

Superconductivity in the TiO and NbO Systems

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This paper presents electrical resistivity and superconductivity studies for the B1 (NaCl) structure oxides of titanium, vanadium, and niobium. In samples of nominal composition TiO_x , VO_x , and NbO_x , x was varied from 0.8 to 1.2. It was found that all three of these oxides exhibit room-temperature electrical resistivities characteristic of metallic behavior. With decreasing temperature, the resistivity drops steeply in the case of NbO_x , but remains steady or rises somewhat in the case of TiO_x and VO_x , depending on the exact value of x . It is suggested that in TiO_x and VO_x there is a large resistivity component due to scattering of carriers by disordered vacancies. Superconductivity was observed in NbO_x ($T_c = 1.38$ K, $x = 1.0$) and TiO_x ($T_c = 1.0$ K, $x = 1.07$). In the latter case the material showed a well-defined maximum of T_c as a function of composition, with $T_c < 0.05$ K for $x < 0.85$ and $x > 1.20$. Several VO_x samples remained normal to 0.07 K.

1. INTRODUCTION

The occurrence of superconductivity in many of the B1 structure carbides and nitrides of the transition elements, such as TiN, VN, NbC, and NbN, is well known and has been extensively investigated.¹⁻³ Less attention has been paid to those oxides which occur in the same structure, namely, TiO, VO, and NbO. Some time ago we reported⁴ TiO and NbO to be superconducting in the vicinity of 1 K. A more detailed investigation of the electrical and superconducting behavior of these two compounds has now been completed, and we have determined that VO is not a superconductor down to the millidegree region.

It is characteristic of compounds of the above type that the electronic properties are strongly influenced by deviations from the stoichiometric formula TX. For both TiO and VO there is an extraordinarily wide range of compositions for which the B1 structure is stable. The titanium compound exists as single-phase material for nominal compositions between $\text{TiO}_{0.8}$ and $\text{TiO}_{1.2}$.⁵⁻⁸ Ehrlich⁵ suggested that this unusually wide phase region is associated with a large vacancy population on both lattice sites. Density measurements by Denker⁹ indicate that with increasing oxygen content the true formula is given by $\text{Ti}_{0.92}\text{O}_{0.74}$ at one extreme, and by $\text{Ti}_{0.79}\text{O}_{0.96}$ at the other. Similarly, vanadium monoxide exhibits a phase field at least as wide as that of TiO, plus a high vacancy content.¹⁰ NbO is reported to possess an equilibrium vacancy concentration as high as 25% on both lattice sites, but differs from the two other monoxides by having a narrow phase field.¹¹

The nonsuperconducting electrical properties of TiO were extensively investigated by Denker,¹² who found that the room-temperature electrical resistivity of electron-beam zone-melted material lies around $300 \mu\Omega\text{-cm}$, irrespective of composition. For the majority of compositions the resistivity was also found to increase slowly with decreasing temperature, an unusual feature for metallic materials. The electrical properties of VO were studied from room temperature to about 100 K by Kawano *et al.*¹³ The results suggest that VO is a low-energy gap semiconductor in this temperature range. Low-temperature magnetic susceptibility data were also obtained on the same samples, with the interesting conclusion that for samples of composition $\text{VO}_{1.15}$ and $\text{VO}_{1.26}$ there are well-defined antiferromagnetic Néel transitions at 4.6 and 7.0 K, respectively. The electrical resistivity of NbO does not seem to have been previously investigated.

The present work began primarily as a study of superconductivity in these compounds. It was later extended to include electrical resistivity measurements from room temperature down to 1 K. Compositions were investigated across the entire cubic phase field in the case of TiO and VO, and deep into the alloy zones on either side of the narrow cubic region of NbO. Our electrical resistivity data agree quite well with the results of Denker¹² and Kawano *et al.*,¹³ but cover a somewhat wider range of temperatures. We have also investigated the effect of heat treatment on resistivity, which turns out to be very dramatic in the case of TiO samples of low oxygen content.

More detailed studies on the critical temperature of superconducting TiO has confirmed the occurrence of a well-defined maximum of T_c centered at about $\text{TiO}_{1.07}$. The critical temperature drops off to below 50 mdeg at both ends of the single-phase region. This unusual effect will be discussed in terms of our limited knowledge of the system's electronic structure.

