

Superconductivity of Some Transition Metal Compounds

A. NØRLUND CHRISTENSEN, S. E. RASMUSSEN, AND G. THIRUP

Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark

Received February 21, 1979; in revised form August 6, 1979

Single crystals of niobium carbonitride were made by zone melting growth methods and single crystals of γ -NbN and δ -NbN by zone annealing crystal growth. The crystals are nonstoichiometric in contrast to the niobium carbonitride or niobium nitride prepared in reaction with nitrogen gas and niobium-niobium carbide mixtures and niobium metal, respectively. The transition temperature for superconductivity (T_c) decreases with increasing deviation from stoichiometry, and a determination of T_c is a nondestructive determination of this deviation. An instrument using the Wheatstone bridge principle is described and T_c values are listed for some nonstoichiometric single crystals of niobium carbonitride and niobium nitride.

The cubic transition metal nitrides, TiN, ZrN, δ -NbN, and solid solutions of niobium nitride and niobium carbide have attracted much interest in relation to the relatively high transition temperatures for superconductivity, T_c , of these compounds (1) (see Table I). Until recently these materials were only available as polycrystalline specimens. Crystal growth methods have now been developed for these transition metal nitrides, and single crystals of sufficient size are now available to measure the phonon dispersion curves for the nitrides, using inelastic neutron scattering.

TABLE I
TRANSITION TEMPERATURE FOR SUPERCONDUCTIVITY^a

	T_c (K)
TiN	5.5
ZrN	10.0
δ -NbN	15-17.3
γ -NbN	8.9
NbN _{0.7} C _{0.3}	17.8

^a Reference (1).

Single crystals of the cubic solid solutions of niobium nitride and niobium carbide are obtained by zone melting of polycrystalline rods of mixtures of the two compounds (2). Single crystals of TiN, ZrN, and δ -NbN are made by zone annealing and annealing growth, where the metals react with nitrogen gas during the growth process (2). The preparation involves thus diffusion of nitrogen in the solid state and the nitrogen content of the crystals is dependent upon annealing temperature, ambient gas pressure, and duration of the annealing experiment. Specimens often show a nitrogen concentration gradient with decreasing nitrogen content inward from the surface. The nitrogen content can be increased by extension of the annealing periods as illustrated in Table II and possibly also by variation of the annealing temperature and the nitrogen gas pressure. The composition of the nitrides can be determined by chemical analysis or by measuring the unit-cell parameters in the cases where a relation between the composition and the unit-cell parameters is known. This is the case for TiN and ZrN (2).

TABLE II
EXPERIMENTAL CONDITIONS FOR PREPARATION AND T_c VALUES OF NIOBIUM NITRIDE

Experiment No. and code	Method of preparation ^a	N ₂ gas pressure (MPa)	Temp. (°C)	Time (hr)	Composition from chemical analysis	T_c (K)
1 NbN 211177	A	2.0	1800	0.01	NbN _{1.07}	14.4
2 NbN 020678	B	1.7	2100	95	NbN _{0.75} ^b	<6.8
3 NbN 140177	C	1.9	2200	111	NbN _{0.78} ^b	10.5
4 NbN 150678	C	1.7	2320	191	NbN _{0.89}	12.1
5 NbN 100778	C	1.7	2320	307	NbN _{0.93}	13.3

^a A, polycrystalline preform made as described in Ref. (3); B, annealing; C, zone annealing.

^b The compound is γ -NbN.

The relatively high values for the transition temperature for superconductivity listed for the compounds in Table I refer to materials with compositions close to the stoichiometric composition. The single-crystal growth methods used in this investigation often result in crystals with nitrogen contents smaller than that of a stoichiometric crystal. The transition temperature for superconductivity of these compounds is known to decrease with increasing deviation from stoichiometry. Simultaneously, the soft mode nature of the phonon dispersion curves is less pronounced or possibly absent for crystals with compositions deviating from stoichiometry. Before considerable efforts are invested in physical measurements on single crystals where the effects under investigation are very sensitive to the stoichiometry, such as the above-mentioned soft mode nature, it is desirable to apply a fast, reliable, and nondestructive method of investigation of the stoichiometry that in this case could be deduced from a determination of T_c . The purpose of the present paper is to describe such a fast and uncomplicated method of determining T_c using a relatively simple instrument for induction measurements of the samples, and to report values for T_c for single crystals of some nonstoichiometric transition metal nitrides and carbonitrides.

