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An X-Ray and Neutron Diffraction Investigation of the Crystal Structure of γ-NbN

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The compound γ-NbN was made by annealing of niobium in nitrogen. X-Ray and neutron diffraction show the compound to be tetragonal, the space group is $I4/mmm$ (No. 139) with $a=4.377(4)$, $c=8.719(3)$ Å. The unit cell contains 8 formula units of $NbN_{0.801(1)}$.

Single crystal X-ray intensity data were measured on an automatic diffractometer with equiinclination Weissenberg geometry using Mo$K\alpha$ radiation ($\lambda=0.71069$ Å) reflected from a graphite monochromator crystal and a scintillation counter. Single crystal neutron intensity data were measured on an automatic four-circle diffractometer using 0.53 Å neutrons.

Least-square refinements gave the final $R(F)$-value 4.5 % for the neutron diffraction data and the $R(F)$-value 5.0 % for the X-ray diffraction data. The structure is a superstructure of the sodium chloride structure. The nitrogen sublattice has filled sites and partly vacant sites. The niobium atoms are coordinated octahedrally with the ligands of the nitrogen sublattice. The longest and shortest niobium–nitrogen distances within the octahedra are 2.226(1) and 2.133(1) Å, respectively.

In the system niobium–nitrogen two phases with related structures are known: δ-NbN is cubic with the sodium chloride structure, and γ-NbN is tetragonal with a modulated sodium chloride structure. At room temperature δ-NbN exists in the composition range $NbN_{1.06}$—$NbN_{0.86}$, and γ-NbN in the range $NbN_{0.79}$–$NbN_{0.75}$.[1-3] The two compounds can be made by zone annealing of niobium in nitrogen at temperatures up to 2100 °C and pressures up to 2 MPa. γ-NbN is transformed to δ-NbN on heating with a transition temperature of approximately 1800 °C.[4] The unit cell parameter for δ-NbN varies between $a=4.382$ and $a=4.395$ Å, dependent upon the deviation from stoichiometry. A Guinier powder pattern of γ-NbN can be indexed with a tetragonal cell with the parameters $a=4.385\rightarrow4.386$, $c=4.310\rightarrow4.335$ Å, also dependent upon the composition. However, single crystal precession photographs of γ-NbN show some additional weak reflections,[4] which can be indexed with a superstructure cell $a_T=2a$, and $c_T=2c$. From a neutron diffraction investigation of a powder containing γ-NbN and β-Nb_2N, a structure was proposed for γ-NbN where the vacant positions in the nitrogen sublattice were partly ordered, and it was suggested that this was the origin of the superstructure reflections of the neutron diffraction powder pattern.[4] The nature of the phase transition δ-NbN→γ-NbN would thus be a partial ordering of the vacant sites in the nitrogen sublattice possibly combined with a modulation of some atomic coordinates.

In X-ray diffraction of γ-NbN the niobium atoms contribute on an average 97 % of the intensity. Thus X-ray data may not yield sufficient information about the nitrogen atom positions. The intensities of some superstructure reflections indicate that at least some of the atoms in the niobium sublattice are shifted to non-special positions. For neutron diffraction the nitrogen atoms contribute on an average 60 % of the intensity. Neutron diffraction data may thus give information about both sorts of atoms and especially these data may be used to determine the occupancy of the sites in the nitrogen sublattice. It was therefore decided to investigate the structure of γ-NbN using a combination of single crystal X-ray and neutron diffraction methods.

Only a few structures and superstructures of transition metal nitrides have been investigated

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previously, and none of these investigations have included structure factor calculations and structure refinements on sets of single crystal X-ray or neutron diffraction data. The crystal structure of γ-NbN has been investigated by Terao [5] by combining information from electron diffraction diagrams and from X-ray powder patterns. The structure was described with a tetragonal unit cell with $a=4.382$ Å and $c=8.632$ Å ($a_T=a$, $c_T=2a$), but no space group was assigned to the structure. It contains eight niobium atoms and six nitrogen atoms, that is two Nb_4N_3 formula units. All atoms are at special positions, and of the eight possible sites in the nitrogen sublattice six positions are filled and two positions are vacant. This structure is sometimes referred to in the literature as the Nb_4N_3 type structure.

The structure of γ-NbN (Nb_4N_3) was further studied by Oya and Onodera [6] using electron diffraction of thin films of γ-NbN. Although the electron diffraction pattern given in Ref. 6 for γ-NbN clearly shows a diffraction pattern that can only be indexed with a unit cell $a_T=b_T=2a$ or $a_T=2a$ and $c_T=2a$ the structure was described with the same unit cell as in Ref. 5 as a structure with ordered vacant sites in the nitrogen sublattice. No space group was assigned to the structure.

