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Preparation and Properties of Compact Cubic δ-NbN_{1-x}

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Compact δ-NbN_{1-x} was prepared by heating niobium wire for several days in nitrogen at 4 MPa pressure and temperatures of 1 723 to 1 923 K. The samples obtained had compositions between $NbN_{0.924}$ and $NbN_{0.975 \pm 0.002}$ and were coarse-grained. The lattice parameter increases with the nitrogen content from $a = 0.43884$ nm for $NbN_{0.924}$ to $a = 0.43913$ nm for $NbN_{0.975}$. From the determination of the lattice parameters up to 1 073 K the coefficient of linear thermal expansion as a function of temperature was evaluated. The microhardness $HV_{0.1}$ decreases from $1\,300 \pm 80 \cdot 10^7\,Nm^{-2}$ for $NbN_{0.924}$ to $1\,080 \pm 60 \cdot 10^7\,Nm^{-2}$ for $NbN_{0.975}$. The occupancies of both the niobium and the nitrogen sublattices were calculated using experimental density data. The occupancy of the niobium sublattice decreases linearly with increasing nitrogen content. An extrapolation gives 2.9 ± 0.4% vacancies in both sublattices for stoichiometric δ-NbN.

(Keywords: B 1 Niobium nitride; Microhardness; Thermal expansion; Vacancy concentration)

Herstellung und Eigenschaften von kompaktem, kubischem δ-NbN_{1-x}

Kompaktes δ-NbN_{1-x} wurde durch mehrtägiges Erhitzen von Niobdraht in Stickstoff bei einem Druck von 4 MPa und Temperaturen von 1 273 bis 1 923 K hergestellt. Die dabei erhaltenen Proben hatten Zusammensetzungen von $NbN_{0.924}$ bis $NbN_{0.975 \pm 0.002}$ und zeigten ein grobkörniges Gefüge. Der Gitterparameter steigt mit dem Stickstoffgehalt von $a = 0.43884$ nm für $NbN_{0.924}$ bis $a = 0.43913$ nm für $NbN_{0.975}$ an. Von einer Bestimmung der Gitterparameter bis 1 073 K wurde der lineare thermische Ausdehnungskoeffizient erhalten. Die Mikrohärte $HV_{0.1}$ sinkt von $1\,300 \pm 80 \cdot 10^7\,Nm^{-2}$ für $NbN_{0.924}$ auf $1\,080 \pm 60 \cdot 10^7\,Nm^{-2}$ für $NbN_{0.975}$ ab. Die Besetzung sowohl des Niob- als auch des Stickstoffteilgitters wurde unter Verwendung von experimentell gemessenen Dichten bestimmt. Die Besetzung des Niobteilgitters fällt mit zunehmendem Stickstoffanteil linear ab. Eine Extrapolation dieser Werte ergibt für stöchiometrisches δ-NbN einen Leerstellenanteil von 2.9 ± 0.4% auf beiden Teilgittern.

Introduction

The refractory mononitrides with the B 1 type structure are of considerable interest since they combine a number of exceptional physical properties such as high superconducting transition temperatures, high melting points and high microhardness. They exist within a rather broad range of homogeneity whereas the physical properties change with composition within the limits of that range.

Many studies have been made of the niobium-nitrogen system; these were reviewed by *Toth*[1]. *Brauer, Elliot* and *Guard* and their coworkers[2—6] and recently *Brauer* and *Kern*[7] have investigated the system Nb—N and several tentative constitution diagrams were proposed[3, 5—9]. Further, *Storms* et al.[10, 11] have derived several values for pure δ-NbN by extrapolation from $Nb_wC_xN_yO_z$ phases. However, there are still some open questions about the stability of some phases with respect to the influence of oxygen, ordering of nitrogen within the nitrogen sublattice and phase relationships[2, 3, 6, 12—18]. The transition temperature[7, 18] as well as the exact nature of the γ-Nb_4N_{3-x}—δ-NbN_{1-x} phase transition have not been completely clarified, since X-ray, neutron and electron diffraction investigations as carried out by several investigators[14, 18—22] led to contradictory results.

Cubic δ-NbN_{1-x} crystallizes in the *fcc* sodium chloride structure and is considered to be a high-temperature modification[3] which undergoes a phase transition to η-NbN and/or γ-Nb_4N_3, depending on the stoichiometry, at a temperature of 1 503–1 643 K. This high-temperature modification can be easily frozen in by cooling.

