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Preparation and Crystal Structure of β-Nb_2N and γ-NbN

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Samples of the niobium nitrides β-Nb_2N and γ-NbN have been obtained from the elements by sintering of niobium in nitrogen at 2100 °C (γ-NbN) or by zone melting of δ-NbN in nitrogen. In the zone melting δ-NbN is converted to β-Nb_2N and γ-NbN.

Based on a neutron diffraction powder pattern of a sample containing β-Nb_2N and γ-NbN the structures are proposed for the two compounds.

β-Nb_2N is trigonal, the space group is $P\bar{3}1m$ (No. 162) with $a = 5.267(2)$ Å, $c = 4.988(1)$ Å and three formula units per unit cell. The composition of the sample investigated is $NbN_{0.46(1)}$. γ-NbN is tetragonal, the space group is $P4/m$ (No. 83) with $a = 8.742(3)$ Å, $c = 8.592(3)$ Å, and 32 formula units per unit cell. The composition of the sample investigated is $NbN_{0.64(1)}$.

The phase diagram for the system niobium-nitrogen is complex and only partly investigated.[1] The crystal data for three of the phases found in the system are listed in Table 1.[1] All three compounds are non-stoichiometric. β-Nb_2N is trigonal, but the structure of the phase has not been investigated. The lattice parameter a of the hexagonal cell is almost independent of the composition, whereas the lattice parameter c increases rapidly from 4.955 Å for $Nb_2N_{0.8}$ to 4.995 Å for Nb_2N.[2] A structure for Nb_2N has been proposed with the niobium atoms in a hexagonal closepacking and the nitrogen atoms randomly distributed in the octahedral holes of the packing.[2]

Table 1. Unit cell parameters for β-Nb_2N, γ-NbN, and δ-NbN, Ref. 1. (Room temperature).

Phase	Crystal structure	Lattice parameters in Å N-poor boundary		N-rich boundary
β-Nb_2N	trigonal	$a = 3.056$	→	$a = 3.056$
		$c = 4.955$	→	$c = 4.996$
γ-NbN	tetragonal	$a = 4.385$	→	$a = 4.386$
		$c = 4.310$	→	$c = 4.335$
δ-NbN	cubic	$a = 4.382$	→	$a = 4.395^a$

^{a} corresponds to the stoichiometric composition.

γ-NbN is tetragonal and has a distorted sodium chloride structure,[3] but the structure of the phase has not been investigated. The unit cell parameter ratio c/a approaches 1 with increasing temperature and nitrogen content. The lattice parameter a of the tetragonal cell is almost independent of the composition, whereas the lattice parameter c increases with increasing nitrogen content, see Table 1. δ-NbN is cubic and has the sodium chloride structure.[3] The lattice parameter a increases from 4.382 Å for $NbN_{0.86}$ to 4.395 Å for NbN. It is possible to increase the stability of δ-NbN at high nitrogen pressures to the composition $NbN_{1.062}$. For this composition the niobium sub-lattice is defective,[4] and the unit cell parameter is smaller than 4.395 Å. δ-NbN is metallic and becomes superconductive at $T_c = 17.3$ K. The purpose of this investigation was to produce well characterized specimens of β-Nb_2N, γ-NbN and δ-NbN, so that crystal structures and other physical properties could be investigated. In the following the formulae β-Nb_2N, γ-NbN, and δ-NbN will be used for the nonstoichiometric compounds.

EXPERIMENTAL

Sample preparation and X-ray technique. Attempts have been made to prepare single crystals of β-Nb_2N, γ-NbN, and δ-NbN by a floating zone crystal growth technique. The starting materials for the crystal growth experiments were powders of Nb of the nominal purity 99.8 % and nitrogen gas of the nominal purity 99.99 %. The metal powder was placed in rubber moulds which were sealed, evacuated and pressed at an isostatic pressure of 5000 atm to produce rods. The rods were either sintered in pure nitrogen to produce rods of niobium nitride or were zone melted in pure helium (99.99 % He) to produce solid bars of niobium. The experimental conditions for sintering are listed in Table 2.

