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Electrical Resistivity of NbO*

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The resistivity of NbO_x ($0.99 \leqslant x \leqslant 1.03$) boules containing 3 to 5 grains is reported for the range 77–900°K. The material is an excellent conductor with a positive temperature coefficient of resistivity. The results are compared with some earlier work, which seems to require correction, and with unpublished work which is confirmed by this study.

Introduction

While it has been known since 1858 that NbO exhibits metallic characteristics (*1*), surprisingly little information is available on the physical characterization and properties of this material. Aside from work published in 1933 which established that the metallic conductivity of NbO persists into the liquid helium temperature range (*2*), most of the remaining work has been initiated in the last decade. This will be listed briefly under several headings:

(a) Several phase diagrams have been reported (*3–6*) as part of a comprehensive investigation of the NbO system; the results are not concordant.

(b) Crystal structure studies (*7–12*) are generally in good accord; the most complete study involved neutron diffraction techniques by which the locations of the atoms in the unit cell were ascertained. NbO is a member of the *Pm*3*m* space group, with 25% of cations and anions missing in an ordered manner from the parent rocksalt structure.

(c) Galvanic cell and other thermodynamic measurements (*13–16*) have been carried out, but the need for further complete measurements is evident.

(d) Phase and composition studies have been reported which indicate in NbO_x a homogeneity region of $0.98 \leqslant x \leqslant 1.03$ at room temperature (*17*).

(e) It has been established that NbO is a superconductor (*2*) below 1.5°K.

(f) Electrical properties of this compound have been explored by Pollard in an unpublished thesis (*17*) and by Pollard and Reed in a laboratory report (*18*); this work requires extension. The electrical, thermoelectric, and galvanic properties of NbO at the Nb-rich and NbO_2-rich phase boundaries have been investigated by Roberson and Rapp (*19*) in the range 0–900°C. Their resistivities are much higher than those reported in Refs. (*17*) and (*18*). In view of the paucity of data and their conflicting nature, a reexamination of the electrical properties of NbO was thought to be highly desirable.

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Experimental

A variety of samples of NbO_x in the composition range $0.98 \leqslant x \leqslant 1.03$ were grown by first melting appropriate amounts of high purity Nb metal and Nb_2O_5 in an arc and subsequently pulling boules by the Czochralski–Kyropoulos technique from the relatively cool central zone of the peripherally heated arc melter (*20–22*). Care was taken to exclude impurities; the arc was struck in an inert atmosphere of gettered argon. The boules, weighing several grams each, were polycrystalline and contained approximately 3–5 grains. The niobium oxygen ratios in the different boules were determined by reoxidizing a known weight of the sample to Nb_2O_5. The stoichiometry ratios quoted below are accurate to within ±0.005 units. One sample was doped with tungsten at the 2 at. % level.

Specimens for the resistivity measurements were cut in the shape of rectangular parallelepipeds approximately 8 × 1 × 1 mm in size. Four-probe resistivity measurements in the temperature range 77–900°K were made on an automated device with provision for periodic reversals in current direction.

The lead wires were spot welded on to the specimen by a capacitance discharge welder. The measurements were made in an atmosphere of helium. Current was supplied by a constant current source; it was repeatedly verified in various runs that the sample exhibited ohmic behavior. The voltage signals were amplified via a dc amplifier and displayed on the y axis of an x–y recorder. The temperature was monitored by means of a thermocouple pressed against the sample through a thin mica sheet; the output, relative to a reference junction of ice water, was also amplified and displayed along the x axis of the recorder. The average of the voltage readings obtained in the forward and reversed current direction was used as the voltage in response to the input current.

Results

The variation of resistivity ρ vs temperature T for five samples is displayed in Fig. 1. The following points are noteworthy:

(1) In all cases the resistivity increased linearly with temperature in the 77–900°K range, confirming the metallic nature of the samples under investigation.

(2) The temperature coefficients of resistivity are comparable to values encountered for normal metals such as Cu, Au, and Fe.