The niobium-rich phase boundary of δ-NbN_{1-x} is temperature dependent and is situated between $NbN_{0.86}$—$NbN_{0.88}$ at room temperature[3, 9]. Nitrogen-rich compositions have been reported up to $NbN_{1.063}$ by *Brauer* and *Kirner*[23] by nitriding Nb powder at up to 16 MPa. *Rögener*[24, 25] was able to obtain compact samples of $NbN_{1.05}$ at 1 733 K and 4.2 MPa nitrogen pressure and *Horn* and *Saur*[26] reported the formation of $NbN_{1.04}$ at 1 923 K and 10 MPa nitrogen pressure. The formation of films of δ-NbN_{1+x} with a nitrogen content even up to N/Nb = 1.5 prepared by reactive sputtering have also been reported[13, 27].

Measurements of the nitrogen partial pressure as a function of composition of δ-NbN_{1-x} were carried out by *Shchurik* and *Tomilin*[28], *Zhikharev* and *Kharina*[29], and recently by *Brauer* and *Kern*[7]. A log $p(N_2)$ vs. N/Nb plot yields a straight line. The pressure ranges investigated in these studies were limited to those below atmospheric.

The melting point of δ-NbN_{1-x} was studied by *Ettmayer* et al.[30] at nitrogen pressures up to 8.1 MPa. δ-NbN_{1-x} does not melt congruently even at 8.1 MPa but decomposes to β-Nb_2N_{1-x}. Similar observations were made during trial runs with the purpose of growing δ-NbN_{1-x} single crystals by zone melting[31—34].

The nitrogen content significantly influences the lattice parameter. According to *Storms*[10] the lattice parameter of δ-NbN_{1-x} increases with increasing nitrogen content but levels off before reaching the stoichiometric composition, whereas *Brauer* and *Kirner*[23] gave the vertex value of the lattice parameter close to N/Nb = 1.00.

The thermal expansion of NbN_{1-x} was measured by *Timofeeva* and *Shvedova*[35] on $NbN_{0.95}$ (from lattice parameters at 93 and 300 K, $\alpha = 4.3 \cdot 10^{-6}\,K^{-1}$), by *Bogdanov* et al.[36] on $NbN_{0.99}$ in the range of 293–1 173 K

($\alpha = 6.74 \cdot 10^{-6} + 3.36 \cdot 10^{-9}$ T, T/°C) and by *Samsonov* and *Verkhoglyadova*[37] on $NbN_{1.0}$ ($\alpha = 10.1 \cdot 10^{-6}\,K^{-1}$).

The microhardness of δ-NbN_{1-x} was measured by *Politis* and *Rejman*[9] on compact samples between $NbN_{0.755}$ and $NbN_{0.969}$ and was found to decrease significantly with increasing nitrogen content. Microhardness data for hot-pressed specimens of NbN_{1-x} are given by *Verkhoglyadova* et al.[38].

The density values of powder samples of δ-NbN_{1-x} were reported by *Brauer* et al.[2,3,23]. The density decreases with increasing nitrogen content. At N/Nb < 1 the nitrogen sublattice is partially unoccupied and at N/Nb > 1 the niobium sublattice develops vacancies. However, density measurements on powder samples may lead to erroneous results due to incomplete wetting of the powder particles by the immersion liquid. *Storms*[10] reported vacancy concentrations (extrapolated values of $Nb_wC_xN_yO_z$ compounds) of several samples from N/Nb = 0.839 to 1.063.

The preparation of compact NbN_{1-x} from Nb wire at elevated nitrogen pressures—for the purpose of measuring the transition temperature of superconductivity—was described by *Rögener*[24], *Sellmaier*[39], *Hechler* and *Saur*[40], *Horn* and *Saur*[26] and by *Bernhardt*[41]. The latter obtained a composition of N/Nb = 0.86 at 10.1 MPa and 1 673 K. Finally, the preparation of δ-NbN_{1-x} single crystals by means of RF zone annealing was reported by *Scheerer*[31], who started with perforated Nb samples to shorten the diffusion length and obtained samples with compositions near the niobium-rich phase boundary with relatively high oxygen contents. *Christensen* et al.[32,33] prepared samples by zone annealing of NbN_{1-x} samples in nitrogen and came closer to the stoichiometric composition. Since the diffusion rates of nitrogen in δ-NbN are rather low the samples so obtained may exhibit nitrogen concentration gradients. Thus, samples of larger sizes prepared by such annealing techniques do not necessarily represent an equilibrium state but have been used for neutron diffraction measurements.