The rods of niobium nitride were zone melted in an ADL MP crystal growth furnace using the zone melting procedure previously reported.[5] The experimental conditions for these crystal growth experiments are listed in Table 3.

Table 2. Experimental conditions for the preparation of rods of δ-NbN by sintering. Raw material Nb.

Preform No.	A[a]	B	C	D	E
1	8.3	*	30	–	2
2	10	2	11.8	1700	4
3	1.7	5	7	–	3.5

[a] A: N_2 gas pressure in atm. B: R.F. sintering coil No. * indicates the use of a zone melting coil. C: Power kW. D: Temperature of specimen measured with pyrometer. E: Duration of sintering in h.

Table 3. Experimental conditions for the zone melting of niobium nitrides. Preform of NbN.

Experiment No.	A[a]	B	C	D	E
NbN 1	17.0	2	13.7	64	50
NbN 2	19.5	2	15.9	130	10
NbN 3[b]	15.5	5	20.0	45	10
NbN 4	1.3	9	13.6	38	7.5
NbN 5[b]	11.5	9	15.0[c]	30	20
	16.5	9	11.4[d]		7.5
NbN 6[b]	16.5	9	9.0 to 13.0	55	10
NbN 7	2.0	9	13.4[c]	30	20
	17.0	9	17.0[d]	16	2.0

[a] A: N_2 gas pressure in atm. B: R.F. coil No. C: Power kW. D: Length of zone melted specimen. E: Growth rate in mm h^{-1}. [b] Preform of Nb. [c] First pass. [d] Second pass.

Guinier powder photographs obtained with a Guinier powder camera with Cu$K\alpha_1$, $\lambda = 1.54051$ Å or Co$K\alpha_1$, $\lambda = 1.78892$ Å and with sodium chloride, $a_{NaCl} = 5.6389$ Å or germanium, $a_{Ge} = 5.6576$ Å as an internal standard, and optical metallography have been used to characterize the specimens. The results indicated that single crystals of δ-NbN cannot be obtained with a zone melting technique at the experimental conditions used. The sintered rods of δ-NbN are converted to specimens containing β-Nb_2N and γ-NbN in the zone melting procedure.

The solid bars of niobium were sintered in pure nitrogen using the experimental conditions listed in Table 4. The specimens were examined using optical metallography, and Guinier powder patterns were taken of the specimens as well. The results indicate that niobium by this treatment is converted to γ-NbN.

All the lines in the X-ray diffraction powder pattern of γ-NbN can be indexed with a tetragonal cell with $a_\gamma = 4.392(2)$ Å and $c_\gamma = 4.321(3)$ Å. However, precession photographs of a multidomain twinned specimen of γ-NbN show weak additional reflections corresponding to the unit cell parameters $a_T = 2a_\gamma$, and $c_T = 2c_\gamma$.

X-Ray powder patterns of a sample containing β-Nb_2N and γ-NbN were obtained with a powder diffractometer at temperatures from room temperature to 1700 °C. From these powder patterns the unit cell parameters for

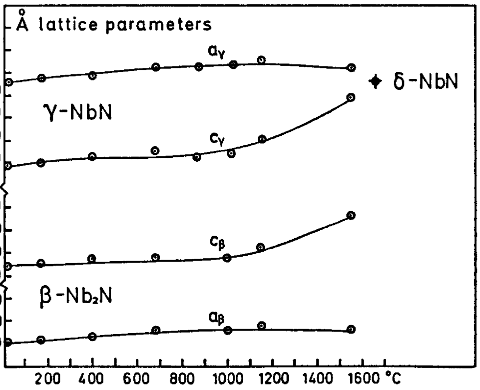

Fig. 1. The variation of the unit cell parameters of β-Nb_2N and γ-NbN with temperature. The values given are for the two subcells that can index the X-ray powder patterns but not the neutron powder patterns.

