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The Crystal Structure of Nb_2Be_{17}*

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Nb_2Be_{17} is rhombohedral with $a = 5{\cdot}599$ Å, $\alpha = 82{\cdot}84°$. The dimensions of the triply primitive hexagonal cell are $a = 7{\cdot}409$, $c = 10{\cdot}84$ Å. The space group is $R\bar{3}m$, and there is one Nb_2Be_{17} unit in the rhombohedral cell. Each Nb atoms has 19 Be neighbors at 2·57 to 2·85 Å (2·72 Å average). There are four types of Be atoms: Be_{I} has 1 Nb neighbor at 2·57 and 13 Be at 2·23 to 2·47 Å; Be_{II} has 2 Nb at 2·85 and 10 Be at 2·13 to 2·25 Å; Be_{III} has 2 Nb at 2·62 and 10 Be at 2·13 to 2·47 Å; Be_{IV} has 3 Nb at 2·68, 2·76, and 2·84 Å and 9 Be at 2·10 to 2·31 Å.

Introduction

Crystallographic methods have been used to establish the existence and structures of $NbBe_2$, $NbBe_3$ (Sands, Zalkin & Krikorian, 1959), and $NbBe_{12}$ (von Batchelder & Raeuchle, 1957).

Powder photographs indicated the presence of a fourth phase, with about 90 mol.% beryllium. We have succeeded in preparing single crystals of this phase, establishing its composition as Nb_2Be_{17}, and determining its structure.

Experimental

Nb_2Be_{17} was prepared by reacting a weighed mixture of the pure elements for one-half hour at 1200–1450 °C. in an inductively heated molybdenum crucible with 10^{-4} mm. Hg vacuum. The starting materials were 100- to 200-mesh powders with less than 0·2% metallic impurities; the starting composition was $NbBe_{9.7}$.

To obtain single crystals for an X-ray structure study, the above material was fused in a BeO crucible under a partial atmosphere of argon. Approximately 90% of the sample fused at 1800 °C., whereas fusion was not detected at 1725 °C. The fused chunk was crushed and sieved, and a suitable single crystal was selected from the material that passed a 200-mesh but not a 325-mesh sieve.

Chemical analyses and a density determination were run on the fused portion. Analyses were carried out by Schoeller's method (Schoeller & Powell, 1955). To insure complete separation, the pH was maintained at 4·2 to 5·5 for the niobium precipitation and at 5·5 to 8·0 for the beryllium precipitation. A second precipitation was performed to give a more complete separation. Compositions of two samples were determined as (1) 55·3% Nb and 44·8% Be, and (2) 54·7% Nb and 44·8% Be; the theoretical values for Nb_2Be_{17} are 54·8% Nb and 45·2% Be.

Oscillation and Weissenberg photographs with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) show a rhombohedral unit cell with

$$a = 5{\cdot}599 \pm 0{\cdot}002 \text{ Å}, \quad \alpha = 82{\cdot}84 \pm 0{\cdot}04°.$$

The dimensions of the triply primitive hexagonal cell are

$$a = 7{\cdot}409 \pm 0{\cdot}002 \text{ Å}, \quad c = 10{\cdot}84 \pm 0{\cdot}01 \text{ Å}.$$

The diffraction symmetry is characteristic of space groups $R\bar{3}m$, $R3m$, and $R32$.

The volumes of Nb and Be atoms, obtained from the elemental metals, are 18 Å^3 and 8 Å^3, respectively; assuming these volumes to be additive, the volume of one Nb_2Be_{17} formula unit is estimated to be 172 Å^3. The volume of the rhombohedral unit cell is 171·8±0·2 Å^3, establishing the composition Nb_2Be_{17}. The calculated density is 3·28 g.cm.$^{-3}$; the pycnometrically measured density of a sample whose composition by chemical analysis is $NbBe_{8.4}$ is 3·31 g.cm.$^{-3}$.

The single crystal selected for the structural investigation was a plate of dimensions 0·12×0·04×0·03 mm. The rhombohedral *c*-axis was parallel to the 0·12-mm. edge of the crystal.

The intensities of 100 rhombohedral *hk*0 reflections, of which 30 were too weak to be observed, were measured with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) on a General Electric XRD-5 X-ray spectrometer equipped with a single crystal orienter. No absorption corrections were made.