The structure of $TiN_{0.61}$ was studied by Nagakura and Kusunoki [7] using electron diffraction and microscopy. The unit cell parameters are $a_T=a$ and $c_T=2a$, and all the observed reflections satisfy the condition $h+k+l=2n$, so the structure was described in space group $I4_1/amd$ with eight titanium atoms in site 8*e* with $z=0.25\pm0.018$, four nitrogen atoms in site 4*b*. The structure has thus a partial ordering of the vacant sites in the nitrogen sublattice and a modulation of the *z*-coordinates of the titanium atoms. In the atomic layers with $z=r/4\pm0.018$ the modulation of the *z*-coordinates in the diagonal directions [110] is alternating as $r/4+0.0018$ and $r/4-0.0018$, with $r=1$ or 3.

Finally, the structure of $VN_{0.81}$ was investigated by Onozuka [8] using electron diffraction and microscopy. The tetragonal unit cell has $a_T=2a$ and $c_T\approx2a$ and the structure is described in the space group $P4_2/nmc$, although the stated systematic absences *hhl* with $l=2n+1$ and *h*00 with $h=2n+1$ are not the conditions limiting possible reflections in that space group. The model of the structure has no modulation of the atomic coordinates in the two sublattices, but has a partial ordering of vacant sites in the nitrogen sublattice.

EXPERIMENTAL

Sample preparation. A specimen of γ-NbN was made by zone annealing of niobium in nitrogen. Approximately 1 cm^3 of the specimen was further annealed in nitrogen at 2 MPa, 2100 °C for 100 h. The sample was now γ-NbN with the composition $NbN_{0.78}$ estimated from the values of its unit cell parameters. A Guinier photograph of part of the sample, using germanium, $a_{Ge}=5.6576$ Å, as an internal standard, gave the tetragonal unit cell (based on the large cell) $a=8.754(3)$, $c=8.719(3)$ Å.

X-Ray diffraction technique. X-Ray diffraction data were measured on an automatic diffractometer with equiinclination Weissenberg geometry using a scintillation counter and Mo$K\alpha$ radiation, $\lambda=0.71069$, reflected from a graphite monochromator crystal. A single crystal of dimensions $0.038\times0.108\times0.083$ mm was used. The crystal was mounted along the [100] direction. A total of 17241 reflections was measured. The intensities were corrected for absorption using Wells' method [9] ($\mu=128$ cm^{-1}). Averaging gave a total of 223 independent reflections with $I>3\sigma(I)$. Of these 52 reflections belonged to the small cell and 117 reflections were superstructure reflections.

Neutron diffraction technique. A single crystal with a volume of 46 mm^3 was cut from the specimen using spark erosion. Laue back reflection photographs showed that the crystal was of good quality and was used to orient the crystal along the [001] direction. The crystal had a rather irregular shape. The surface could be described by nine faces with the Miller indices: (00$\bar{1}$), (00$\bar{1}$), (543), (9 $\bar{1}\bar{1}$ 0), (5 $\bar{1}$0 9), ($\bar{3}$ 4 0), ($\bar{1}$ 0 0), ($\bar{7}$ $\bar{6}$ 8), (5 $\bar{4}$ $\bar{3}$).

Neutron diffraction data (data I) were measured on a four-circle diffractometer at DR3, Risø, using 1.07 Å neutrons, and the ω-scan technique. A total of 3555 reflections was measured, the measuring time for each reflection was approximately 15 min. The measured reflections were selected to give an even distribution in reciprocal space, leaving out some that were expected to be small according to a structure factor calculation using the suggested structure [4] in space group $P4/m$. Some of the strongest reflections were measured twice. Data reduction gave a total of 517 reflections with $I>0$. An absorption correction with $\mu(\text{calc})=0.14$ cm^{-1} was included in the data reduction. Of the 517 reflections 26 belonged to the small cell and 491 were superstructure reflections. This set of data was used in the preliminary model calculations. Extinction and multiple scattering effects made it necessary to measure another set of neutron diffraction data (data II) on the four-circle diffractometer D9 at the high flux reactor at the Laue-Langevin Institute in Grenoble using 0.53 Å neutrons. The single crystal used for data I was reduced in size to a volume of

27 mm^3 using spark erosion. Its surfaces could be described by nine faces with the Miller indices: (0 0 1), (0 0 $\bar{1}$), (1 1 0), ($\bar{1}$ $\bar{1}$ 0), (1 $\bar{1}$ 0), ($\bar{1}$ 1 0), (1 0 0), (6 $\bar{3}$ $\bar{5}$), ($\bar{16}$ $\bar{20}$ $\bar{3}$). A hafnium filter was used to remove second order contamination. All strong reflections with $\sin\theta/\lambda < 1.6$ and a large number of selected weak reflections with $hkl > 0$ were measured, in all 1900, and in addition the 800 strongest of these were measured for $h < 0$. The reflections were selected as described above, and the set of data was reduced in the same way as for data I giving a total of 632 reflections with $I > 3\sigma(I)$. Of these 632 reflections 81 belonged to the small cell. By measuring a few selected strong reflections at different diffractometer geometry it was found that double reflection and thus probably also extinction corrections in this set of data could be neglected.

