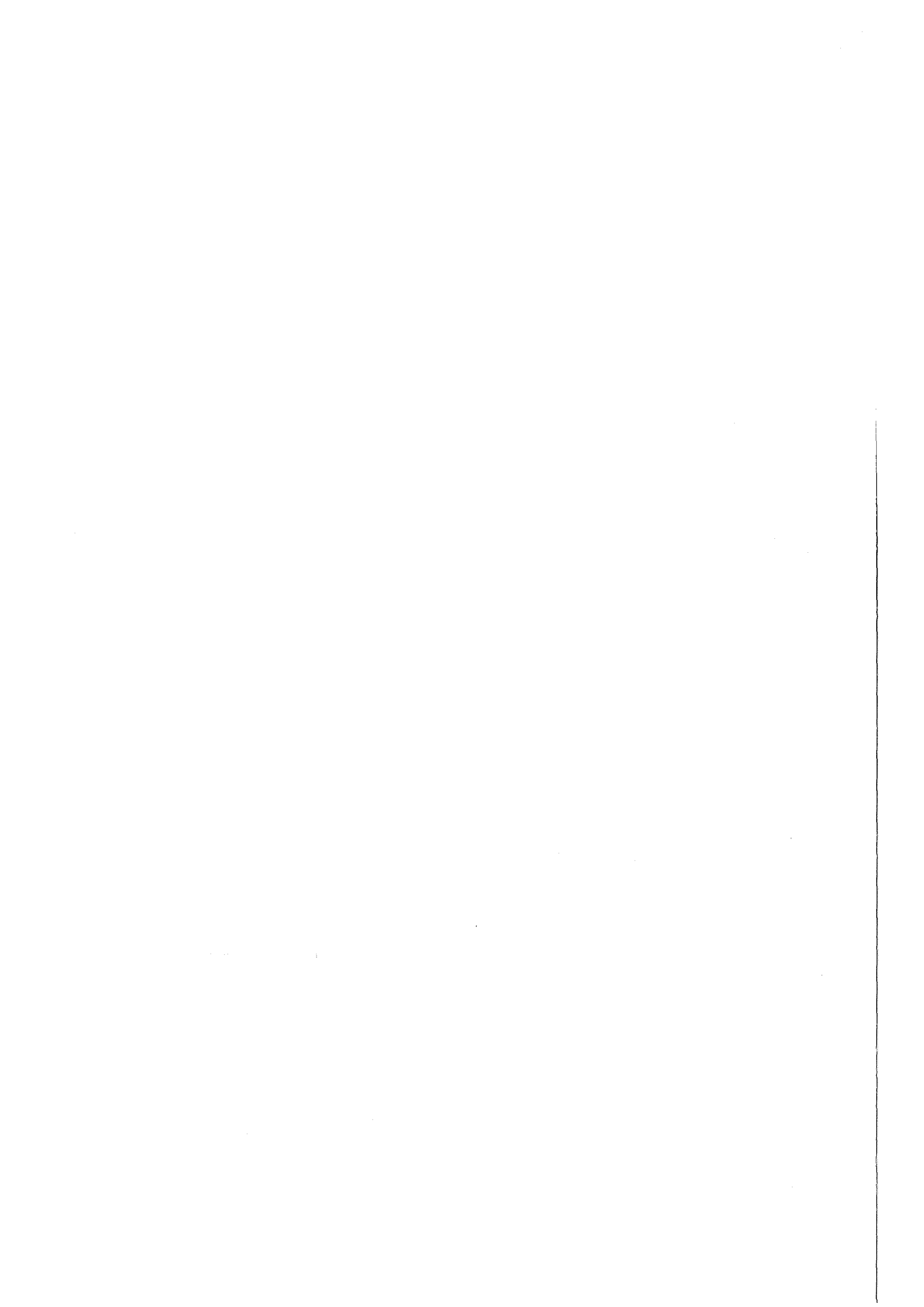


KfK 4409
September 1988

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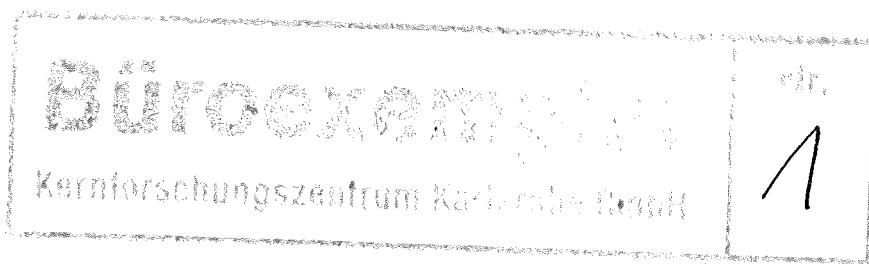
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Presence of Small Amounts of Aluminum During Sputtering