The purpose of this work is to contribute to the knowledge about the physical properties of δ-NbN_{1-x} on the basis of compact and carefully characterized samples.

Experimental

Sample Preparation

The starting material was niobium wire of 1 mm diameter and a length of 10 mm. The composition of this material was 99.73 ± 0.02 wt% Nb, 0.25 ± 0.02 wt% Ta, 200 ppm oxygen, 50 ppm nitrogen and 5 ppm hydrogen. The tantalum content was taken into account and the measurements and results were corrected accordingly.

The nitridation was performed in a high-temperature cold wall autoclave equipped with a resistively heated tungsten tube. The construction of this equipment is described elsewhere[42]. The sample was wrapped in several layers of zirconium foil to prevent oxygen contamination and placed in the center of the heating tube by means of a molybdenum loop. The temperature was controlled by adjusting the electric power and measured optically with a pyrometer through a quartz viewing port. The nitrogen was of high purity (> 99.999 vol% N_2) and had a total of only 5 vpm oxygen and carbon containing gases. A further purification did not seem necessary. In order to obtain a nitrogen concentration as high as possible at a given temperature the pressure was held at 4 MPa (measured with a

Bourdon type manometer). For each successive run the samples of the previous run were used at a lower temperature. The annealing times and temperatures are given in Table 1. The nitridation cycles were stopped by turning off the electric power. The specimen cooled to room temperature within about 20 s. An estimate of the nitrogen pickup during cooling, using the diffusion coefficients of N in NbN at 1 783 and 1 888 K given by *Levinskii* et al.[43], led to a nitrogen-rich surface layer of about 2–4 μm thickness that does not influence the analytical results with compact samples (however, this would cause an inhomogenous nitrogen concentration in powder particles because of their high surface-to-volume ratio).

The δ-NbN_{1-x} samples were of the same shape as the starting material and had a metallic luster with a just perceptible light yellowish tinge.

Chemical Analysis

The nitrogen analysis was performed by a modified *Dumas* method as described by *Kern* and *Brauer*[44] using 50 mg of finely powdered nitride. 200 mg of a mixture of 50 mol% Cu and 50 mol% CuO that had been heated at 973 K in vacuum before use were employed as an oxidant. The analysis was performed at 1 123 K in flowing CO_2 as a carrier gas. In order to remove traces of oxygen or CO, which could have formed during the reaction, the carrier gas was first passed over heated pure and oxidized copper nets and then absorbed in 50 wt% aqueous KOH in an azotometer where the evolved nitrogen was measured volumetrically.

The niobium content of the obtained nitrides as well as the tantalum content of the starting material was determined by completely oxidizing the samples in a platinum crucible in air to Nb_2O_5 (and Ta_2O_5). The combustion was performed at $1\,073 \pm 5$ K until constant weight was achieved. This required 4 h for the nitride samples and 7 h for the niobium wire.

The oxygen content was analyzed by vacuum hot extraction with a nickel bath in a carbon crucible.

Lattice Parameters and Thermal Expansion

Lattice parameters were measured with a Philips powder diffractometer PW 1040 with Ni-filtered Cu-K_α radiation. The diffraction angles of the (511), (422) and (420) lines were measured and calibrated against high-purity silicon powder[45]. The diffraction lines (especially in back reflection) showed excellent splitting of the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines indicating a homogeneous composition throughout the specimen.

The thermal expansion of the lattice was measured with a high temperature attachment to the diffractometer manufactured by *A. Paar*, Graz, Austria, equipped with a resistively heated molybdenum strip. The powdered specimen was spread directly on the surface of the strip. The temperature was measured with a Pt/PtRh thermocouple tightly squeezed into a borehole of the molybdenum strip and positioned in the focus area of the goniometer. The goniometer readings were corrected by applying a linear function $\Delta\theta\,[f(\theta)]$[46] derived from diffraction lines of high-purity silicon powder. During these measurements the high-temperature attachment was filled with high-purity nitrogen of atmospheric pressure.