2. EXPERIMENTAL

The melting points of the transition metal monoxides are approximately 1750°C (TiO), 1800°C (VO), and 1915°C (NbO). It was found that all three compounds could be satisfactorily prepared by levitation melting a suitable mixture of the pure metal and a higher oxide (either TiO_2 , V_2O_5 , or Nb_2O_5) in an atmosphere of pure argon. The samples were melted and dropped into a water-cooled copper mold. In a few selected samples the composition of the end product was checked by weight-gain measurements obtained by oxidation at 1000°C to constant weight. The composition, thus derived, agreed with the nominal composition to within 1%. For all samples the total weight was determined before and after melting. A weight loss of more than a few milligrams in a 5-g ingot caused the sample to be rejected. Such losses were usually due to splashing of the molten material rather than to any noticeable decomposition of the compounds, all of which appear to be quite stable in liquid form. TiO and NbO exhibit a golden color, whereas VO is silvery gray.

Marked differences were noted in the mechanical properties of the various oxides prepared by levitation melting. All these materials are brittle and have a tendency to crack quite easily. This is not a problem in the case of the superconducting tests, since powdered or fragmented samples are acceptable for magnetic testing. However, for electrical resistance measurements it was necessary to prepare specimens of more regular shape. The as-cast ingots were usually cylinders about $\frac{1}{4}$ in. in diameter and about $\frac{1}{2}$ in. long. Using a diamond saw, bars of rectangular cross section were cut from these cylinders for electrical measurements, and the surplus pieces of the cylinder were used for x-ray and analytical studies.

Difficulty was experienced due to the presence in the cast samples of hairline cracks, which were evident in the surfaces exposed by cutting. These cracks appeared frequently in the TiO samples, to a lesser extent in VO, and hardly at all in NbO. The samples used for resistivity measurements were selected for absence of cracks from a large number of different cast samples at each composition.

In order to check the possible influence of small cracks on the absolute values of the measured resistivities, a different set of resistivity samples was prepared as follows. Materials at several compositions were ground to a fine powder, pressed into rectangular bars, and sintered in vacuo at about 1400°C. The resulting specimens were somewhat porous, with densities around 90% of the cast value. The measured electrical resistivity was corrected downwards by the factor $(\rho_a/\rho_c)^{3.5}$, where ρ_a and ρ_c are the actual and cast densities, respectively. Corrected resistivity values lay within about 5% of these obtained for cast samples of the same composition, indicating that the latter values are reliable.

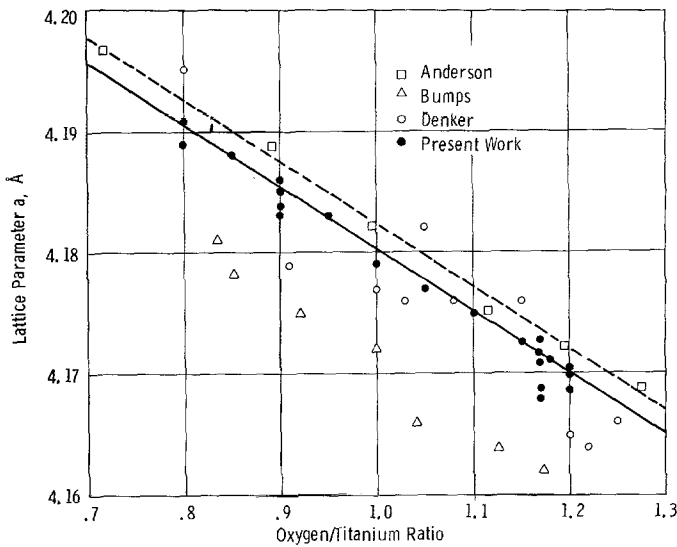


Fig. 1. Lattice parameter of titanium monoxide as a function of oxygen-to-titanium ratio.

The single-phase character and composition of every sample was checked by x-ray examination in a 57.3-mm powder camera. Lattice parameters corrected for absorption are plotted for TiO as a function of nominal composition in Fig. 1, where data due to earlier investigators are also shown. The full line is drawn through the points obtained in the present work, while the dotted line represents the data of Andersson *et al.*¹⁴ Evidently these two sets of data are in excellent agreement except for a slight relative shift, which is probably due to differences in standards between the two laboratories involved. The data of Bumps *et al.*⁸ and Denker⁹ both exhibit much more scatter than those represented by the two lines of Fig. 1. Denker's data are generally clustered about the two lines, but those of Bumps *et al.* are displaced downwards by about 10 mÅ. The equation of the straight line obtained from the present work on TiO is

$$a = 4.2311 - 0.0508 (\text{O/Ti}) \quad (1)$$

The lattice parameter of vanadium oxide also varies with the oxygen-to-vanadium ratio, but this dependence was not studied in detail in the present work. A value of 4.073 Å was observed for the stoichiometric compound VO. In the case of niobium oxide, no composition dependence could be detected, and the measured lattice parameter was 4.211 Å.