Experimental

Preparation of Transition Metal Compounds

The experimental conditions for the preparation of some transition metal nitrides and carbonitrides are listed in Tables II and III, respectively. Polycrystalline rods of niobium nitride and niobium carbonitride are obtained in a fast reaction between rods of pressed niobium powder or rods of mixtures of niobium and niobium carbide powder and nitrogen gas (3). Specimens made in this way have a composition close to stoichiometry or are slightly overstoichiometric with respect to nitrogen. Single crystals of the nitrides (Table II) were obtained by zone annealing growth methods described previously (2). Stoichiometry can only be approached when long annealing periods are applied at high temperatures. Single crystals of niobium carbonitrides can be obtained by zone melting growth (2, 4). Crystals obtained in this way are nonstoichiometric. The nitrogen content can be increased by application of zone annealing growth methods (Table III).

The metal contents of the specimens were determined gravimetrically. The nitrides or the carbonitrides were kept in a platinum crucible in an electric furnace at 1000°C for 1 hr, and were by this treatment converted to the respective metal oxide. Carbon in the carbonitrides was released as CO₂ by ignition

TABLE III
EXPERIMENTAL CONDITIONS FOR PREPARATION AND T_c VALUES OF NIOBIUM CARBONITRIDE

Experiment No. and code	Method of preparation ^a	N ₂ gas pressure (MPa)	Temp. (°C)	Time (hr)	Composition from chemical analysis	T_c (K)
1 NbN-NbC 031276	A	2.0	1800	0.01	Nb _{1.0} N _{0.76} C _{0.28}	16.4
2 NbN-NbC 130876	A	2.0	1800	0.01	Nb _{1.0} N _{0.60} C _{0.37} □ _{0.03}	16.9
3 NbN-NbC 310178	B	2.0	—	—	Nb _{1.0} N _{0.44} C _{0.26} □ _{0.30}	<7.4
4 NbN-NbC 221177	B	9.0	—	—	Nb _{1.0} N _{0.47} C _{0.31} □ _{0.22}	<6.5
5 NbN-NbC 240677	C	1.9	2200	96	Nb _{1.0} N _{0.30} C _{0.52} □ _{0.18}	<6.8
6 NbN-NbC 070777	C	1.9	2200	110	Nb _{1.0} N _{0.48} C _{0.35} □ _{0.17}	15.0
7 NbN-NbC 220278	C	1.7	2300	111	Nb _{1.0} N _{0.64} C _{0.25} □ _{0.13}	9.4
8 NbN-NbC 090278	C	1.4	2300	130	Nb _{1.0} N _{0.67} C _{0.15} □ _{0.18}	10.4

^a A, polycrystalline preform made as described in Ref. (3); B, zone melted; C, zone annealed.

at 1000°C and was collected and determined by titration with sodium hydroxide. The nitrogen percentages were determined as the differences between the measured metal and carbon percentages and 100. The results of the chemical analyses are listed in Tables II and III.

The experimental conditions for the preparation of some niobium- and vanadium-containing alloys are listed in Table IV.

The Instrument for Measuring Superconducting Transition Temperatures and the Measuring Technique

The principle in the T_c measurements used here is a determination of the unbalance in a

Wheatstone bridge containing the sample in a detector unit and kept at cryogenic temperatures. The unbalance of the bridge and the temperature is recorded simultaneously and the transition to superconductivity is indicated by a discontinuity in the unbalance of the bridge. The detector is mounted on a loading stick for a top-loaded (Fig. 1) Thor flow cryostat (Thor Cryogenics Ltd., Henly Road, Berinsfield, Oxon, England). It consists of two coils wound on a nylon coilform, each having 50 turns of 0.5-mm-diameter Cu wire. In the coilform are placed two calibrated germanium cryogenic temperature sensors (CryoCal Inc., Minneapolis, Minn.) and a 100-mW heating