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Postfach 3640, 7500 Karlsruhe 1

ISSN 0303-4003

IMPROVEMENTS IN THE PROPERTIES OF NbN LAYERS THROUGH THE PRESENCE OF SMALL AMOUNTS OF ALUMINUM DURING SPUTTERING

Pure phase B1 NbN layers could be sputtered in our laboratory only with a maximum T_c of 15.9 K and a residual resistance ratio RRR of <0.9 . Samples with a T_c of up to 16.7 K invariably had a large fraction of hexagonal foreign phase. If under similar conditions one sputters layers in the presence of small amounts of Al, one obtains pure B1 phase NbN layers with a maximum T_c of 16.9 K. The RRR rises to values of up to 1.16. The specific resistance drops from typical values of around $400 \mu\Omega\text{cm}$ to values as low as $73 \mu\Omega\text{cm}$. The width of the X-ray lines drops occasionally, indicating increased grain size. Al acts like a catalyst, being substituted with less than 0.03 at% for a high T_c layer. When Al is substituted for Nb in detectable quantities both T_c and the lattice parameter drop. To verify the above results the experiment was repeated in a magnetron rather than a RF sputter system with similar outcome.

VERBESSERUNG IN DEN EIGENSCHAFTEN VON NbN SCHICHTEN DURCH GEGENWART VON KLEINEN MENGEN VON ALUMINIUM WÄHREND DES SPUTTERNS

Phasenreine B1 NbN Schichten konnten in unserem Labor nur mit maximalem T_c von 15.9 K und einem Restwiderstandsverhältnis von <0.9 hergestellt werden. Proben mit einem T_c bis zu 16.7K hatten immer einen großen Anteil von hexagonaler Fremdphase. Wenn man unter gleichen Bedingungen Schichten in Gegenwart kleiner Mengen von Aluminium durch Sputtern herstellt, erhält man phasenreine Schichten mit einem T_c bis 16.9 K. Das Restwiderstandsverhältnis steigt auf Werte bis zu 1.16. Der spezifische Widerstand fällt von typischen Werten um $400 \mu\Omega\text{cm}$ auf Werte bis zu $73 \mu\Omega\text{cm}$. Die Breite der Röntgenlinien nimmt gelegentlich ab, was auf erhöhte Korngrößen hinweist. Das Aluminium wirkt wie ein Katalysator, da es für eine hoch- T_c Schicht mit weniger als 0.03 at% substituiert wird. Wenn Niob durch Aluminium in meßbaren Mengen ersetzt wird, fällt sowohl T_c als auch der Gitterparameter. Um obige Resultate zu reproduzieren, wurde das Experiment in einer Magnetron- statt HF-Anlage mit ähnlichen Resultaten wiederholt.

1. INTRODUCTION

In the last few years numerous publications have appeared on NbN (1-8) and extensive literature cited therein. For very recent work see the proceedings of the LT18 (8).

The interest lies partly in the development of superconducting junctions (2). On the other hand the critical currents of up to 10^7 A/cm² are very high and hence the development of this material for high current conductors (3,4,8) will continue, as long as the new oxidic superconductors do not reach comparable high current densities in bulk form.

Furthermore it will continue to be needed for applications where radiation resistance is important, such as accelerators and fusion reactors. One should be aware that NbN is about a factor of 10^4 more resistant to radiation damage (9). A brief version of this paper has been presented at the International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity (10).

2. EXPERIMENTAL

The sputtering conditions for the two systems are summarized in Table 1. The substrate temperature for optimum T_C was in the range of 820-880°C. The optimum N_2 partial pressure for magnetron sputtering was 1.4 Pa. The special method to determine the lattice parameters a_0 of stressed films is described in ref. 11 and in particular the simplification pointed out in 12 is used. Not applying this method may cause an error of as large as 1% in a_0 .