When heated to 1663 °C the diffraction lines from γ-NbN have disappeared and the diagram has lines of δ-NbN ($a = 4.372$ (5) Å). When the sample is cooled to room temperature the diffraction diagram shows again the lines from γ-NbN without any diffraction lines from δ-NbN.

Table 4. Experimental conditions for sintering of rods of niobium and niobium nitride.

Exp. No.	A[a]	B	C	D	E
NbN 8[c]	15.7	1350	24	γ-NbN+β-Nb_2N	unchanged
NbN 9[b]	17.0	1480	89	γ-NbN+Nb	main product Nb
NbN 10[b]	17.0	2000	66	γ-NbN	crystal twinned
NbN 11[b]	20.00	2100	112	γ-NbN	crystal twinned
NbN 12[c]	20.0	2100	90	γ-NbN	crystal twinned

[a] A: N_2 gas pressure in atm. B: Temperature of specimen °C measured with pyrometer. C: Duration of sintering in h. D: Composition of specimen. E: Comments. [b] Niobium. [c] Niobium nitride.

the two compounds were calculated, and the results of these measurements are shown in Fig. 1. No internal standard has been used in the determination of these unit cell parameters.

Neutron diffraction technique. A neutron diffraction powder pattern of a sample containing β-Nb_2N and γ-NbN was measured at room temperature using a triple-axis spectrometer with an energy analyser at the DR3 reactor at Risø. This instrument was chosen to obtain a low background intensity of the diagram. The sample was placed in a 12 mm diameter cylindrical vanadium container. The neutron wave length was 1.6886 Å (reflection from a (111) plane of a Ge monochromator). The diffraction pattern is shown in Fig. 2.

Crystal data and structure refinement. The diffraction pattern showed only reflections belonging to the two compounds β-Nb_2N and γ-NbN. The reflections from β-Nb_2N could be indexed with a hexagonal unit cell with $a_H = \sqrt{3}a_\beta$, and $c_H = c_\beta$, where a_β and c_β are comparable with the unit cell parameters for β-Nb_2N listed in Table 1. The reflections from γ-NbN could be indexed with a tetragonal unit cell with $a_T = 2a_\gamma$ and $c_T = 2c_\gamma$, where a_γ and c_γ are comparable with the unit cell parameters for γ-NbN listed in Table 1. The unit cell parameters for the two components are listed in Table 5.

The reflections for β-Nb_2N (except those within brackets in Fig. 2) could be completely

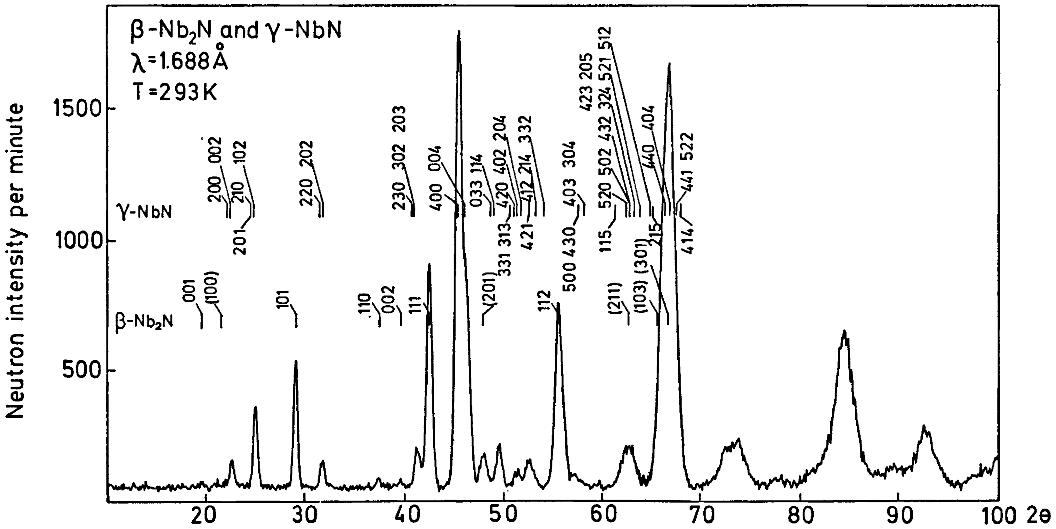

Fig. 2. Neutron diffraction powder pattern of a sample containing β-Nb_2N and γ-NbN.

