Vacancy Order in Nb_6C_5

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Niobium carbide has the sodium chloride type structure in the composition range $NbC_{0.77-0.99}$. Diffuse neutron scattering experiments with a single crystal of $NbC_{0.73}$ have shown a short-range order where the niobium atoms are shifted 0.03 Å away from the first nearest neighbour vacant site of the carbon sublattice.[1] A V_6C_5 type[2] superstructure of niobium carbide is obtained when samples of $NbC_{0.80-0.85}$ are annealed below 1000 °C.[3] The trigonal unit cell (using hexagonal setting) of the long-range ordered phase is related to that of the cubic cell as: $a_{hex}=\sqrt{3/2}\cdot a_c$, $c_{hex}=2\sqrt{3}\cdot a_c$, and the space group is $P3_1$ (No. 144). The superstructure is ideally made of $Nb-C_5\square$ octahedra where one site of the carbon sublattice is vacant. A neutron powder diffraction investigation has shown that the niobium atoms in the $Nb-C_5\square$ octahedra are shifted away from the vacant site in the same way as in the short-range order case.[3] However, the investigation indicated that the vacant site contained some scattering density. The investigation reported below was made to clarify this observation.

A single crystal of $NbC_{0.83}$ was annealed in a HP-crystal growth unit with an ambient He gas pressure of 0.4 MPa. The crystal was kept at 1100 °C for 1 h and was then slowly cooled to 600 °C over 45 h. This annealing time is considerably shorter than that used in Ref. 3 where the powder samples were annealed for 15 days in vacuum. The powder samples (Ref. 3) showed a scattering contribution at the vacant carbon site of 20 to 44 % of the scattering contribution of a carbon atom.

The long-range ordered superstructure is known from electron microscopy to form multidomain twins.[4] As the direction of c_{hex} is along the 111 directions of the cubic cell, this fact is understandable. A cubic single crystal of $NbC_{0.83}$ may thus be annealed to a sample with four directions for c_{hex} ([$\bar{1}11$], [$\bar{1}\bar{1}1$], [$1\bar{1}1$], and [111] of the cubic cell). A sample of the annealed crystal with dimensions 2×2×2 mm^3 was used in a measurement on the four circle single crystal neutron diffractometer at Risø, using 1.02 Å neutrons. The cubic setting was first used to align the sample and the eight superstructure reflections of the class $\{\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}\}$ were measured. This corresponds to {003} planes using hexagonal setting of the four possible twin directions. This measurement confirmed that the sample had scattering contributions from four superstructure crystals. However, no electron microscopy measurements were made of the specimen to confirm the multidomain nature of the twins, as reported in Ref. 4. The $(\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2})$ reflection with greatest intensity was chosen as (003) in the superstructure cell to be used in the data collection. The superstructure reflections will not have scattering contributions from the twin crystals with the three other directions of c_{hex}. The basis reflections that can also be indexed with the cubic unit cell will have scattering contributions from crystals with the four c_{hex} directions. This means that the superstructure reflections and the basis reflections will not be on the same scale in the differaction measurements.

A structure factor calculation was made using the results of Ref. 3, so that the measurements could be restricted to the strongest superstructure reflections and the basis reflections. The measurements were made using the $\omega-2\theta$ scan technique with two standard reflections for every twenty reflections. The measuring time for each reflection was approximately 20 min. After data reduction 150 reflections with $I>10\ \sigma(I)$ were used in the structure factor calculations ($b_{Nb}=7.054$ fm, $b_C=6.648$ fm).[5]

Due to the nature of the sample (twins) used in the diffraction experiment, it was not possible to refine thermal parameters of the atoms of the model, and the data showed severe extinction effects. Table 1 shows parameters arrived at in the refinement. The vacant site C6 (Refs. 2 and 3) has a significant scattering density, thus confirming the observations made in Ref. 3. Average values of the Nb–C distances of the six octahedra show the same tendency as observed previously of a shift of the niobium atom away from the vacant, or the less occupied, carbon site. The average distances are Nb–C6 (vacant): 2.27(3) Å, Nb–C (trans

0302-4377/85 $2.50

Table 1. Results of least-squares refinement with LINUS.[6] Standard deviations on coordinates 0.005 and on occupancies 0.06.[a]

Atom	Occupancy	x	y	z
Nb1	1	0.421	−0.122	0.254
Nb2	1	−0.242	−0.460	0.247
Nb3	1	0.089	0.227	0.251
Nb4	1	−0.241	−0.124	0.083
Nb5	1	0.449	0.207	0.084
Nb6	1	0.116	−0.451	0.076
C1	0.93	0.101	−0.460	0.325
C2	0.75	−0.229	−0.124	0.335
C3	1.00	0.430	0.219	0.331
C4	0.82	−0.216	0.229	0.159
C5	0.71	0.463	0.569	0.167
C6	0.52	0.111	−0.111	0.167

[a] $R(F)$=6.4 %, $R(F^2)$=4.2 %. a_{hex}=5.464, c_{hex}=15.422 Å.

to C6): 2.20(3) Å, Nb−C (average of four): 2.22(3) Å. The two last average distances include all carbon atoms except C6.

In the formation of the ideal superstructure of $NbC_{0.83}$ (built of $Nb-C_5\square$ octahedra) by an annealing process, five carbon sites must change occupancy from 0.83 to 1.00 and one from 0.83 to 0.0. This is a time consuming diffusion process. The sample investigated is not as close to this ideal superstructure as the powder samples investigated in Ref. 3. These were annealed at 960 °C for 15 days. It is possible that considerably longer annealing times are necessary to obtain the ideal superstructure.

In a comparison of the vacancy ordered structure of niobium carbide with that of niobium nitride it may be noted that the vacancy ordered structure of γ-NbN was described previously as a structure with some completely vacant nitrogen sites.[7] A single crystal neutron diffraction investigation showed, however, a measurable scattering density of the vacant nitrogen site.[8] The structures of Nb_6C_5 and γ-NbN have thus "vacant" sites with some scattering contribution.

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1. Moisy-Maurice, V., de Novion, C.H., Christensen, A.N. and Just, W. *Solid State Commun. 39* (1981) 661.
2. Venables, J.D., Kahn, D. and Lye, R.G. *Phil. Mag. 18* (1968) 177.
3. Landesmann, J.P., Christensen, A.N., de Novion, C.H., Lorenzelli, N. and Convert, P. *J. Phys. C 18* (1985) 809.
4. Billingham, J., Bell, P.S. and Lewis, M.H. *Phil. Mag. 25* (1972) 661.
5. Koester, L. and Rauch, H. *Summary of Neutron Scattering Lengths,* FKA, Jülich 1981.
6. Busing, W.R., Martin, K.O. and Levy, H.A. *ORFLS: A Fortran Crystallographic Least-Squares Program,* Report ORNL-TM 305, Oak Ridge National Laboratory, Oak Ridge 1962. *LINUS* is a 1971 version of *ORFLS.*
7. Terao, N. *Jpn. J. Appl. Phys. 4* (1965) 353.
8. Christensen, A.N., Hazell, R.G. and Lehmann, M.S. *Acta Chem. Scand. A 35* (1981) 111.

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