Determination of the structure

The apparent equivalence in the intensities of the reflections with the same hexagonal l index suggests that the locations of the six Nb atoms are along the 3-fold axes of the hexagonal cell. The variation of the intensities as a function of l, and in particular the near absence of reflections for which $l = 8$ suggests that the Nb atoms occupy the $R\bar{3}m$ positions 6*c*:

$$\pm(0,0,z) + (0,0,0;\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3})$$

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Table 1. *Atomic parameters in* Nb_2Be_{17} (*hexagonal*)

Position	Atom	*x*	*y*	*z*	*B* (Å²)
6(*c*)	Nb	0·0000	0·0000	0·1599 ± 0·0004	0·56
6(*c*)	Be_{I}	0·000	0·000	0·397 ± 0·005	0·5
9(*e*)	Be_{II}	0·500	0·000	0·000	1·6
18(*g*)	Be_{III}	0·297 ± 0·010	0·297 ± 0·010	0·500	1·5
18(*h*)	Be_{IV}	0·164 ± 0·004	0·836 ± 0·004	0·994 ± 0·003	0·3

with $z \approx 0{\cdot}16$. (*International Tables for X-ray Crystallography*, 1952.)

In the $NbBe_3$ (Sands, Zalkin & Krikorian, 1959) and $NbBe_{12}$ (von Batchelder & Raeuchle, 1957) structures 5·6 Å distances are associated with linear Nb–Be–Nb units and 7·4 Å distances with linear Nb–Be–Be–Nb units. Applying this association of distances to Nb_2Be_{17} we obtain a trial structure of the correct stoichiometry and $R\bar{3}m$ symmetry. The beryllium parameters, in terms of $R\bar{3}m$ and hexagonal axes, are

6 Be_I in 6(*c*): $\pm(0,0,z)+(0,0,0;\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3})$, with $z = 0{\cdot}40$,
9 Be_{II} in 9(*e*): $(\tfrac{1}{2},0,0;\ 0,\tfrac{1}{2},0;\ \tfrac{1}{2},\tfrac{1}{2},0)+(0,0,0;\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3})$,
18 Be_{III} in 18(*g*): $\pm(x,0,\tfrac{1}{2};\ 0,x,\tfrac{1}{2};\ x,x,\tfrac{1}{2})+(0,0,0;\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3})$ with $x = 0{\cdot}33$,
18 Be_{IV} in 18(*h*): $\pm(x,\bar{x},z;\ x,2x,z;\ 2\bar{x},\bar{x},z)+(0,0,0;\ \tfrac{1}{3},\tfrac{2}{3},\tfrac{2}{3};\ \tfrac{2}{3},\tfrac{1}{3},\tfrac{1}{3})$ with $x = 0{\cdot}167$, $z = -0{\cdot}01$.

These parameters were refined by repeated application of the least-squares method to the rhombohedral *hk*0 data. Isotropic temperature factors for each atom were included in the refinements. The Berghuis *et al.* (1955) scattering factors for beryllium were used. The niobium scattering factors were calculated from the formula

$$f = [(f_0+\Delta f')^2+(\Delta f'')^2]^{\frac{1}{2}},$$

where the f_0's are the Thomas–Fermi scattering factors (Klug & Alexander, 1954), and $\Delta f'$ and $\Delta f''$ are the dispersion corrections for niobium with Mo $K\alpha$ radiation (Dauben & Templeton, 1955). It is easily shown that, for least-squares purposes, this formula is an exceptionally good approximation when the relative contribution of the other atoms to the structure factors is small.

After the least-squares refinements the reliability factor, $R = \Sigma|F_o-F_c|/\Sigma|F_o|$, was 0·067. The hexagonal $R\bar{3}m$ Nb_2Be_{17} parameters are listed in Table 1. The standard deviations of these parameters were evaluated by the method of Cruickshank (1949). The calculated and observed structure factors, with hexagonal indexing, are listed in Table 2. The interatomic distances calculated from the parameters of Table 1 are listed in Table 3. The probable errors of these distances were computed according to Cruickshank & Robertson (1953).

