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The Crystal Structures of $NbBe_2$ and $NbBe_3$*

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$NbBe_2$ has a face-centered cubic cell, $a = 6{\cdot}535$ Å; the space group is $Fd3m$; and there are eight formula units in the unit cell. Each niobium atom is surrounded by 12 Be atoms at 2·71 Å and 4 Nb atoms at 2·83 Å. Each beryllium atom has 6 Nb atoms at 2·71 Å and 6 Be atoms at 2·31 Å as nearest neighbors.

$NbBe_3$ has a rhombohedral cell with $a = 7{\cdot}495$ Å, $\alpha = 35{\cdot}43°$; the space group is $R\bar{3}m$, and there are three formula units in the unit cell. There are two kinds of niobium atoms. Nb_I has 18 Be and 2 Nb nearest neighbors at average distances of 2·78 Å and 2·95 Å, respectively; Nb_{II} has 12 Be and 4 Nb nearest neighbors at average distances of 2·64 Å and 2·88 Å, respectively.

Introduction

The structure of $NbBe_{12}$ was determined by von Batchelder & Raeuchle (1957). White & Burke (1955) mention a cubic $NbBe_2$ phase. A hexagonal $NbBe_3$ phase with $a = 4{\cdot}57$ Å and a large c axis was reported by Baenziger, Wilson & Snow (1946). We have obtained single crystals of $NbBe_2$ and $NbBe_3$, and the detailed structural analyses of these compounds have been completed.

Experimental

The Nb–Be compounds were prepared by reaction of niobium and beryllium powder mixtures in a vacuum induction furnace. Reactants were 200-mesh niobium of 99·9% purity and 100-mesh beryllium of 99% purity. Samples were heated in molybdenum crucibles for about 20 minutes at 1350–1500 °C. under a vacuum of 10^{-4} mm. Hg. Negligible crucible attack was noted. In order to grow single crystals of suitable size, samples were reheated in BeO crucibles to 1600 °C. in vacuum for about 10 minutes. The resulting samples were crushed, and crystals were selected for X-ray examination.

The cell constants and diffraction symmetries of $NbBe_2$ and $NbBe_3$ were obtained from Weissenberg, precession, and powder photographs using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). Intensity measurements were carried out 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.

Structure determinations

$NbBe_2$

$NbBe_2$ has a face-centered cubic cell with

$$a = 6{\cdot}535 \pm 0{\cdot}002 \text{ Å} .$$

The diffraction symmetry and extinction conditions are characteristic of space groups $Fd3$ and $Fd3m$. Furthermore, reflections with $h+k+l = 4n+2$ are very weak or absent.

As no accurate density measurements were available, the number of atoms per unit cell was deduced from a calculation of atomic volumes. In the elemental metals, niobium and beryllium atoms occupy 18 Å^3 and 8 Å^3, respectively. A $NbBe_2$ group is thus estimated to occupy 34 Å^3; the unit cell can accommodate about eight such groups. This type of calculation was carried out on other beryllium intermetallics of known structure and was found to give reliable results. The X-ray density of $NbBe_2$ is 5·28 g.cm.$^{-3}$.

The atoms occupy special positions for which there is no distinction between space groups $Fd3$ and $Fd3m$. These positions, which are uniquely determined, are

8 Nb in $8a$: $(0, 0, 0;\ \frac{1}{4}, \frac{1}{4}, \frac{1}{4}) +$ face-centering;
16 Be in $16d$: $(\frac{5}{8}, \frac{5}{8}, \frac{5}{8};\ \frac{5}{8}, \frac{7}{8}, \frac{7}{8};\ \frac{7}{8}, \frac{5}{8}, \frac{7}{8};\ \frac{7}{8}, \frac{7}{8}, \frac{5}{8}) +$ face-centering.

This structure is one of the cubic Laves or Friauf phases ($MgCu_2$ type) (Friauf, 1927), of which $AgBe_2$ (Misch, 1936; Winkler, 1938) and $TiBe_2$ (Misch, 1936; Ehrlich, 1949) are other examples.

