8
6	8	8	18	-19
6	8	10	93	-92
6	8	12	16	11
6	9	7	49	-49
6	9	9	19	-19
6	9	11	16	11
6	9	13	59	-57
6	10	8	17	-13
6	10	10	129	126
6	10	12	10	9
6	11	7	23	28
6	11	9	56	-57
6	11	11	26	-31
6	12	8	67	-66
6	12	12	26	-22
6	13	7	13	-13
6	13	9	31	32
7	7	8	48	-51
7	7	10	17	-17
7	7	12	9	-3
7	7	14	44	-55
7	8	9	29	29
7	8	11	110	108
7	8	13	78	-76
7	9	8	32	-30
7	9	10	25	26
7	9	12	17	15
7	10	9	66	-63
7	10	11	10	3
7	11	8	97	-99
7	11	10	95	96
7	12	9	*10	9
7	13	8	17	-19
8	8	8	167	181
8	8	10	47	-48
8	8	12	92	98
8	9	9	36	38
8	9	11	23	-24
8	10	10	57	-57
8	11	9	33	30
9	9	10	25	-25

Table 3. *Atomic parameters of* Ru_3Be_{17}

Atom	Position	*x*	*y*	*z*	*B*
Ru	24(*g*)	0	0·1879 ± 0·0001	0·3014 ± 0·0001	0·2 Å²
Be_1	48(*h*)	0·2010 ± 0·0011	0·1140 ± 0·0011	0·3434 ± 0·0011	1·1
Be_2	24(*g*)	0	0·2305 ± 0·0015	0·0914 ± 0·0015	0·9
Be_3	24(*g*)	0	0·4055 ± 0·0012	0·3488 ± 0·0012	0·2
Be_4	16(*f*)	0·1645 ± 0·0010	0·1645 ± 0·0010	0·1645 ± 0·0010	0·9
Be_5	12(*e*)	0·1956 ± 0·0017	0	½	0·2
Be_6	12(*d*)	0·4065 ± 0·0023	0	0	1·2

Å³, suggesting the composition Ru_6Be_{35} with four of these formula units per unit cell.

The 24 Ru atoms were found, by interpretation of the three-dimensional Patterson function, to occupy positions 24(*g*) of space group *Im*3: body-centering $\pm(0, y, \pm z;\ z, 0, \pm y;\ y, \pm z, 0)$ (*International Tables for X-ray Crystallography*, 1952), with $y=0{\cdot}19$, $z=0{\cdot}31$. The relationship, $y+z=\frac{1}{2}$, which these unrefined parameters obey, has been observed for the metalloid atoms in the isostructural compounds $CoAs_3$ (Oftedal, 1928), $CoSb_3$ (Rosenqvist, 1953), $RhSb_3$ (Zhuravlev & Zhdanov, 1956), and $IrAs_3$ and $IrSb_3$ (Kjekshus & Pedersen, 1961). A consequence of this relationship is that no new vectors would be added to the vector set if an atom were placed at the origin. However, the magnitudes of the vectors would be changed, and quantitative consideration of the heights of the Patterson peaks shows that, in this case, there is no heavy atom at the origin and the above interpretation of the Patterson is, in fact, unique if the space group is *Im*3.

The contributions of the Ru atoms to the structure factors were computed, and the resulting signs were applied to the observed structure factors which were then used in calculating the three-dimensional Fourier synthesis. The positions of 136 beryllium atoms were obtained from this Fourier map. In terms of space group *Im*3 they are:

48 Be_1 in 48(*h*): $\pm(x, \pm y, \pm z;\ z, \pm x, \pm y;\ y, \pm z, \pm x)$ + body-centering, with $x=0{\cdot}20$, $y=0{\cdot}11$, $z=0{\cdot}34$,
24 Be_2 in 24(*g*) with $y=0{\cdot}23$, $z=0{\cdot}09$,
24 Be_3 in 24(*g*) with $y=0{\cdot}40$, $z=0{\cdot}35$,
16 Be_4 in 16(*f*): $\pm(x, \pm x, \pm x)$ + body-centering, with $x=0{\cdot}16$,
12 Be_5 in 12(*e*): $\pm(x, 0, \frac{1}{2};\ \frac{1}{2}, x, 0;\ 0, \frac{1}{2}, x)$ + body-centering, with $x=0{\cdot}20$,
12 Be_6 in 12(*d*): $\pm(x, 0, 0;\ 0, x, 0;\ 0, 0, x)$ + body-centering, with $x=0{\cdot}40$.