(3) According to the trends exhibited in Fig. 1, the more nearly stoichiometric samples are associated with the lowest resistivities.

(4) The resistivities are low, near $x = 1$, and at 77°K, and 300°K, $\rho \simeq 10^{-6}$ and $\rho \simeq 10^{-5}$ Ω cm, respectively. These values are comparable to those of the element Nb from which the oxide is derived.

(5) Doping with tungsten at the 2 at. % level does not significantly reduce the resistivity observed with the best available sample.

It is not possible to compare the present data with the early work by Meissner, Franz, and Westerhoff (*2*), because these investigators failed to specify their results in terms of resistivities. However, it may be noted that the temperature dependence of their resistivities is much lower than that reported here. The resistivities of Fig. 1 are roughly six order of magnitude below those cited by Roberson and Rapp (*19*). Undoubtedly, much of the discrepancy is to be attributed to the fact that these workers performed two-probe measurements on sintered pellets under conditions that did not preclude the formation of a two-phase mixture.

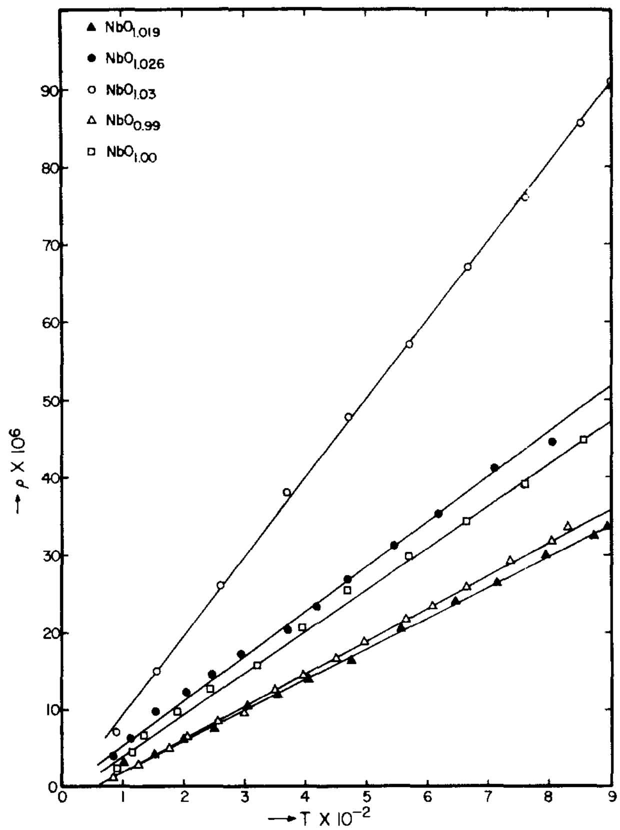

FIG. 1. Resistivity versus temperature for various NbO samples. The sample labelled $NbO_{0.99}$ was doped with 2 at % tungsten. Resistivity in micro-ohm-cm; T in °K.

The present work does, however, agree in all essentials with the results of Pollard (*17*) and of Pollard and Reed (*18*). These workers also noted in the stoichiometry range $0.982 \leqslant x \leqslant 1.008$ a linear rise in ρ with T, but theirs is smaller than that reported here. Below 77°K their curves flatten out and approach a value of 10^{-6} Ω cm, before the material becomes a superconductor at approximately 1.5°K. Our results obtained with large-grained boules exhibit conductivities at 77°K quite comparable to those of Pollard and Reed, whose experiments were performed on single crystals.

The metallic characteristics reported here make it quite plausible that the incorporation of potential donors such as W into the lattice should not dramatically affect the resistivity characteristics of the sample, and that variations in stoichiometry should likewise alter the electrical characteristics only to a slight extent. The highest lying curve in Fig. 1 was obtained with a sample whose composition was very close to the upper limit of the homogeneity range. In this instance small clusters of an incipient second phase may have been present.

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