TABLE IV
EXPERIMENTAL CONDITIONS FOR PREPARATION OF SOME NIOBIUM- AND VANADIUM-CONTAINING ALLOYS AND MEASURED T_c VALUES

Experiment No. and code	Method of preparation	He gas pressure (MPa)	Growth rate (mm hr ⁻¹)	Composition from X-ray analysis	T_c^a (K)
1 Nb ₃ Al 300377	Zone melting	1.0	10	Nb ₃ Al	17.4
2 Nb ₃ TaGe 040777	Zone melting	0.1	10	Nb ₅ Ge ₃	<6.4
3 Nb ₃ Ga 120576	Zone melting	0.3	20	Nb ₃ Ga	8.2-7.6
4 Nb ₅ InSb 020676	Zone melting	1	10	Nb ₃ Sb + In	<7.5
5 MoVTi 051274	Zone melting	0.3	15	?	<6.4
6 VB 090377	Zone melting	0.5	10	VB	<7.2

^a < followed by a number indicates that no superconducting phase transition was observed by cooling to the temperature indicated.

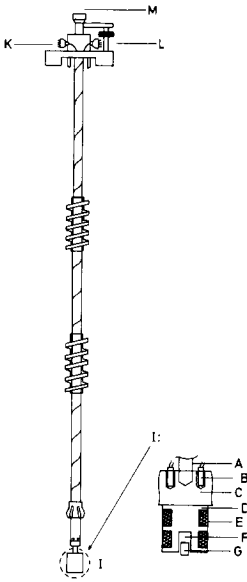


FIG. 1. Sketch of the loading stick with the detector unit. The letters in inset I indicate: A, lower part of the stick; B, cryogenic resistors; C, Cu block; D, nylon coilform; E, coil; F, cavity for the specimen; G, nylon plug. The small heating coil is placed just outside the cavity and is not shown. On the top of the loading stick are connections to: K, the heating coil; L, the cryogenic resistors; M, the Wheatstone bridge.

coil. One of these is kept at an extra cryoresistor. The other is fed with a constant current from a Thor constant current source (Thor Cryogenics Ltd.), and its variation in resistance with temperature is measured on a digital voltmeter. The specimen is placed in one of the two coils of the detector unit thus introducing an asymmetry in the magnetic field in its coils. The asymmetry suddenly changes when the transition to superconductivity takes place.

The abrupt change in the asymmetry is measured with the electronic circuit shown in Fig. 2. A detailed description of the electronic circuit may be obtained from the authors.

Only the detector coils of the electronic circuit are placed on the loading stick. The Wheatstone bridge and the transformer T_1 are placed in a small box on top of the loading

stick. As the impedance of the detector coils is rather low, it is necessary to have soldered connections between the coils and the rest of the bridge in order to avoid the influence of contact resistance of a plug connection. The rest of the electronic circuit is mounted on a print card. The instrument uses a supply potential of ± 15 V with a current of 30 mA. Its sensitivity can be checked at room temperature by introducing a 2-mm-diameter and 2-mm-long Cu specimen in the detector unit. This yields a 70-mV change in the dc-output potential. When the instrument is used for a determination of T_c , the specimen with a volume of 3 to 10 mm³ is placed in the detector unit, and the loading stick is placed in the flow cryostat. Approximately 1 hr is necessary to cool the specimen from 77 to 6 K. During this period the dc-output potential will change. Figure 3 displays this unbalance vs time for three specimens and the transitions to superconductivity.

Results and Discussion

The instrument described above was used to measure the T_c values listed in Tables II, III, and IV. The instrument was first used to measure T_c for Nb and Nb₃Al. The value found was 8.6 K for Nb and 17.3 K for Nb₃Al

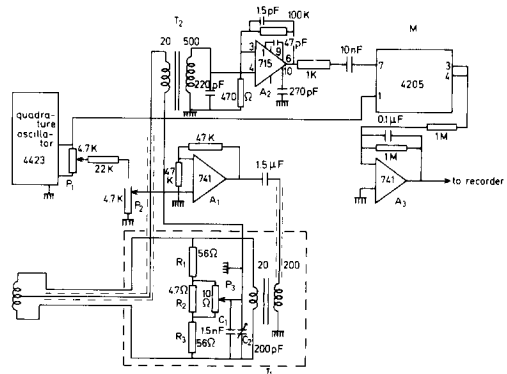


FIG. 2. Diagram of the electronic circuit.