The substrates were mounted on a resistively heated Ta-strip. For the RF-runs four substrates were used, while for the magnetron-runs single substrates were employed. The geometry was chosen such that there was an Al-gradient along the substrates. The composition of the samples was partly characterized by an electron microprobe. For the T_C measurements the resistive four point method was used. The 1% onset points are given.

Table 1 Preparation Conditions for $\text{Nb}_{1-x}\text{Al}_x\text{N}$

	RF-Sputtering	Magn.-Sputtering
Substrate temperature/°C	790-910	820-1100
N ₂ partial pressure/Pa	0.4	0.3-2.1
Ar+N ₂ pressure/Pa	2.0	5.2-15.5
Power/W	500 (RF)	300 (DC)
Voltage/V	≈1800	≈570
Distance anode/cathode/mm	≈40	≈45
area fraction Al-Nb	0-3%	0-5%
diameter cathode/mm	150	75

3. RESULTS AND DISCUSSION

Reuschenbach (13) analyzed by Rutherford backscattering and X-ray analysis a Nb layer on Al_2O_3 nitrided at 1450°C by Remeika (6). See sample C4113M in Table 2 and its remarkably high RRR. Fig. 1 (Fig. 14 in ref. 13) shows the Rutherford backscattering spectrum of the nitrided Nb layer. A few at% of Nb appear to be missing near the rearside of the layer extending until the middle. A corresponding excess of Al appears to be visible above the Al edge of the substrate. This makes it plausible that a substrate reaction has taken place and Al has diffused into the rearhalf of the layer. This is not surprising as Al is soluble in Nb up to 23 at% and substrate reactions of Nb on Al_2O_3 are known to take place at temperatures above 900°C

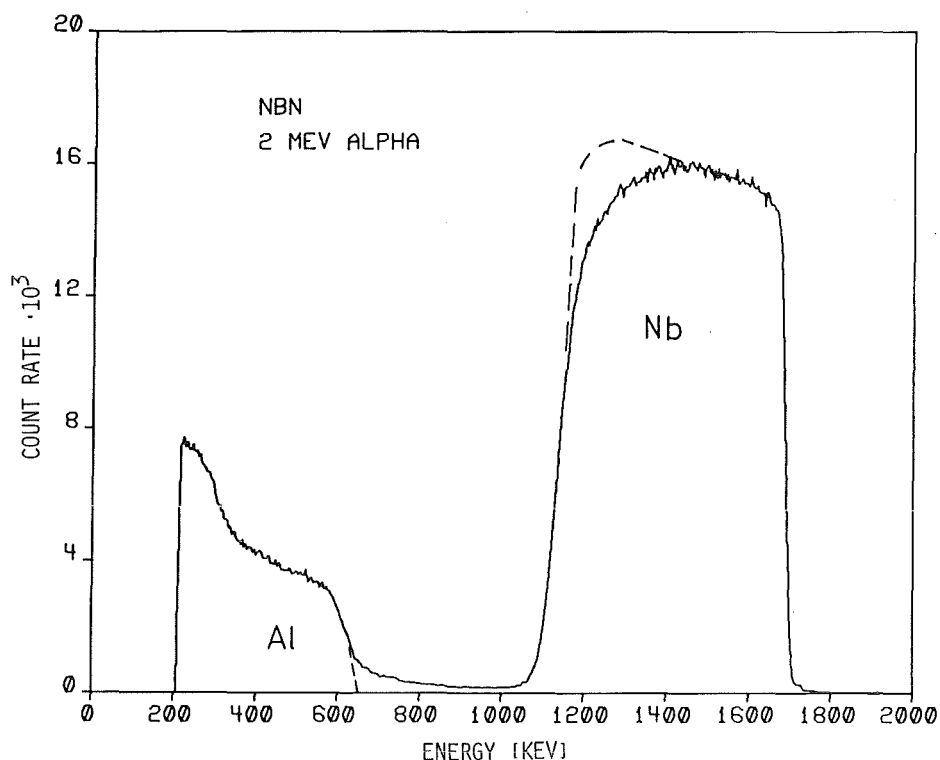


Fig. 1 Rutherford backscattering spectrum of the niobided Nb layer, sample C4113M.