Metallography, Microhardness and Density Measurements

The compact δ-NbN_{1-x} specimens were embedded in thermosetting resin and diamond polished. The microstructure in Fig. 1 reveals that the samples were very coarse-grained and completely pore-free which is most important for the determination of the density.

The microhardness was measured at room temperature at four different loads (0.51–1.61 N). From these values the *Meyer's* index was established and the microhardness at 0.98 N (0.1 kp) calculated.

The specific density was determined by the immersion method. Tribromomethane was chosen as the immersion liquid because of its relatively high density and low volatility. The density of the immersion liquid as a function of temperature was measured between 291 and 301 K (18–28 °C). The sample was suspended with a stainless steel wire (0.07 mm ∅). The influence of buoyancy and surface tension was taken into account accordingly.

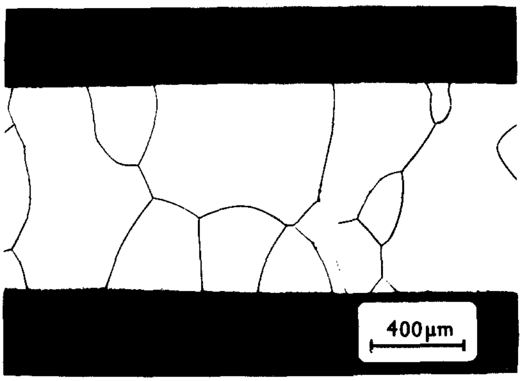

Fig. 1. Microstructure of a δ-NbN$_{1-x}$ sample (etched with HF + HNO_3)

Results and Discussion

Composition

The maximum nitrogen content of the samples was N/Nb = 0.975 ± 0.002. No samples with hyperstoichiometric nitrogen content could be observed, which is in contrast to the findings of *Rögener*[24] but in agreement with *Sellmaier*[39] and *Horn* and *Saur*[26]. These authors had not analyzed the nitrogen content directly but had calculated it from the weight gain of the sample. The samples in the present study were analyzed carefully for their true nitrogen content. Since the oxygen content of our samples was well below 150 ppm in each case (see Table 1) an oxygen stabilization effect can be ruled out.

Other investigators who had prepared compact samples did not report their conditions of synthesis exactly[9, 33], or had samples with much higher oxygen contents[31].

Table 1. *Experimental conditions and results*

Sample	Nitrogen pressure $p(N_2)$	Annealing temperature K	Annealing time h	Composition $1-x$ (N/Nb)	Lattice parameter a/nm		
					298 K	(T/K)	
	± 4%	± 10 K		± 0.002	± 0.00002	± 0.00005	± 10
NbN 1	4 MPa	1 923	76	0.924	0.43884	0.44178	(1 073)
NbN 2	4 MPa	1 823	166	0.953	0.43899	0.44168	(973)
NbN 3	4 MPa	1 723	259	0.975	0.43913	0.44062	(673)

	Coefficient of linear thermal expansion $\alpha = \frac{A}{2a_T} T^{-\frac{1}{2}} + \frac{B}{a_T}$		Oxygen content ppm	Microhardness $HV_{0.1}$ (0.98 N) $10^7\,Nm^{-2}$	Specific density gcm^{-3} (300 K)	Sublattice occupancy (%)	
						Nb	N
	$A \cdot 10^4$	$B \cdot 10^6$	± 20 rel%	± 6%	± 0.0050	± 0.4%	± 0.4%
NbN 1	—0.983	5.706	129	1 300	8.2395	98.9	91.2
NbN 2	—1.002	6.037	75	1 185	8.2050	98.1	93.6
NbN 3	—1.138	6.621	125	1 080	8.1820	97.7	95.5

Lattice Parameter

The variation of the lattice parameter with composition according to the present study as compared to the findings of other investigators is shown in Fig. 2. The results of our measurements are in very good agreement with the values of *Brauer* et al.[3,23], *Politis* and *Rejman*[9], and *Storms*[10]. In the composition range investigated in this work no indication of a deviation from the linearity of the lattice parameter vs. composition was observed. The slope of the function lattice parameter vs. composition is rather small. Thus δ-NbN_{1-x} exhibits a behavior intermediate between that of δ-VN_{1-x}[47] and that of δ-TaN_{1-x}[48]. This behavior can be attributed to the decreasing occupancy in the niobium sublattice when the equiatomic composition is approached, whereas the vanadium sublattice in δ-VN_{1-x} is almost fully occupied throughout the homogeneity range (analogous data for δ-TaN_{1-x} have not yet been collected).