STRUCTURE REFINEMENT

Independent of this work, a single crystal neutron diffraction investigation of the structure of γ-NbN was recently made by Heger and Baumgartner.[10] The investigation was made on a multidomain twinned crystal having three crystal orientations. The structure was described in space group *I4/mmm* with the unit cell parameters $a_T = 4.386(4)$, and $c_T = 8.683(5)$ Å. In the structure refinement 78 reflections with $I > 2.5\sigma(I)$ were used, corresponding to scattering contributions from one out of the three crystal orientations of the twinned crystal specimen.

In the previous investigation[4] of the structure of γ-NbN, precession photographs showed superstructure reflections which were indexed with the unit cell $a_T = 2a$ and $c_T = 2c$, and the X-ray and neutron diffraction data collections were made under this assumption. However, precession photographs taken of a number of different crystal specimens from the same bulk crystal of γ-NbN showed variation in the intensities of the superstructure reflections. The hypothesis that the crystals used in the X-ray and neutron diffraction data collections were multidomain twinned crystals could thus not be ruled out. The data were according to this hypothesis reindexed, and in the structure refinements the model used by Heger and Baumgartner[10] was used. The structure was thus refined in the space group *I4/mmm* (No. 139) with the unit cell parameters $a = 4.377(2)$, $c = 8.719(3)$ Å. The least-squares program LINUS[11] was used with the scattering length 0.711 and 0.94 (in units of 10^{-12} cm) for Nb and N, respectively.[12] In order to use all the measured diffraction data in the structure refinements the least-squares program was modified to add the scattering contributions from the three crystal orientations of the crystal specimen. Each of these had its own scale factor. The results of the refinements including the three scale factors are listed in Table 1.

After the structure was solved and refined using the neutron diffraction data II, the structure was refined using the X-ray diffraction data. The coordinates listed in Table 1 were used as starting

Table 1. Results of the refinements of the structure of γ-NbN.

Atom	Site	x	y	z	U_{11}[a]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Multiplicity Theor.	Found
Neutron diffraction data II												
N1	2*a*	0	0	0	53(1)	53(1)	0	0	0	0	0.25	0.051(1)
N2	2*b*	0	0	1/2	49(1)	49(1)	52(2)	0	0	0	0.25	0.25
N3	4*d*	0	1/2	1/4	58(1)	58(1)	57(2)	0	0	0	0.50	0.50
Nb1	4*e*	0	1/2	0	41(2)	78(2)	38(2)	0	0	0	0.50	0.50
Nb2	4*c*	0	0	0.2447(1)	49(1)	49(1)	86(3)	0	0	0	0.50	0.50
$R = 4.5$ %, scale factors: 1.663(5), 1.068(12) and 0.854(12). 758 intensities.												
X-Ray diffraction data												
N1	2*a*	0	0	0	73(7)[b]	0	0	0	0	0	0.25	0.051(1)
N2	2*b*	0	0	1/2	73(7)[b]	0	0	0	0	0	0.25	0.25
N3	4*d*	0	1/2	1/4	73(7)[b]	0	0	0	0	0	0.50	0.50
Nb1	4*e*	0	1/2	0	54(8)	75(8)	95(8)	0	0	0	0.50	0.50
Nb2	4*c*	0	0	0.2438(1)	81(7)	81(7)	101(8)	0	0	0	0.50	0.50
$R = 5.0$ %, scale factors: 0.0811(8), 0.0512(16) and 0.0358(16). 272 intensities.												

[a] The anisotropic temperature factor parameters are multiplied by 10^4. [b] Isotropic temperature factor multiplied by 10^4.

parameters and only positions and temperature factor parameters for the niobium atoms and the scale factor were refined. The atomic scattering factors reported by Cromer and Mann[13] for Nb and N were used. The results of this refinement are listed in Table 1. A list of structure factors of the neutron data II and the X-ray data is available on request.

DISCUSSION

The structure investigation confirms that the origin of the superstructure reflections of γ-NbN is a combination of partly ordered vacant sites in the nitrogen sublattice and a shift out of the positions with $z=1/4$ and $z=3/4$ for one of the atoms in the niobium sublattice. The modulation of the niobium sublattice found by using the X-ray data is in acceptable agreement with that found using the neutron diffraction data II.