The volume calculation predicted the presence of 140 Be atoms per unit cell. The 136 Be atoms found leave holes of radius 2·81 Å around the 2(*a*) positions $(0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. However, four atoms cannot be added to the structure without destroying the cubic symmetry. The possibility of placing a third of a Be atom in each of the 12(*d*) positions, with $x=0{\cdot}1$, was tested in the course of the least squares refinements. The temperature factors of these fractional atoms increased rapidly, reaching 8·7 Å² after two cycles. Similar results occurred when Be atoms were placed in the 2(*a*) positions. Furthermore, the energy required to transfer a Be atom from the lattice to a hole of 2·81 Å radius would be of the order of the energy necessary to vaporize the atom. Finally, a difference Fourier was computed after refinement of the 136 Be and 24 Ru atoms. The largest peak on this difference map corresponded to about 1·5 electrons near a Be_4 atom; the next largest peaks amounted to only about 0·5 electron. The most negative region was at the origin. Since there are no other holes of sufficient size to accommodate additional atoms, the conclusion was reached that there are only 136 Be atoms per unit cell, and the formula of this phase is Ru_3Be_{17}.

The Ru_3Be_{17} parameters were refined on an IBM 709 using the least squares program of Busing & Levy (1959). Individual isotropic temperature factors for each atom were included in the refinements. Constant weighting factors were applied. The atomic scattering factors used were those of Thomas & Umeda (1957) for Ru, and Ibers (1957) for Be. The final reliability factor, $R=\Sigma|F_o-F_c|/\Sigma|F_o|$, was 0·052. Omitting the unobserved reflections, R was 0·049. The standard error of fit, $[\Sigma|F_o-F_c|^2/(m-n)]^{\frac{1}{2}}$, was 4·83 ($m=506$ was the number of observations, $n=20$ was the number of parameters being refined). The observed and calculated structure factors are listed in Table 2. The refined parameters are given in Table 3. The standard errors of the parameters were computed by Busing & Levy's program.

Discussion

The nearest neighbor interatomic distances of Ru_3Be_{17} are listed in Table 4. The standard deviations of these distances were computed by the method of Cruickshank & Robertson (1953).

The point symmetry at a Ru atom is C_s–m. Its neighbors include four Be_1, two Be_2, three Be_3, two Be_4, and one Be_5 arranged at the vertices of a truncated tetrahedron. Four additional neighbors, consisting of two Be_1 atoms at 2·38 Å, one Be_2 atom, and one Be_6 atom, lie on the axes of the hexagonal faces of the truncated tetrahedron. This configuration about the heavy atom (Fig. 1) has also been observed in $NbBe_2$ and $NbBe_3$ (Sands, Zalkin & Krikorian, 1959) and in $ReBe_{22}$ (Sands, Johnson, Zalkin, Krikorian & Kromholtz, 1962).

Table 4. *Interatomic distances in* Ru$_3$Be$_{17}$

Ru	–2 Be$_1$	2·474 ± 0·012 Å
	–2 Be$_1$	2·379 ± 0·013
	–2 Be$_1$	2·464 ± 0·013
	–1 Be$_2$	2·429 ± 0·017
	–2 Be$_2$	2·501 ± 0·009
	–1 Be$_3$	2·525 ± 0·013
	–2 Be$_3$	2·528 ± 0·006
	–2 Be$_4$	2·441 ± 0·018
	–1 Be$_5$	2·610 ± 0·010
	–1 Be$_6$	2·442 ± 0·013
Be$_1$	–1 Ru	2·474 ± 0·012
	–1 Ru	2·379 ± 0·013
	–1 Ru	2·464 ± 0·013
	–2 Be$_1$	2·195 ± 0·021
	–1 Be$_1$	2·585 ± 0·025
	–1 Be$_2$	2·202 ± 0·019
	–1 Be$_3$	2·230 ± 0·017
	–1 Be$_3$	2·188 ± 0·015
	–1 Be$_4$	2·048 ± 0·017
	–1 Be$_5$	2·197 ± 0·013
	–1 Be$_6$	2·716 ± 0·014
Be$_2$	–1 Ru	2·429 ± 0·017
	–2 Ru	2·501 ± 0·009
	–2 Be$_1$	2·202 ± 0·019
	–1 Be$_2$	2·073 ± 0·033
	–2 Be$_4$	2·174 ± 0·020
	–1 Be$_6$	2·249 ± 0·029
Be$_3$	–2 Ru	2·528 ± 0·006 Å
	–1 Ru	2·525 ± 0·013
	–2 Be$_1$	2·188 ± 0·015
	–2 Be$_1$	2·230 ± 0·017
	–1 Be$_3$	2·143 ± 0·027
	–1 Be$_5$	2·062 ± 0·017
	–1 Be$_5$	2·041 ± 0·021
	–2 Be$_6$	2·282 ± 0·017
Be$_4$	–3 Ru	2·441 ± 0·018
	–3 Be$_1$	2·148 ± 0·017
	–3 Be$_2$	2·174 ± 0·020
Be$_5$	–2 Ru	2·610 ± 0·010
	–4 Be$_1$	2·197 ± 0·013
	–2 Be$_3$	2·062 ± 0·017
	–2 Be$_3$	2·041 ± 0·021
	–2 Be$_6$	2·457 ± 0·021
Be$_6$	–2 Ru	2·442 ± 0·013
	–4 Be$_1$	2·716 ± 0·014
	–2 Be$_2$	2·249 ± 0·029
	–4 Be$_3$	2·282 ± 0·017
	–2 Be$_5$	2·457 ± 0·021
	–1 Be$_6$	2·118 ± 0·052