Table 5. Composition, unit cell parameters and space group for β-Nb_2N and γ-NbN.

Formula	Composition	Unit cell parameters in Å		Space group
		a	*c*	
β-Nb_2N	$NbN_{0.46(1)}$	5.267(2)	4.988(1)	$P\bar{3}1m$ (No. 162)
γ-NbN	$NbN_{0.64(1)}$	8.742(3)	8.592(3)	$P4/m$ (No. 83)

resolved from reflections belonging to γ-NbN, and were used in the refinement of the structure of β-Nb_2N. The program F418 by Rietveld using a refinement on the profile intensities of the reflections was used.[6] The size of the unit cell for β-Nb_2N indicates that the cell contains three formula units and that the structure is of the ε-Fe_2N type[7] with space group $P\bar{3}1m$. In this space group the metal atoms can be placed in the 6*k* site with $x=0.3333$ and $z=0.25$, and the nitrogen atoms can be placed in the 2*d* and in the 1*a* sites. The diffraction data were not sufficient to permit a refinement of all possible parameters in the structure. The positional parameters of niobium have been fixed at the values mentioned above and all temperature factor parameters have been given the value zero. The parameters refined are a scale factor and two occupancy factors for site 6*k* and 2*d*. The results of the refinement are listed in Table 6. The niobium site and one of the nitrogen sites are only partly occupied corresponding to the composition of the β-Nb_2N sample investigated: $Nb_2N_{0.93(2)}$. The results of the refinement have been used to calculate all possible contributions from β-Nb_2N to the diffraction pattern (Fig. 2) from $2\theta = 10°$ to $2\theta = 70°$. These calculated contributions have been subtracted from the diffraction pattern to give a difference pattern with contributions only from γ-NbN.

The reflections of γ-NbN shown in Fig. 2 have been used in the refinement of the structure of γ-NbN, using the same refinement program as for β-Nb_2N. The composition of γ-NbN has been reported to be in the range $NbN_{0.75-0.79}$,[2,3] and the structure has been assumed to be a distorted sodium chloride structure. The formula Nb_4N_3 has been proposed for γ-NbN.[9] The size of the unit cell for γ-NbN indicates that the cell contains 32 formula units (assuming the composition NbN). The distortion of the sodium chloride structure is most likely related to the non-stoichiometry of the compound. For γ-NbN the space group $P4/m$ has been assumed with the possible positions of the atoms listed in Table 7. As the unit cell has a shorter *c*-axis than *a*-axis, the distortion of the structure is likely to be due to nitrogen vacancies in planes parallel to the 001 plane and to deviations of the *z*-parameters for the atoms from the values 0,1/4, 1/2, and 3/4.

The diffraction data were not sufficient to permit a refinement of all possible parameters in the structure. The temperature factor parameters have been set to zero and some positional parameters have been given fixed values (Table 7). The *z*-parameter for Nb9 and Nb10 and for the nitrogen atoms N1, N6, N7, and N8 have been refined, as well as occupancy factors for all the nitrogen atoms and a scale factor. The final values of parameters giving an acceptable agreement between the observed and the calculated diffraction pattern are listed in Table 7. The nitrogen site 8*l* (N1) is only partly occupied, and the two nitrogen sites 4*k* (N3) and 2*g* (N7) are vacant. From this the composition of the sample of γ-NbN investigated is $NbN_{0.64(1)}$.