As already mentioned, the electrical resistivity measurements were made on samples cut to regular shape. A four-probe technique was employed, with measuring currents of a few milliamperes. Temperatures between 1 K and 100°C were obtained with a sample probe of large heat capacity fitted with a thermocouple and a germanium resistance thermometer. The probe was either immersed in cryogenic fluid or was allowed to drift slowly between the various fixed points.

Temperatures below 1 K were necessary for most of the present superconducting measurements. These were obtained using several ^3He and adiabatic demagnetization cryostats which already existed in our two laboratories. In the ^3He region the superconducting transitions were monitored within the inductor of a 16-kHz resonant circuit. At lower temperatures a low-frequency mutual inductance bridge was employed. Temperatures in this region were usually determined by magnetic thermometry, using either potassium chrome alum or cerium magnesium nitrate. However, germanium and carbon resistance thermometers were also employed as secondary standards. It should be remarked that despite the variety of techniques employed, T_c values were reproducible within a few percent when the samples were checked in different cryostats.

3. RESULTS

3.1. Titanium Monoxide

Values of the electrical resistivity of various cast TiO_x samples are given at a few characteristic fixed temperatures in Table I and are plotted vs. temperature for a wide range of compositions in Fig. 2. The rather high level of the resistivity in a metallic sense and its relatively slow variation with temperature is reminiscent of the behavior of high-concentration alloys with dominant impurity scattering. In this case it seems reasonable to assume

TABLE I
TiO_x Electrical Resistivity Values

Oxygen-to-titanium ratio	Resistivity (298 K), $\mu\Omega\text{-cm}$	Resistivity (78 K), $\mu\Omega\text{-cm}$	Resistivity (4 K), $\mu\Omega\text{-cm}$
0.80	281	294	296
0.87	303	283	287
0.95	285	275	277
1.05	311	363	378
1.00	290	314	318
1.12	296	381	406
1.17	309	415	443
1.20	331	483	512

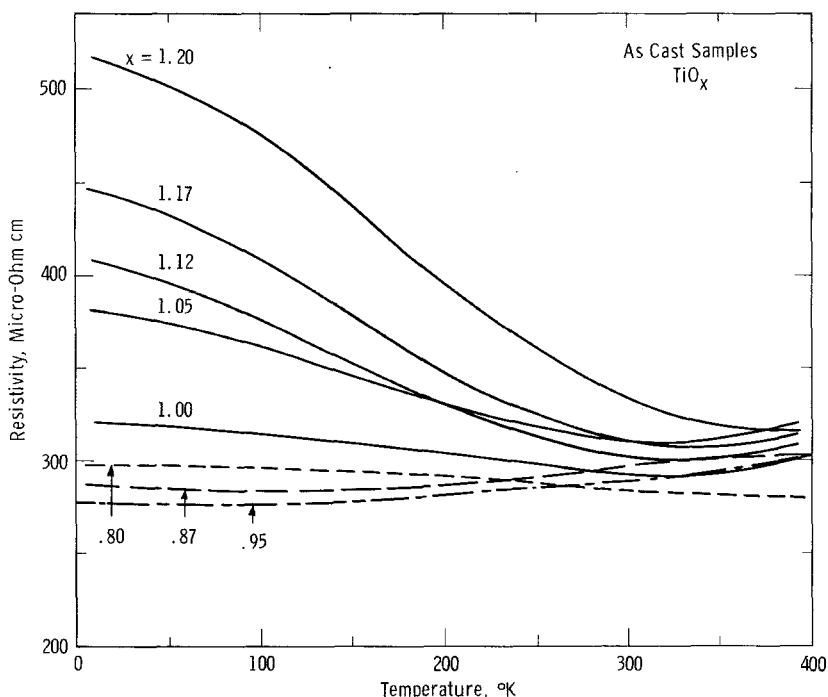


Fig. 2. Electrical resistivity vs. temperature for as-cast, single-phase samples of TiO_x , various x values.

that vacancies are the principal scattering centers, since they are known to exist in high concentrations in TiO .⁹

Figure 2 also indicates that with increasing oxygen content, the resistivity develops a pronounced negative temperature coefficient. This is unexplained by a simple, fixed vacancy scattering picture, and we cannot interpret it at the present time. It may possibly be due to temperature-activated motion of vacancies or, alternatively, to the appearance of a small energy gap in the electronic structure.