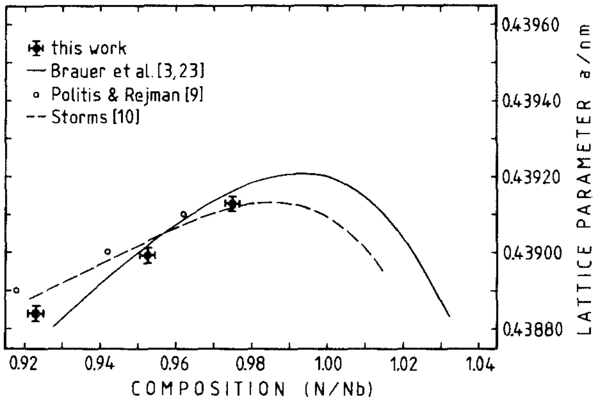

Fig. 2. Lattice parameter of δ-NbN_{1-x} vs. composition

Thermal Expansion

The variation of the lattice parameter with temperature is shown in Fig. 3. It is noteworthy that the sample with the highest nitrogen content undergoes a nitrogen loss at temperatures higher than 673 K (nitrogen pressure: 100 kPa), resulting in a decrease of the lattice parameter. Thus the highest temperature where measurements could be made was 673 K. The other samples did not exhibit this behavior up to 973 K ($NbN_{0.953}$) and 1 073 K ($NbN_{0.924}$). This observation can be attributed to a lower nitrogen dissociation pressure.

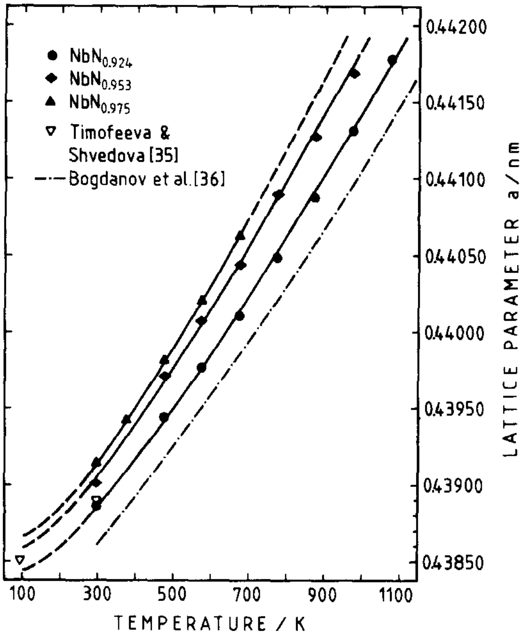

Fig. 3. Lattice parameter of δ-NbN$_{1-x}$ as a function of temperature

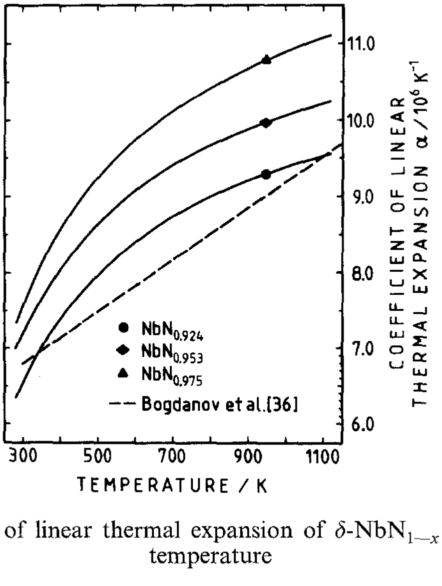

Fig. 4. Coefficient of linear thermal expansion of δ-NbN$_{1-x}$ as a function of temperature

The function lattice parameter vs. composition (Fig. 3) fits the following equation very closely:

$$a_T = a_{298} + A \cdot T^{1/2} + B \cdot T \qquad (1)$$

where a_T and a_{298} are the lattice parameters (nm) at the temperature T and at 298 K respectively, T is the absolute temperature, and A and B are coefficients that can be calculated by a least squares fit of the data. A and B are listed in Table 1. The values of the present study agree well with the findings of *Bogdanov* et al.[36] on $NbN_{0.99}$ with respect to the slope of the expansion curve but not with respect to absolute values. The lattice parameter at room temperature as found by *Bogdanov* et al.[36] is too low and/or the nitrogen content is too high compared with accepted values shown in Fig. 2.