In the refinement of the structure for the two compounds the atomic scattering length

Table 6a. Results of the refinement of the structure of β-Nb_2N.[a]

Atom	Atom site	*x*	*y*	*z*	Multiplicity Theor.	Calc.
Nb	6*k*	0.3333	0	0.2500	0.5	0.385(6)
N1	2*d*	1/3	2/3	1/2	0.16667	0.095(6)
N2	1*a*	0	0	0	0.08333	0.08333

[a] Scale factor = 0.0717, $R = 10.6$ %, $R(F^2) = 13.1$ %. (For definition of *R* (profile) and $R(F^2)$ (nuclear) see Ref. 8).

for Nb and N were 0.711 and 0.940 (× 10^{-12} cm), respectively.[10]

Table 6b. Observed and calculated intensities for β-Nb_2N and γ-NbN. Reading from left to right the columns are: *hkl* I_{calc} I_{obs}.

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BETA NIOBIUM NITRIDE    4 2 0     307    309
0 0 1     21    183     4 0 2     428    441
1 0 1   5529   5011     2 0 4     419    556
1 1 0    121    288     4 2 1      57    105
0 0 2   .365    231     4 1 2     595   1026
1 1 1  11146  11447     2 1 4     402    347
1 1 2  10687  12538     3 3 2     100     30
                        5 0 0       0     25
                        4 3 0       0     48
GAMMA NIOBIUM NITRIDE   4 0 3     206    983
2 0 0    705    472     3 0 4      13     66
0 0 2    479    768     1 1 5      60     72
2 1 0   1297   2125     5 2 0     256    218
2 0 1    110    167     5 0 2     227    211
1 0 2   1124   1107     4 3 2     453    423
2 2 0    360    559     4 2 3     310    317
2 0 2    785    562     3 2 4     308    333
2 3 0    520    370     2 0 5     261    262
3 0 2    458    684     5 2 1     159    142
2 0 3   .311    868     5 1 2     154    127
4 0 0  26517  25952     2 1 5     237    154
0 0 4  11435  11591     4 4 0   14600  15468
0 3 3    376    503     4 0 4   25620  27174
1 1 4    193    298     4 4 1     261    282
3 3 1      5      3     5 2 2       2      2
3 1 3     83     48     4 1 4      21     23
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CONCLUSION

The crystal growth investigation indicates that single crystals of δ-NbN cannot be obtained from sintered rods of δ-NbN using a zone melting technique at the experimental conditions used. It also shows that single crystals of β-Nb_2N or γ-NbN cannot be obtained in a floating zone crystal growth experiment as this always results in formation of a specimen containing β-Nb_2N and γ-NbN in a lamella structure. The pure phase γ-NbN can, however, be obtained by sintering of niobium in pure nitrogen.

The neutron diffraction investigation shows that β-Nb_2N has the ε-Fe_2N structure (Fig. 4). A model for the structure of γ-NbN where some of the niobium-nitrogen layers are completely occupied, and where some of the layers have vacancies at the nitrogen atom positions (see Fig. 3), fits best to the diffraction data. This model can yield an explanation of the fact that the unit cell parameter c for γ-NbN is increasing and the unit cell parameter a is constant with increasing nitrogen content of γ-NbN. The unit cell parameter a is fixed by the fully occupied layer for $z=0$. When the

Table 7. Results of the refinement of the structure of γ-NbN.[a]

Atom	Atom site	x	y	z	Multiplicity Theor.	Calc.
Nb1	1*a*	0	0	0	0.125	0.125
Nb2	1*b*	0	0	1/2	0.125	0.125
Nb3	1*c*	1/2	1/2	0	0.125	0.125
Nb4	1*d*	1/2	1/2	1/2	0.125	0.125
Nb5	2*e*	0	1/2	0	0.250	0.250
Nb6	2*f*	0	1/2	1/2	0.250	0.250
Nb7	4*j*	0.2500	0.2500	0	0.500	0.500
Nb8	4*k*	0.2500	0.2500	1/2	0.500	0.500
Nb9	8*l*	0.2500	0.0	0.243(7)	1.000	1.000
Nb10	8*l*	0.5000	0.2500	0.256(7)	1.000	1.000
N1	8*l*	0.2500	0.2500	0.202(6)	1.000	0.29(2)
N2	4*k*	0.2500	0.0	1/2	0.500	0.500
N3	4*k*	0.5000	0.2500	1/2	0.500	0.0
N4	4*j*	0.2500	0.0	0	0.500	0.500
N5	4*j*	0.5000	0.2500	0	0.500	0.500
N6	2*h*	1/2	1/2	0.288(7)	0.250	0.250
N7	2*g*	0	0	0.2500	0.250	0.0
N8	4*i*	0	1/2	0.253(5)	0.500	0.500