The structure was confirmed by the measurement of the intensities of 43 hhl reflections. A single isotropic temperature factor $B = 0{\cdot}4$ Å^2 was applied to all atoms, and the hhl structure factors were calculated from the atomic parameters, using the Thomas–Fermi scattering factors for Nb (Klug & Alexander, 1954) and the Berghuis *et al.* (1955) scattering factors for beryllium. The reliability coefficient,

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

was 0·076.

The nearest neighbor distances in $NbBe_2$ are given in Table 1.

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Table 1. *Interatomic distances in* $NbBe_2$

Nb– 4 Nb	2·830±0·001 Å
–12 Be	2·709±0·001
Be– 6 Nb	2·709±0·001
– 6 Be	2·310±0·001

$NbBe_3$

$NbBe_3$ is rhombohedral with

$$a = 7{\cdot}495\pm0{\cdot}007 \text{ Å}, \quad \alpha = 35{\cdot}43\pm0{\cdot}04^\circ .$$

The dimensions of the triply primitive hexagonal cell are

$$a = 4{\cdot}561\pm0{\cdot}005, \quad c = 21{\cdot}05\pm0{\cdot}02 \text{ Å} .$$

The diffraction symmetry is characteristic of space groups $R\bar{3}m$, $R3m$, and $R32$. The volume of an $NbBe_3$ group is estimated to be 42 Å^3; the number of such groups in the hexagonal unit cell is nine. The calculated density is 4·72 g.cm.$^{-3}$.

The uniformity in intensity of all reflections with the same hexagonal l index suggests placing the niobium atoms along the three-fold axes. The Patterson projection onto the hexagonal c-axis, $P(w)$, leads to the following atomic positions, in terms of $R\bar{3}m$:

3 Nb_I in $3a$: $(0, 0, 0)+(0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3})$;
6 Nb_{II} in $6c$: $\pm(0, 0, z)+(0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}; \frac{2}{3}, \frac{1}{3}, \frac{1}{3})$
with $z = 0{\cdot}14$.

(*International Tables of X-ray Crystallography*, 1952).