The present data are qualitatively similar to the earlier results of Denker¹² for TiO , particularly as regards the temperature variation of resistivity. Unfortunately, there are noticeable quantitative discrepancies between the two sets of data. The resistivities obtained in the present work are generally higher than those of Denker, particularly for samples near the middle of the phase diagram. For example, the residual resistivity of our TiO sample was $318 \mu\Omega\text{-cm}$, compared to $175 \mu\Omega\text{-cm}$ observed by Denker. These differences are too large to be attributed to experimental error.

The source of the discrepancy seems to lie in the method of preparation of the samples. In the present work the samples were cooled very rapidly by dropping molten material into a cold crucible. Denker utilized an electron-beam zone-refining process in which gradual cooling of the specimens can be expected. Denker also noted that one of his samples, stoichiometric TiO, showed a marked decrease of residual resistivity when annealed below 1000°C. This suggested to us that the results for the electron-beam zone-refined samples might be affected by involuntary annealing during preparation and led us to investigate the effect of heat treatment on the cast samples of the present work.

A series of cast TiO_x samples for which electrical data had already been obtained were annealed for 72 h at 800°C. This produced a marked decrease of resistivity at all temperatures, as shown for three representative samples in Fig. 3. The greatest change of resistivity occurred for the lowest

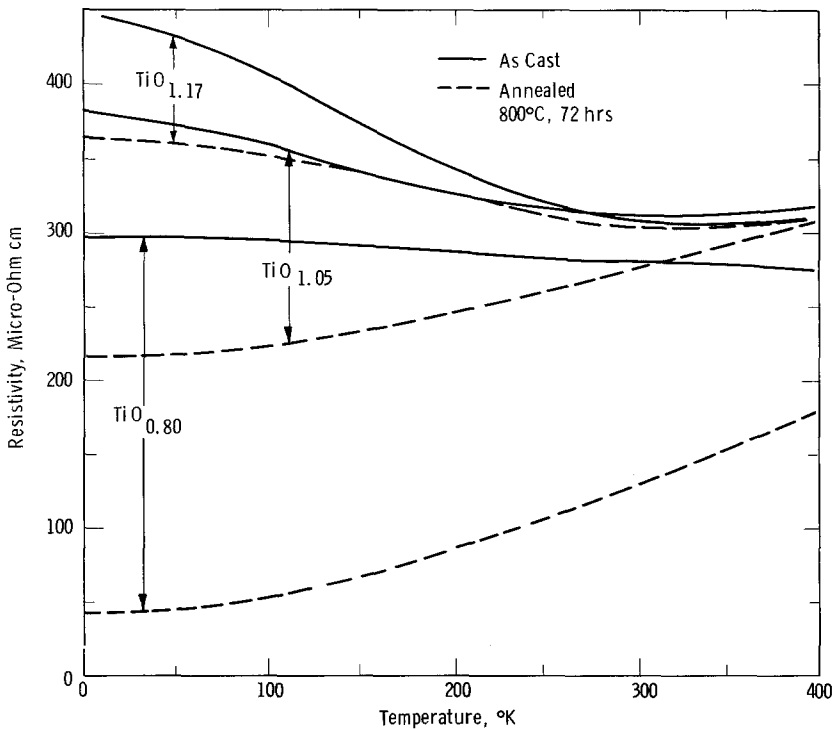


Fig. 3. Effect of 800°C annealing on the electrical resistivity vs. temperature curve of TiO_x , various x values.

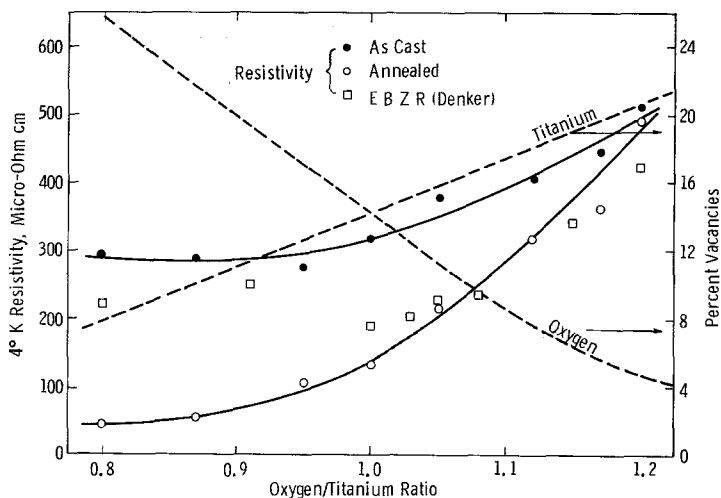


Fig. 4. Effect of 800°C annealing on the electrical resistivity of titanium monoxide at 4.2 K, and the percentage of titanium and oxygen vacancies as a function of the oxygen-to-titanium ratio.

oxygen content sample, $\text{TiO}_{0.8}$, and the effect was largest near absolute zero. This phenomenon is further illustrated in Fig. 4, where the residual resistivity before and after annealing is plotted as a function of composition.