Table 2. *Calculated and observed structure factors for the rhombohedral* (001) *projection of* Nb_2Be_{17} (*hexagonal indices*)

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
2	$\bar{1}$	0	46	56	7	$\bar{2}$	3	34	-31	12	$\bar{3}$	6	12	11	8	1	10	14	-13
4	$\bar{2}$	0	55	64	9	$\bar{3}$	3	29	-26	1	3	7	26	26	10	0	10	<12	-11
6	$\bar{3}$	0	40	40	11	$\bar{4}$	3	24	-20	3	2	7	29	28	1	5	11	< 4	< 1
8	$\bar{4}$	0	40	41	13	$\bar{5}$	3	14	-14	5	1	7	24	24	3	4	11	< 8	- 3
10	$\bar{5}$	0	24	20	0	2	4	38	-41	7	0	7	18	16	5	3	11	< 6	< 1
12	$\bar{6}$	0	25	22	2	1	4	33	-35	9	$\bar{1}$	7	17	16	7	2	11	< 8	- 1
14	$\bar{7}$	0	14	13	4	0	4	26	-26	11	$\bar{2}$	7	14	13	9	1	11	< 1	< 1
1	0	1	31	31	6	$\bar{1}$	4	26	-25	13	$\bar{3}$	7	<16	8	0	6	12	22	24
3	$\bar{1}$	1	27	28	8	$\bar{2}$	4	24	-22	0	4	8	< 1	< 1	2	5	12	17	14
5	$\bar{2}$	1	24	24	10	$\bar{3}$	4	12	-11	2	3	8	< 7	- 6	4	4	12	24	20
7	$\bar{3}$	1	12	11	12	$\bar{4}$	4	11	-13	4	2	8	< 7	- 4	6	3	12	14	12
9	$\bar{4}$	1	17	15	14	$\bar{5}$	4	<15	- 8	6	1	8	<10	- 2	8	2	12	16	15
11	$\bar{5}$	1	11	10	1	2	5	17	17	8	0	8	< 9	- 3	1	6	13	16	16
13	$\bar{6}$	1	<14	7	3	1	5	13	13	10	$\bar{1}$	8	<12	- 2	3	5	13	18	16
0	1	2	23	-25	5	0	5	15	14	12	$\bar{2}$	8	<11	- 2	5	4	13	16	15
2	0	2	25	-26	7	$\bar{1}$	5	<10	10	1	4	9	29	-30	7	3	13	11	11
4	$\bar{1}$	2	17	-16	9	$\bar{2}$	5	<12	8	3	3	9	34	-32	9	2	13	<16	11
6	$\bar{2}$	2	14	-15	11	$\bar{3}$	5	<13	7	5	2	9	26	-25	0	7	14	<13	2
8	$\bar{3}$	2	14	-13	13	$\bar{4}$	5	<13	4	7	1	9	25	-22	2	6	14	< 4	< 1
10	$\bar{4}$	2	<12	- 8	0	3	6	37	40	9	0	9	17	-17	4	5	14	< 1	- 1
12	$\bar{5}$	2	<13	- 7	2	2	6	42	44	11	$\bar{1}$	9	17	-14	6	4	14	<12	1
14	$\bar{6}$	2	<14	- 5	4	1	6	26	25	0	5	10	17	-20	1	7	15	<13	-10
1	1	3	49	-57	6	0	6	39	38	2	4	10	22	-22	3	6	15	<12	-10
3	0	3	53	-61	8	$\bar{1}$	6	21	18	4	3	10	13	-14	5	5	15	10	- 9
5	$\bar{1}$	3	39	-40	10	$\bar{2}$	6	24	21	6	2	10	21	-18	0	8	16	11	-13

Table 3. *Interatomic distances in* Nb_2Be_{17}

Nb–1 Nb	3·463 ± 0·009 Å	Be_{III}–2 Nb	2·62 ± 0·04 Å
–1 Be_I	2·57 ± 0·05	–2 Be_I	2·47 ± 0·07
–3 Be_{II}	2·849 ± 0·003	–2 Be_{II}	2·13 ± 0·01
–6 Be_{III}	2·62 ± 0·04	–2 Be_{III}	2·20 ± 0·08
–3 Be_{IV}	2·76 ± 0·05	–1 Be_{III}	3·01 ± 0·15
–3 Be_{IV}	2·84 ± 0·05	–2 Be_{IV}	2·30 ± 0·05
–3 Be_{IV}	2·68 ± 0·05	–2 Be_{IV}	2·19 ± 0·03
Be_I–1 Nb	2·57 ± 0·05	Be_{IV}–1 Nb	2·76 ± 0·05
–1 Be_I	2·23 ± 0·10	–1 Nb	2·84 ± 0·05
–3 Be_{II}	2·25 ± 0·04	–1 Nb	2·68 ± 0·05
–6 Be_{III}	2·47 ± 0·07	–1 Be_I	2·31 ± 0·07
–3 Be_{IV}	2·31 ± 0·07	–2 Be_{II}	2·16 ± 0·03
Be_{II}–2 Nb	2·849 ± 0·003	–2 Be_{III}	2·30 ± 0·05
–2 Be_I	2·25 ± 0·04	–2 Be_{III}	2·19 ± 0·03
–4 Be_{III}	2·13 ± 0·01	–2 Be_{IV}	2·10 ± 0·05
–4 Be_{IV}	2·16 ± 0·03		