Table 2. *Calculated and observed structure factors for* $NbBe_3$

h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
−8	1	67	62	−3	9	85	92	0	33	<45	−19	4	7	205	198
−8	4	<50	−25	−3	12	<31	23	0	36	162	133	4	10	35	−37
−8	7	63	68	−3	15	196	212	0	39	<49	−25	4	13	157	144
−8	10	<70	−13	−3	18	51	−47	0	42	95	70	4	16	67	61
−8	13	<62	46	−3	21	187	196	0	45	<34	10	4	19	<51	−30
−8	16	<49	23	−3	24	<41	−10	0	48	<47	22	4	22	161	146
−7	2	<61	19	−3	27	73	73	1	1	281	353	4	25	49	−40
−7	5	<61	11	−3	30	87	82	1	4	120	−132	4	28	133	109
−7	8	88	88	−3	33	<45	−10	1	7	349	447	4	31	<49	−20
−7	11	<58	−36	−3	36	86	99	1	10	90	−93	4	34	44	38
−7	14	122	90	−3	39	<50	−25	1	13	179	191	4	37	67	49
−7	17	<59	−16	−3	42	62	65	1	16	113	115	4	40	<49	−14
−7	20	<59	48	−2	1	300	337	1	19	<20	−10	4	43	59	50
−7	23	<59	30	−2	4	137	−136	1	22	209	208	5	2	39	39
−7	26	<31	−10	−2	7	273	314	1	25	94	87	5	5	39	24
−6	3	39	−31	−2	10	56	−55	1	28	192	163	5	8	164	149
−6	6	114	94	−2	13	199	211	1	31	<41	−10	5	11	82	−68
−6	9	<57	42	−2	16	86	85	1	34	<58	48	5	14	184	157
−6	12	<46	30	−2	19	42	−44	1	37	65	54	5	17	<55	−24
−6	15	92	110	−2	22	200	203	1	40	<55	−18	5	20	93	77
−6	18	<61	−38	−2	25	49	−52	1	43	86	73	5	23	59	45
−6	21	107	100	−2	28	156	144	2	2	106	110	5	26	<48	−10
−6	24	<36	10	−2	31	<45	−28	2	5	<18	−10	5	29	115	91
−6	27	<71	44	−2	34	56	48	2	8	239	271	5	32	<71	−26
−6	30	<49	39	−2	37	66	64	2	11	78	−82	5	35	89	61
−5	1	133	127	−2	40	<50	−18	2	14	287	310	6	0	194	171
−5	4	49	−54	−2	43	70	62	2	17	81	−78	6	3	<139	−31
−5	7	182	181	−1	2	100	93	2	20	110	112	6	6	107	94
−5	10	40	−37	−1	5	59	59	2	23	108	102	6	9	<57	42
−5	13	91	88	−1	8	317	365	2	26	<11	10	6	12	<46	30
−5	16	47	54	−1	11	142	−146	2	29	142	129	6	15	133	110
−5	19	<17	−10	−1	14	291	320	2	32	65	−52	6	18	61	−38
−5	22	85	115	−1	17	51	−49	2	35	120	103	6	21	124	100
−5	25	57	−47	−1	20	155	150	2	38	<49	11	6	24	<26	10
−5	28	>69	91	−1	23	89	85	2	41	<63	20	6	27	59	44
−5	31	<39	−10	−1	26	<38	−19	3	0	299	326	6	30	<49	39
−5	34	<71	31	−1	29	177	155	3	3	71	−67	7	1	97	75
−4	2	75	67	−1	32	49	−41	3	6	237	241	7	4	<61	−27
−4	5	<22	−10	−1	35	117	100	3	9	83	85	7	7	129	101
−4	8	185	174	−1	38	<7	10	3	12	20	22	7	10	<58	−24
−4	11	55	−57	−1	41	<71	26	3	15	216	218	7	13	70	54
−4	14	212	217	−1	44	59	50	3	18	51	−46	7	16	59	35
−4	17	61	−54	0	3	137	−127	3	21	204	192	7	19	<15	−10
−4	20	90	82	0	6	283	323	3	24	<52	−11	7	22	89	67
−4	23	67	73	0	9	127	132	3	27	84	76	7	25	<54	−28
−4	26	<3	10	0	12	96	94	3	30	92	83	8	2	<50	20
−4	29	74	98	0	15	285	304	3	33	<48	−11	8	5	<13	10
−4	32	38	−39	0	18	116	−109	3	36	117	99	8	8	74	59
−4	35	<59	80	0	21	244	241	3	39	<50	−24	8	11	<59	−21
−4	38	<38	10	0	24	<50	20	3	42	69	65	8	14	<69	72
−3	3	79	−75	0	27	115	102	4	1	214	203	9	0	93	60
−3	6	239	241	0	30	86	79	4	4	90	−84				

Table 3. *Atomic parameters in* $NbBe_3$

Position	Atom	x	y	z	B
3(*a*)	Nb_I	0·0000	0·0000	0·0000	0·6 Å²
6(*c*)	Nb_{II}	0·0000	0·0000	0·1402±0·0002	0·6
3(*b*)	Be_I	0·0000	0·0000	0·5000	0·6
6(*c*)	Be_{II}	0·0000	0·0000	0·3344±0·0020	0·5
18(*h*)	Be_{III}	0·504±0·010	0·496±0·010	0·0818±0·0012	1·2

The structure thus contains linear chains of three niobium atoms.

Beryllium positions may be derived by surrounding the terminal niobium atoms of these linear chains with the beryllium configuration which was found around the niobium atoms in $NbBe_2$. Twenty-one beryllium atoms are placed by this method, and the remaining six are packed around the central niobium of the chain. The structure thus obtained conforms to the diffraction symmetry, and in terms of $R\bar{3}m$ the beryllium positions are:

3 Be_I in 3(*b*): $(0,0,\frac{1}{2})+(0,0,0;\ \frac{1}{3},\frac{2}{3},\frac{2}{3};\ \frac{2}{3},\frac{1}{3},\frac{1}{3})$.