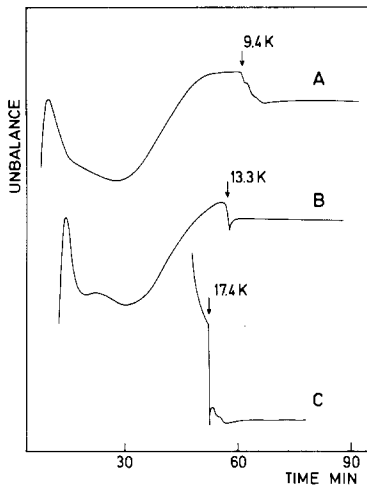


FIG. 3. Display of the unbalance-time diagram for: A, a niobium carbonitride specimen (No. 7, Table III); B, a niobium nitride specimen (No. 5, Table II); and C, a sample of Nb_3Al (No. 1, Table IV).

in acceptable agreement with the values from the literature, 9.1–9.5 and 16.3–17.8 K, respectively (5).

The chemical analysis used in this investigation assumes vacancies to occur only in the nonmetal sublattice of the nitride and carbonitride crystals. It has been shown that NbN and the NbN-NbC system also have vacancies in the metal sublattice near the nitrogen-rich end with up to 4–5% vacant sites in the metal sublattice for compositions close to stoichiometry (6). However, with more than 10% deviation from stoichiometry and with the nitrogen-carbon ratios found here for the carbonitrides, it is acceptable to assume that almost all the vacant sites are found in the nonmetal sublattice, and that the metal sublattice is filled for the niobium carbonitrides investigated and contains a few percent vacant sites for the niobium nitrides with compositions close to stoichiometry.

The investigation shows that T_c for $\delta\text{-NbN}$ decreases with increasing deviation from stoichiometry. The drop in T_c with x (in NbN_x) is almost linear, is more sharp for

these specimens than previously reported for niobium nitride (1), and is similar to that found by Kaiser (7). For niobium carbonitride it is found that the single crystals obtained in zone melting growth contain so many vacancies, even when an ambient nitrogen gas pressure of 9 MPa is used, that the crystals have no transition to a superconducting state at temperatures down to 7 K. By zone annealing of such single crystals the number of vacant sites can be reduced and such single crystals of niobium carbonitride has been found to have T_c values in the range 9–15 K.

Figure 3 shows the niobium carbonitride specimen to have a rather broad transition, the niobium nitride specimen to have a sharper transition, and the Nb_3Al specimen to have a very sharp transition to superconductivity. The last-mentioned transition is similar to that of niobium metal and is characteristic for a sample with a homogeneous composition. The transition for the specimens of niobium carbonitride and niobium nitride indicate that these two samples have composition gradients. As the values of T_c decrease with decreasing nitrogen contents the shape of the curves indicates that such concentration gradients are present in the two specimens, information the measurements can give in addition to the value for the transition temperature. It has previously been observed by microprobe methods (2) that crystals of the transition metal nitrides grown by zone annealing methods have nitrogen concentration gradients with the highest nitrogen contents in the surface layer. Recently, Kaiser (private communication) has shown by investigating Raman spectra of single crystals of $\gamma\text{-NbN}$ and $\delta\text{-NbN}$ that such concentration gradients can be rather large. A specimen with the overall composition $\text{NbN}_{0.75}$ according to chemical analysis had the composition $\text{NbN}_{0.90}$ of a thin surface layer and the composition $\text{NbN}_{0.75}$ below this layer.

Acknowledgments

Specimens for the investigations were cut from larger samples using spark erosion technique. The supplying of a spark erosion machine by Carlsbergfondet is acknowledged. We thank the Physics Department at Risø National Laboratory for the use of the cryogenic equipment.

References

1. L. E. TOTH, "Transition Metal Carbides and Nitrides," Academic Press, New York/London (1971).
2. A. N. CHRISTENSEN AND S. FREGERSLEV, *Acta Chem. Scand. A* **31**, 861 (1977).
3. A. N. CHRISTENSEN, *Acta Chem. Scand. A* **31**, 77 (1977).
4. A. N. CHRISTENSEN AND C. RUSCHE, *J. Cryst. Growth* **44**, 383 (1978).
5. B. W. ROBERTS, "Properties of Selected Superconductive Materials," NBS Technical Note 724, Department of Commerce, National Bureau of Standards, Washington, D.C. (1972).
6. E. K. STORMS, *High Temp. Sci.* **7**, 103 (1975).
7. R. KAISER, *Phys. Status Solidi B* **87**, 565 (1978).