From equation (1) the coefficient of linear thermal expansion as a function of temperature can be calculated:

$$\alpha_T = \frac{A}{2\,a_T} \cdot T^{-(1/2)} + \frac{B}{a} \qquad (2)$$

indicating that in this approximation α is linear with the square root of the reciprocal temperature. The dependence of α upon temperature is depicted in Fig. 4.

Microhardness

The decrease of the *Vickers'* microhardness $HV_{0.1}$ (0.98 N load) with increasing nitrogen content is illustrated in Fig. 5. The values of the present study do not agree well with those reported by *Politis* and *Rejman*[9]. But a linear extrapolation to N/Nb $= 1.000$ gives very nearly the same value ($975 \pm 60 \cdot 10^7\,\mathrm{Nm}^{-2}$) as an extrapolation of the values of these authors[9]. This decrease in the microhardness as N/*Me* approaches unity is observed in all group Va B 1 nitrides[9,47].

Density and Occupancy of Lattice Sites

The occupancy of the lattice sites in the unit cell was calculated using a formula already reported in a previous work[47]. In order to apply this formula there is no need to make further assumptions about the nature of the vacancies (addition or subtraction solid solution).

The results of this calculation as a function of composition are shown in Fig. 6. With the approach to equiatomic composition the occupancy of the niobium sublattice decreases linearly and the occupancy of the nitrogen sublattice increases. A linear extrapolation to N/Nb $= 1.000$—

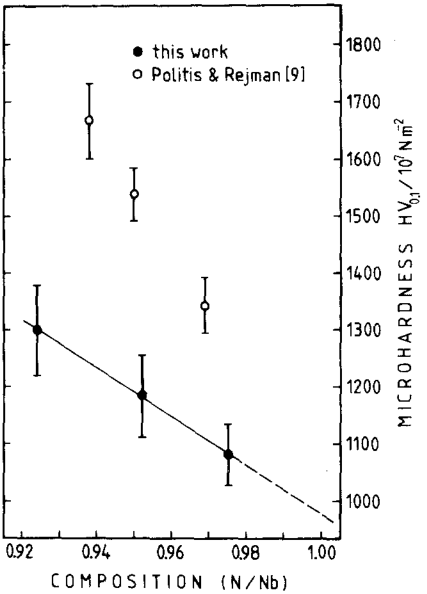

Fig. 5. Microhardness $HV_{0.1}$ of δ-NbN_{1-x} vs. composition

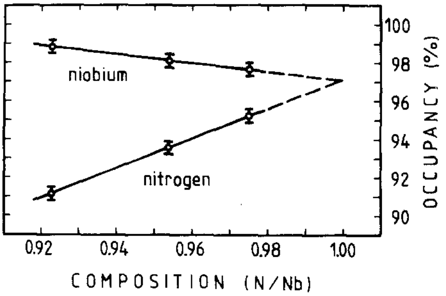

Fig. 6. Occupancy of the niobium and nitrogen sublattices of δ-NbN_{1-x} vs. composition

which probably is in agreement with thermodynamic considerations since both sublattices exhibit vacancies and therefore the entropy term of the free energy of formation would not tend towards inifinite values—gives a vacancy concentration of 2.9 ± 0.4% at the stoichiometric composition NbN. This result is at variance with the value of 13% reported by *Denker*[49] who, unfortunately, did not state the reference. Conversely, *Storms*[10] reported extrapolated values of 2.7% nitrogen and 4.2% niobium vacancies (hyperstoichiometric composition) for conditions of 3.8 MPa nitrogen pressure and 1 646 K, which is in good agreement with the vacancy concentrations for our $NbN_{0.975}$ sample (prepared at 1 723 K and 4 MPa nitrogen pressure) of 4.7 ± 0.4% for at the nitrogen and 2.3 ± 0.4% for the niobium sublattice.

Acknowledgements

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