18 Be_{III} in 18(*h*): $\pm(x,\bar{x},z;\ x,2x,z;\ 2\bar{x},\bar{x},z)$ $+(0,0,0;\ \frac{1}{3},\frac{2}{3},\frac{2}{3};\ \frac{2}{3},\frac{1}{3},\frac{1}{3})$ with $x = 0{\cdot}50$, $z = 0{\cdot}07$;

6 Be_{II} in 6(*c*): $\pm(0,0,z)+(0,0,0;\ \frac{1}{3},\frac{2}{3},\frac{2}{3};\ \frac{2}{3},\frac{1}{3},\frac{1}{3})$ with $z = 0{\cdot}33$.

The intensities of 207 $h0l$ reflections, of which 69 were too weak to be observed, were recorded. The atomic parameters, including isotropic temperature factors for each atom, were refined by repeated application of the least-squares method to these data. The calculated and observed structure factors are listed in Table 2. The reliability coefficient, $R = \Sigma|F_o-F_c|/\Sigma|F_o|$, was 0·10 at the end of the refinements. When the beryllium atoms were omitted from the calculation the reliability coefficient became 0·13.

Further refinement was attempted after correction of the niobium scattering factors for dispersion, using the tables of Dauben & Templeton (1955). Little improvement in the reliability coefficient resulted from this calculation, however, and the changes in the atomic positions were insignificant.

The structure was also confirmed by the computation of the Fourier projection, $\varrho(x,z)$, on which all atoms were clearly visible at the appropriate positions.

The final $R\bar{3}m$ parameters of $NbBe_3$ are listed in Table 3, and Table 4 shows the interatomic distances calculated from these positions. The standard deviations of the parameters were calculated by the method of Cruickshank (1949), and the probable errors of the distances were obtained according to Cruickshank & Robertson (1953).

Discussion

The point symmetry at each niobium atom of the $NbBe_2$ structure is T_d–$\bar{4}3m$. Its nearest neighbors consist of 12 Be atoms at 2·71 Å and 4 Nb atoms at 2·83 Å. The configuration of the beryllium atoms around a niobium atom can be visualized by constructing a regular tetrahedron of edge 6·931 Å about the niobium and cutting off the vertices at the points of trisection of the edges (Fig. 1). The resulting polyhedron has eight faces consisting of four equilateral triangles and four regular hexagons, eighteen edges of length 2·310 Å, and twelve vertices each occupied by a beryllium atom. A niobium atom also has four niobium neighbors at a distance of 2·830 Å along the

Table 4. *Interatomic distances in* $NbBe_3$

Nb_I–	2 Nb_{II}	2·951±0·005 Å
	– 6 Be_{II}	2·634±0·003
	–12 Be_{III}	2·86 ±0·02
Nb_{II}–	1 Nb_I	2·951±0·005
	– 3 Nb_{II}	2·860±0·004
	– 3 Be_I	2·692±0·003
	– 6 Be_{III}	2·59 ±0·01
	– 3 Be_{III}	2·67 ±0·04
Be_I–	6 Nb_{II}	2·692±0·003
	– 6 Be_{III}	2·24 ±0·05
Be_{II}–	3 Nb_I	2·634±0·003
	– 3 Be_{II}	2·634±0·003
	– 3 Be_{III}	2·17 ±0·06
	– 3 Be_{III}	2·17 ±0·06
Be_{III}–	2 Nb_I	2·86 ±0·02
	– 2 Nb_{II}	2·59 ±0·01
	– 1 Nb_{II}	2·67 ±0·04
	– 1 Be_I	2·24 ±0·05
	– 1 Be_{II}	2·17 ±0·06
	– 1 Be_{II}	2·17 ±0·06
	– 2 Be_{III}	2·23 ±0·06
	– 2 Be_{III}	2·34 ±0·06