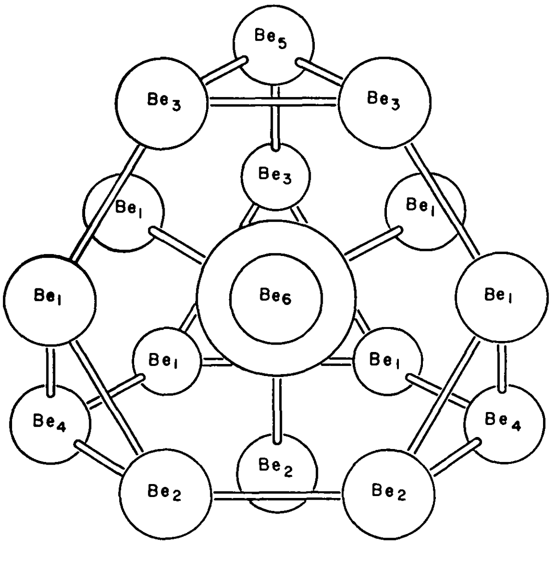

Fig. 1. Nearest neighbors of Ru.

Each of the Be$_1$, Be$_2$, Be$_3$, and Be$_4$ atoms has six beryllium and three ruthenium neighbors arranged at the vertices of two octahedra sharing a face. The vertices of the shared face are in each case occupied by the ruthenium atoms. The Be$_3$ atoms have three additional neighbors, consisting of one Be$_5$ and two Be$_6$ atoms, forming a triangle centered about 1·7 Å from Be$_3$ along the common axis of the octahedra. The Be$_1$ environment also includes this extra triangle, in this case consisting of one Be$_1$, one Be$_5$, and one Be$_6$ atom, but the distances from the central Be$_1$ atom to these atoms are 2·72 Å, 2·20 Å, and 2·59 Å, respectively.

The Be$_5$ atoms occupy positions of point symmetry C_{2v}–*mm*. Each Be$_5$ is surrounded by a prism with quadrilateral bases. The sequence of atoms at the vertices of each base is Be$_1$–Be$_6$–Be$_1$–Be$_3$. The axis of the prism is bisected by a trapezoid whose vertices are occupied by the sequence Be$_3$–Be$_3$–Ru–Ru.

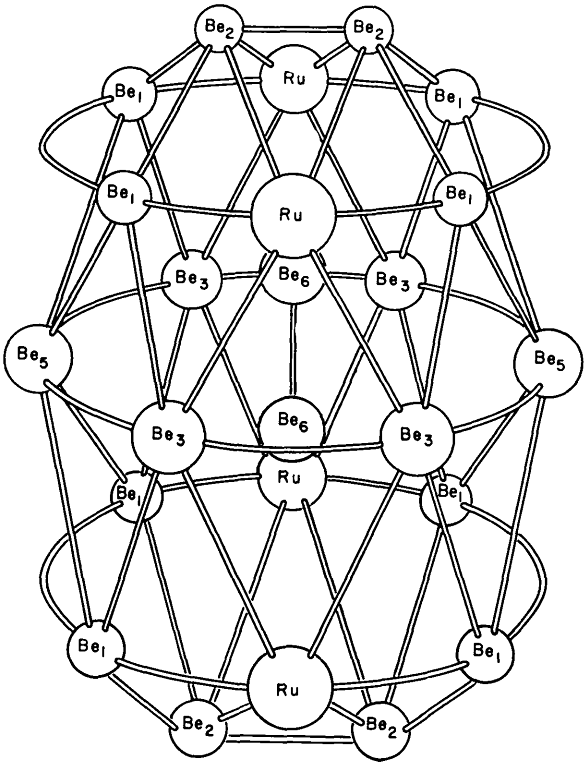

Fig. 2. Environment of two Be$_6$ atoms.