Fig. 2 (Fig. 13 in ref. 13) shows the X-ray diffraction diagram of the same layer. Essentially only the B1-phase is visible. The top half of the picture shows the same diagram with an expanded counts/channel scale. A few very weak peaks of a foreign phase are visible, which however do not stem from Nb₃Al. From the intensities the fraction of foreign phase is estimated to be less than about 0.2 at.%. The information from both figures makes it plausible that Al is substitutional on Nb sites in the B1 phase.

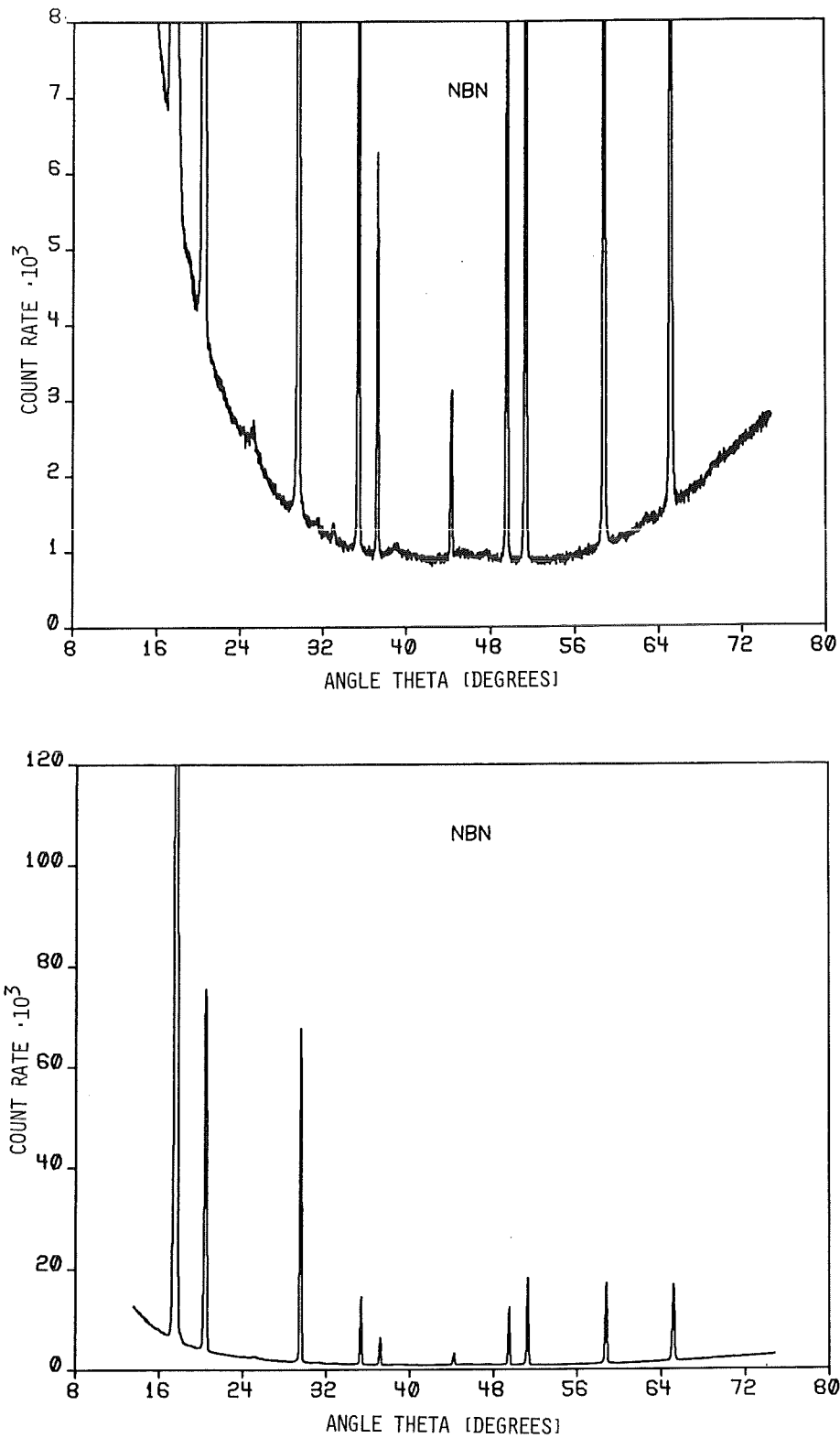


Fig. 2 X-ray diffraction diagram of sample C4113M (bottom half). The top half shows the same diagram with an expanded cfs scale. Note the weak foreign phase peak near $\theta = 26^\circ$.