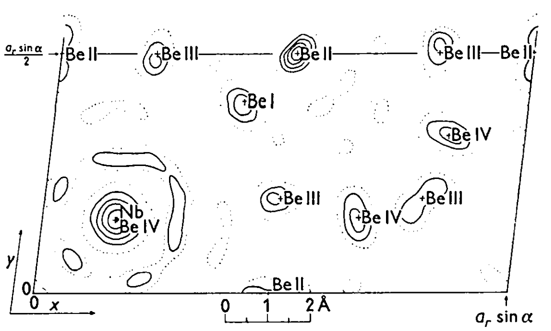

Fig. 1. Electron-density projection onto rhombohedral (001). Contours at arbitrary intervals. Nb contour intervals at 10 times those for Be. Zero contour dotted. *F*(000) not included.

Table 4. Nb_2Be_{17} *powder pattern (hexagonal indices)*

$I_{obs.}$*	d (Å)	*hkl*	$I_{obs.}$*	d (Å)	*hkl*
s	5·50	101	*m*−	2·21	122
m+	4·14	012	*s*−	2·14	300
vs	3·70	110	*m*	2·06	015
m+	3·62	003	*s*	1·85	220
s−	3·08	021	*s*+	1·84	303
m	2·76	202	*m*	1·80	205
s+	2·59	113	*m*−	1·76	131
m	2·50	104	*w*+	1·69	312
m	2·37	211	*s*−	1·65	223

* Visually estimated, Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) X-rays; *vs* = very strong, *s* = strong, *m* = medium, *w* = weak.

The observed structure factors in Table 2 were used to calculate the electron density projected parallel to the rhombohedral *c*-axis. The phases were completely determined by the niobium atoms, and the result (Fig. 1) shows all of the resolvable beryllium atoms close to the least-squares positions.

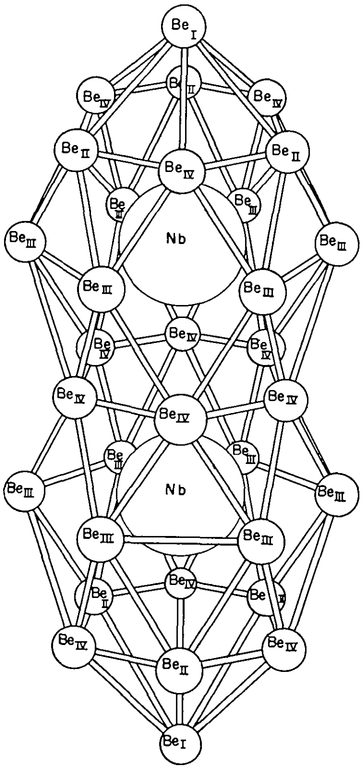

Fig. 2. Be configuration about two Nb atoms in Nb_2Be_{17}.

For identification purposes, the powder pattern is presented in Table 4.

Discussion

Fig. 2 shows the beryllium configuration about two niobium atoms of the Nb_2Be_{17} structure. Each niobium, at a position of C_{3v}–$3m$ point symmetry, has 19 beryllium neighbors. The model shown in Fig. 2 has D_{3d}–$\bar{3}m$ point symmetry, with 32 beryllium atoms forming a cage about the two niobium atoms.

The hexagon of Be_{IV} atoms and the two Be_{II}–Be_{IV} hexagons are not planar. The two hexagons of Be_{III} atoms are required by the space group to be planar, but they are not regular, the Be_{III}–Be_{III} distance alternating between 2·2 and 3·0 Å.

Except for Be_{I}, the beryllium configuration about a single niobium atom is similar to that about Nb_{II} in the $NbBe_3$ structure (Sands, Zalkin & Krikorian, 1959). This beryllium polyhedron was also found around a $TiBe_2$ group in the $TiBe_{12}$ structure (Raeuchle & Rundle, 1952).

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