The Be$_6$ atoms occur in pairs. The environment of such a pair is shown in Fig. 2. The Be$_1$ atoms in this picture serve only to complete the cage, the Be$_6$–Be$_1$ distance (2·72 Å) being too large to be considered an interatomic contact. The Be$_6$–Be$_5$ distance is 2·46 Å.

The hole at the origin is bounded by 12 Be$_2$ atoms at a distance of 2·81 Å. This hole also appears in the CoAs$_3$ structure, where it is bounded by 12 metalloid atoms at a distance varying from 3·1 Å in CoAs$_3$ to 3·5 Å in IrSb$_3$. The electron-to-atom ratios for the Ru$_3$Be$_{17}$ and CoAs$_3$ structures are 2·60 and 2·67, respectively, based on Pauling's valences (1960) of 6 for Ru, 2 for Be, 6 for Co, and 1·56 for As.

We wish to thank Mr Vernon G. Silveira for the powder photography. We are also indebted to Dr William J. Ramsey for helpful discussions.

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Refinement of the Crystal Structure of Co_9S_8

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The structure of Co_9S_8 has been refined in space group O_h^5–$Fm3m$ by the least-squares technique applied to selected single-crystal data. The lattice constant of Co_9S_8 is $9{\cdot}928 \pm 0{\cdot}001$ Å and there are four Co_9S_8 in the unit cell. There are two kinds of cobalt atoms in the structure: one is surrounded by a regular octahedron of sulfur atoms with Co–S distance, $2{\cdot}39 \pm 0{\cdot}03$ Å; the other is surrounded by a tetrahedron of S atoms, one Co–S distance being $2{\cdot}13 \pm 0{\cdot}02$ Å, and the other three being $2{\cdot}21 \pm 0{\cdot}02$ Å. Each of the cobalt atoms with tetrahedral sulfur coordination is also linked to three similarly coordinated cobalt atoms at a distance of $2{\cdot}50 \pm 0{\cdot}02$ Å which is essentially the Co–Co distance in the elementary cobalts. Some comparison is made with the Rh–S coordination in $Rh_{17}S_{15}$ and it is tentatively concluded that an anomaly exists in the apparent sizes of the *octahedrally* coordinated metal atoms.

Introduction

The crystal structure of Co_9S_8 was solved by Lindqvist, Lundqvist & Westgren (1936) from powder data. In their paper, Lindqvist *et al.* point out that several authors had proposed erroneous formulas for this compound or its isomorph pentlandite, ($(Ni,Fe)_9S_8$). Also Alsén (1925), assuming a formula of (Ni,Fe)S for pentlandite, had proposed an apparently erroneous structure.

As was pointed out in a recent paper on the structure of $Pd_{17}Se_{15}$ (Geller, 1962*a*), the interest in Co_9S_8 resulted from the possibility of a close relationship of its structure to that of the isostructural $Pd_{17}Se_{15}$ and $Rh_{17}S_{15}$ crystals. This was particularly so because of the reported (Juza *et al.*, 1935) formula, Rh_9S_8, for the latter compound. Because of some difficulty with the solution of the structures of $Pd_{17}Se_{15}$ and $Rh_{17}S_{15}$, it was decided to check the Co_9S_8 structure with single-crystal data. The single-crystal material used in this analysis was very kindly given to us by Dr J. R. Stubbles*; it had resulted from his investigations on self-diffusion in Co_9S_8.

In our study of the single-crystal data from Co_9S_8, concluded that the structure proposed by Lindqvist *et al.* was essentially correct. The refinement, however, gives a substantially different viewpoint on the Co–S interatomic distances.

Experimental

A slightly imperfect sphere of average diameter 0·28 mm. was made from the single-crystal material with the Bond (1951) sphere grinder. The crystal was aligned along [100] as rotation axis and a set of Weissenberg photographs* taken with Mo $K\alpha$ radiation, for which the absorption coefficient, $\mu = 164{\cdot}0$ cm.$^{-1}$, $\mu R = 2{\cdot}3$. A set of precession-camera photographs was also taken with Mo $K\alpha$ radiation and [100] as precession axis. However only $hk0$ and $hk1$ intensities from the Weissenberg photographs (50 and 24 hr. exposures respectively) were estimated visually, by comparison with a calibrated intensity strip.

The diffraction symmetry of the crystal is $m3m$ with reflections hkl present only when $h+k$ and $k+l$ are even. There are no further systematic absences. Thus the probable space groups are: O_h^5–$Fm3m$, T_d^2–$F\bar{4}3m$ or O^3–$F432$.

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* Customarily, when using Mo $K\alpha$ radiation, the author uses a three film pack with sheets of Cu foil interleaved resulting in a film:film intensity ratio of approximately 4:1.