The nitrogen sublattice has two filled and one partly filled site as indicated in Fig. 1. The previously described structure of Nb_4N_3,[5] had the nitrogen site 4*e* vacant.

When the structure is described by layers of atoms at $z=0$, 1/4, 1/2 and 3/4 (Fig. 1), two layers with $z=0$ and 1/2 have 60.2 % of the nitrogen sublattice filled and the layers with $z=1/4$ and 3/4 have 100 % of the nitrogen sublattice filled. This gives the composition $NbN_{0.801(1)}$ for the crystal investigated in acceptable agreement with the composition $NbN_{0.78}$ deduced from the unit cell parameters of the crystal. In the model suggested previously based on a neutron diffraction powder pattern the layers for $z=1/4$ and 3/4 had identical arrangements of filled, partly filled, and empty sites of the nitrogen sublattice while the layers with $z=0$ and 1/2 had not identical arrangements of the vacant sites. It is to be expected that a single crystal investigation can give a much more detailed model of the structure than that arrived at from a neutron diffraction powder pattern with a very limited number of reflections.

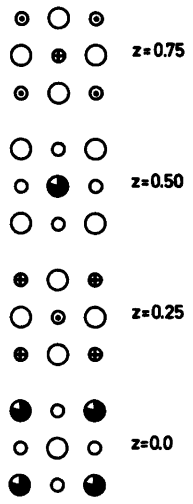

Fig. 1. Packing of the atoms in the layers with $z=0$, 1/4, 1/2 and 3/4. The niobium atoms in the layers with $z=1/4$ and 3/4 are shifted out of the layers in the direction of the partly vacant sites. The black area of the circle indicates the fraction of the atom that is missing statistically.

In the niobium sublattice the atoms in the layer with $z=0$ and 1/2 are placed exactly in the layers and the atoms in the layers with $z=1/4$ and 3/4 are shifted significantly out of these layers. Atoms with positions over the layers are in Fig. 1 shown as a circle with a dot in it, atoms with positions under the layers are shown as a circle with a cross in it.

The niobium atom Nb2 is placed at the layer with $z=1/4$ and over the partly vacant nitrogen site in the layer with $z=0$, and is shifted 0.047(1) Å towards the vacant site. The interatomic distances in the two coordination polyhedra are shown in Fig. 2. The results arrived at in this investigation is in acceptable agreement with the results found by Heger and Baumgartner.[10] As the present neutron diffraction data set contains 758 independent observed intensities in contrast to the 78 intensities used in Ref. 10, this investigation yields a more detailed model with anisotropic temperature factor parameters for all atoms except the sparsely populated nitrogen at site 2*a*. In Ref. 10 the isotropic mean-square displacements of this atom were three to four times greater than for the other atoms in the structure. This was interpreted as a

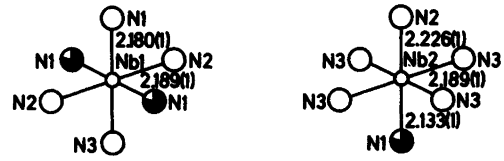

Fig. 2. Coordination polyhedra of the two niobium atoms Nb1 (0, 1/2, 0) and Nb2 (0, 0, 0.2447). Nb1 has a centrosymmetric arrangement of the ligands N1, N2 and N3. Nb2 has four ligands arranged centrosymmetrically, N3, and has in addition the two ligands N1 and N2.

dominant static displacement of the nitrogen atom N1. The present investigation does not support this hypothesis. Refinement showed only a slight tendency towards a higher thermal parameter for N1 but high correlation with the occupation factor, in spite of the inclusion of high order data. Therefore the thermal parameter for N1 was fixed. Anisotropic refinement showed that the other nitrogen atoms are isotropic, whereas the niobium atoms show anisotropy corresponding to the equilibrium position of niobium atom being dependent on whether the neighbouring 2*a* site is occupied or not.

The structure arrived at explains the variation of the unit cell parameter with the temperature for γ-NbN and that the phase transition from γ-NbN to δ-NbN at approximately 1800 °C is an order-disorder transition as the vacant sites in the nitrogen sublattice of δ-NbN are randomly distributed. With increasing temperature the *c*-axis increases and the *a*-axis of γ-NbN is showing a much smaller variation with temperature.[4] The packing of the atoms in the layers with $z=0$ and 1/2, with all the atoms placed in the layers, determines the size of the *a*-axis of the unit cell. In the layers with $z=1/4$ and 3/4 the niobium atoms are displaced from the plane of the layer towards the vacancies. With increasing temperature these displacements will decrease as the vacancies become disordered in δ-NbN and the niobium atoms occupy sites in the planes. This decrease of the displacements will result in an increase of the *c*-axis of γ-NbN.

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