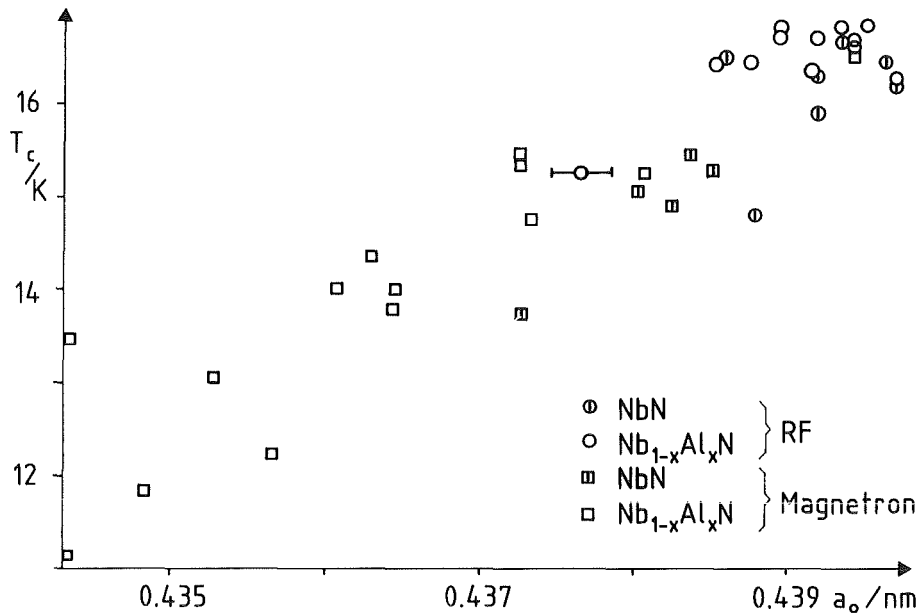


Fig. 3 Plot of T_c vs. lattice parameter a_0 for samples prepared with and without Al in a RF and a magnetron sputtering system.

We now deliberately added Al by preparing layers on single crystal sapphire substrates by reactive sputtering with composite Nb-Al cathodes. For optimum T_c the substrate temperatures were around 850° . Considering the low melting point of Al of 660°C the Al-sticking coefficient is likely to be low. Fig. 3 shows T_c vs. a_0 for layers with the two sputtering systems with and without Al. With rising a_0 and falling Al-content T_c rises. The error bar indicates the error in a_0 . Predominantly points with high T_c were evaluated and are shown.

Table 2 gives the data for selected samples. The highest T_c values are obtained phase pure for RF-prepared samples with Al, from the point at 15.3 K/0.4377 nm to sample NAN3-4R with 16.9 K/0.4395 nm and less than 0.03 at% Al. RF-prepared samples

without Al have lower T_c and contain large fractions of the hexagonal phase, except for the sample at 15.9 K/0.4392 nm with a residual resistance ratio of 0.87. The magnetron prepared samples with Al extend from 13.5 K/0.4343 nm via sample NAN15R with 1.4 at% Al to sample NAN26RR with 16.5 K/0.4394 nm and 1.2 at% Al. The corresponding samples prepared without Al have all lower T_c extending from 13.8 K/0.4373 nm to 15.5 K/0.4384 nm. The sample NAN26RR shows an additional almost single crystalline line with a d-value of 1.0863 nm, to the large angle side of the 400 line with the same texture. Attempts to account for this extra line as superstructure line by doubling or tripling the unit cell were not convincing. However, the line does coincide with a line of a less common NbN phase, probably the ϵ -phase.

Sample NAN3-4R has less Al than the detection limit of 0.03 at%. This makes it probable, that it is not the Al-content but rather the role of Al during the film growth, which leads to phase purity and enhanced T_c . Possibly Al acts similar to a catalyst. More probably Al acts as a flux medium, which is not built into the NbN structure, as often used in the preparation of single crystals. Building Al into the B1-structure leads to a decrease in both T_c and a_o , as evidenced by sample NAN15R with 1.4 at% Al and sample NAN17R with 1.6 at% Al. The a_o -value of layer NAN17R is smaller by 1.2%, that of NAN15R is smaller by 0.7% than stoichiometric samples. Unfortunately, the metal film of the latter has a black layer on top, which is probably carbon, up to 6.2 at% totally. The residual resistance ratio of layer NAN26RR is 1.16, which is the highest which we prepared. Only films containing foreign phase have a larger RRR.