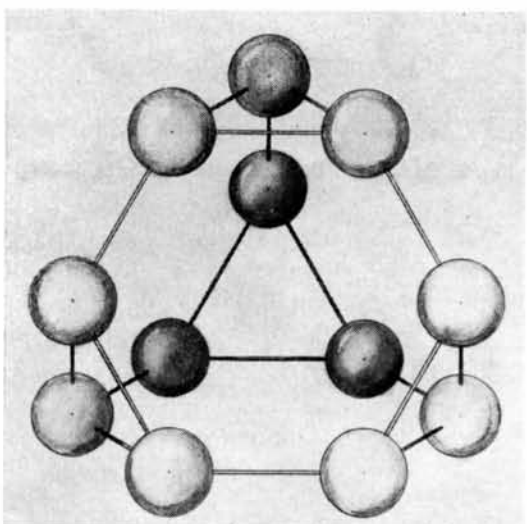

Fig. 1. Packing of Be atoms about Nb in $NbBe_2$, and about Nb_{II} in $NbBe_3$.

lines perpendicular to the hexagonal faces of the beryllium polyhedron. These niobium neighbors form another regular tetrahedron, of edge 4·621 Å. The point symmetry at a beryllium atom is D_{3d}–$\bar{3}m$. Each beryllium atom has six niobium neighbors at 2·709 Å and six beryllium neighbors at 2·310 Å.

The niobium atoms in $NbBe_3$ are of two types: Nb_I has two Nb nearest neighbors at 2·95 Å and eighteen Be nearest neighbors at an average distance of 2·78 Å; Nb_{II} has four Nb nearest neighbors, three at 2·86 Å and one at 2·95 Å, and twelve Be nearest neighbors at an average distance of 2·64 Å. The configuration of nearest neighbors about Nb_{II} is the same as that found about the Nb atoms in $NbBe_2$. The arrangement is distorted in this case, however, and the point symmetry of Nb_{II} is C_{3v}–$3m$. An Nb_I atom has the point symmetry D_{3d}–$\bar{3}m$. It is collinear with its two Nb_{II} neighbors (at 2·95 Å), and it is at the center of the regular hexagon formed by its six Be_{II} neighbors. The twelve Be_{III} neighbors of Nb_I form two smaller hexagons above and below Nb_I, parallel to and rotated 30° with respect to the Be_2 hexagon (Fig. 2). Each beryllium atom has twelve nearest neighbors; the types and distances of these neighbors are shown in Table 4. The Be_{III}–Be_{III} distances are calculated to be alternately 2·23 and 2·34 Å, but they are within experimental error of being equal. Although there are two crystallographically distinct Be_{II}–Be_{III} separations, these distances are calculated to be the same.

The Nb–Nb interatomic distance in metallic niobium is 2·86 Å, and the average Be–Be distance in metallic beryllium is 2·26 Å. All of the Nb–Nb and Be–Be nearest neighbor separations in $NbBe_2$ and $NbBe_3$ are within 4% of these values.

The environment shown in Fig. 2 occurs also in the $CaZn_5$ structure (Haucke, 1940).

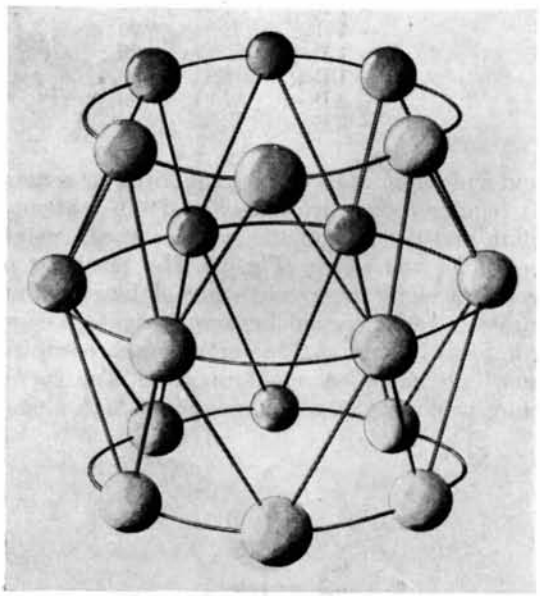

Fig. 2. Packing of Be atoms about Nb_I in $NbBe_3$.

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