[a] Scale factor = 1.8156, R = 8.6 %, $R(F^2)$ = 5.6 % (for observed and calculated intensities see Table 6b). Coordinates that may be used as parameters are listed as decimal fractions with standard deviations in brackets. Where no standard deviations are listed the coordinates have not been refined.

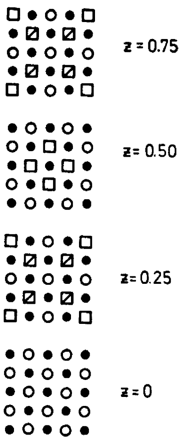

Fig. 3. Niobium-nitrogen layers in the structure of γ-NbN. Filled circles indicate niobium atom positions, and open circles nitrogen atom positions. Open squares are vacant nitrogen atom positions and partly filled squares are partly occupied nitrogen atom positions. The atomic layer for $z=0$ is complete. In the layer for $z=1/4$ approximately three nitrogen atoms are missing, and in the layer for $z=1/2$ four nitrogen atoms are missing.

occupancy of the nitrogen atom sites of the layers for $z=1/4$, $1/2$, and $3/4$ is increased, the spacing between these layers will increase, and the unit cell parameter c will be longer. The nitrogen content in the sample investigated of γ-NbN is low, $NbN_{0.64}$, compared to the values reported previously.[2,3,9]

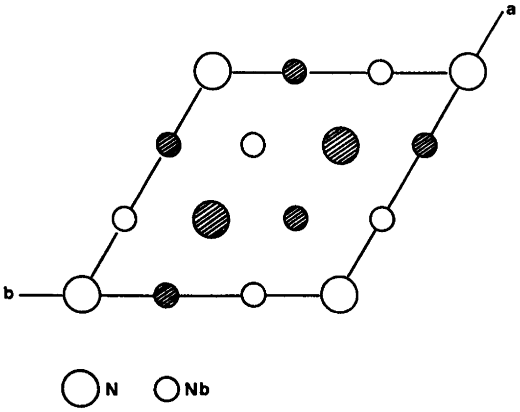

Fig. 4. Projection of the structure of β-Nb_2N along the [001] direction. Nitrogen atoms with $z=0.5$ and niobium atoms with $z=0.75$ are hatched.

This is possible because the sample investigated has been prepared at a temperature higher than that for the samples from Refs. 2 and 3. As the neutron diffraction powder pattern was made on a sample containing both compounds, the structures arrived at for β-Nb_2N and γ-NbN have not been obtained by a traditional refinement procedure. The diffraction data available are not sufficient to permit a refinement of all possible parameters, and the parameters are strongly correlated. Therefore the two structures should only be regarded as structural proposals. The high temperature X-ray powder diffraction investigation shows, that at temperatures between 1550 and 1660 °C and nitrogen gas pressures of 1 atm γ-NbN transforms to δ-NbN as the c/a ratio approaches unity. The transformation from δ-NbN to γ-NbN involves an order-disorder reaction. δ-NbN is cubic and substoichiometric in nitrogen with the vacancies randomly distributed at the nitrogen sites. The transformation from δ-NbN to γ-NbN on cooling of specimens results in formation of samples with a lamella structure and twinning (see Table 4) similar to the twinning formed in a Martensitic phase transformation.

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