The high ρ -value is probably not an inherent property of NbN films, but rather an artifact associated with the typical columnar growth and the possible existence of voids or oxide layers between the columns. Samples NAN26RR and NAN17R have a large excess of oxygen, correlated with a high ρ (RT). Substoichiometric bulk $NbN_{0.9}$ has ρ (RT) = 44.4 $\mu\Omega$ cm and a RRR of

Table 2 Properties of selected samples. RRR means residual resistance ratio

Property/Sample	C4113M	NAN3-4R	NAN15R	NAN26RR	NAN3-3L	NAN17R
T_c /K (Onset)	16.9	16.9	14.4	16.5	16.4	13.5
a_0 /nm	0.4411	0.4395	0.4363	0.4394	0.4386	0.4343
T_s /°C	$T_D=1450$	830	830	900	780	830
P_{N_2} /Pa	-	0.40	1.4	1.4	0.40	2.0
P_{Ar+N_2} /Pa	-	2.0	16	7.6	2.0	15.5
at% Nb	47.7	47.7	48.5	45.3	51.3	45.1
at% Al	<2.4>	<0.03	1.4	1.2	0.9	1.6
at% N	43.4	46.4	43.6	45.1	42.7	46.1
at% O	2.2	3.0	3.8	5.9	3.6	6.0
at% C	4.3	3.0	2.5(<6.2)	2.5	1.5	1.2
Layer thickness/nm	0.48	≈1.0	≈1.0	≈1.0	≈1.0	≈1.0
ρ (RT)/ $\mu\Omega$ cm	76	220	1940	1030	90	2050
RRR	1.27	0.993	0.735	1.160	1.029	≈0.75
Method	Diffusion	RF	Magnetron	Magnetron	RF	Magnetron

1
1

0.98 (14). Sample NAN3-3L (Table 2) with a residual resistance ratio RRR of 1.029 and 0.9 at% Al is representative of RF-films grown with Al where RRR ranges from 0.92 to 1.13 with specific resistance values in the range from 73 to 220 $\mu\Omega\text{cm}$, typically 100 $\mu\Omega\text{cm}$.

The maximum of our T_c vs. a_o data extrapolates to the data of ref. 7. Samples prepared in the RF-system generally have superior properties. That the T_c of the samples in the present study is limited to 16.9 K and not slightly higher is presumably due to the presence of oxygen. The high T_c of up to 17.8 K of the samples of ref. 15 is presumably due to small amounts of Al that diffused into the $\text{NbC}_{1-x}\text{N}_x$ layers during preparation at 1100°C. The authors observed that at 1100°C sapphire yielded higher T_c than quartz substrates.

4. CONCLUSIONS

The presence of small amounts of Al during sputtering improves the properties of NbN layers markedly:

- (i) T_c rises somewhat (0.2-1.0 K),
- (ii) the layers are pure B1-phases,
- (iii) the residual resistance ratio reaches up to values of 1.16,
- (iv) the specific resistance drops to values as low as 73 $\mu\Omega\text{cm}$,
- (v) occasionally the X-ray line width decreases, pointing to the formation of larger grains.

For a high T_c layer the Al is not incorporated in detectable amounts into the film. Possibly Al acts similar to a catalyst. When Al is incorporated, T_c and a_o fall. An alternative explanation is that Al behaves like a flux medium. The small electronegativity difference Nb-Al of 0.1 and the smaller Al-radius probably play a role. The situation is reminiscent of the role of oxygen during the growth of Nb_3Ge films, except that the evidence is more clear-cut.

A similar situation exists when C is substituted for N, or Ti for Nb, even in small amounts (5,16) except that the mechanism is related to the fact that the number of electrons/atom is approaching 4.85, where the highest T_c is observed.

ACKNOWLEDGEMENTS

The authors want to thank O. Meyer for a critical reading of the manuscript and H. Späte for the electron microprobe analyses. They are grateful to L. Reuschenbach for permission to show figs. 1 and 2.

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