It seems likely that the observed drop in resistivity is primarily due to the ordering of vacancies by heat treatment. Watanabe *et al.*¹⁵ have reported superlattice lines in the x-ray diffraction pattern of TiO annealed for long periods at 950°C and have attributed these to vacancy ordering. Similar lines were observed in the x-ray patterns of the present heat-treated samples, particularly at low oxygen contents.

The 4 K resistivity values of Denker's electron-beam zone-refined samples are also plotted in Fig. 4. From a comparison of these values with our own data we conclude that Denker's samples were probably ordered at high oxygen contents and disordered at low oxygen contents. This appears to explain the quantitative differences between the resistivity values of the present work and those of Denker.

The two dotted curves in Fig. 4, corresponding to the right-hand ordinate, show the variation with composition of the titanium and oxygen vacancy concentrations calculated by Denker from x-ray and density data.⁹ The form of the as-cast residual resistivity curve resembles the titanium vacancy plot more than the oxygen vacancy plot, suggesting that titanium

vacancies are the dominant scattering centers. A rough approximation to the residual resistivity curve is given by the expression

$$\rho_0 = 23V(\text{Ti}) + 2V(\text{O}) \mu\Omega\text{-cm}, \quad (2)$$

where $V(\text{Ti})$ and $V(\text{O})$ are the percentage of titanium and oxygen vacancies, respectively. This expression is not an exact representation of the residual resistivity, since the curvature of the latter was too pronounced to permit exact fitting with the almost linear vacancy functions. It should also be emphasized that our conclusion that scattering is mainly due to titanium vacancies is open to criticism on the grounds that we have ignored any possible changes of carrier density across the solid-solution range.

Superconducting critical temperature data for TiO_x samples were derived from transition curves of the type shown in Fig. 5, where the normalized initial differential magnetic susceptibility is plotted vs. temperature for several specimens. Clearly the superconducting critical temperature is quite sensitive to composition in certain regions. The transition widths seem reasonable for unannealed refractory compounds. Bulk superconducting behavior cannot be inferred unambiguously from differential magnetic susceptibility data such as that shown in Fig. 5. Nevertheless, such data is usually reliable when the samples are known to be unequivocally single phase, as was the case in the present work.

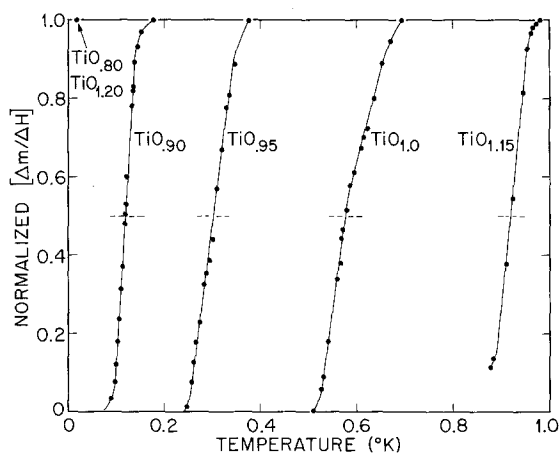


Fig. 5. Onset of superconductivity in titanium monoxide samples; the normalized initial differential magnetic susceptibility is shown as a function of temperature for various compositions.

Figure 6 shows all of the critical temperature data points accumulated for single-phase samples of TiO_x . The horizontal bars with down-directed arrows represent lowest temperatures of measurement at which normal behavior was observed. All of the data points in Fig. 6 are for as-cast samples, but represent a mixture of the data taken in the various cryostats available to us. No systematic differences could be detected between the data from the various sources.

For compositions in the vicinity of $\text{TiO}_{0.9}$ and $\text{TiO}_{1.2}$, where T_c is a rapidly varying function of x (Fig. 6), it was not surprising to observe a fairly wide spread of measured T_c values. Clearly, this can be attributed to small variations of x . However, better reproducibility of T_c might have been anticipated in the vicinity of the flat maximum of T_c centered about $\text{TiO}_{1.07}$. In fact, the observed T_c values at the maximum also scattered over a range much greater than the individual transition width, extending from 0.5 K up to about 1.1 K. The culprit in this case does not seem to be the oxygen-to-

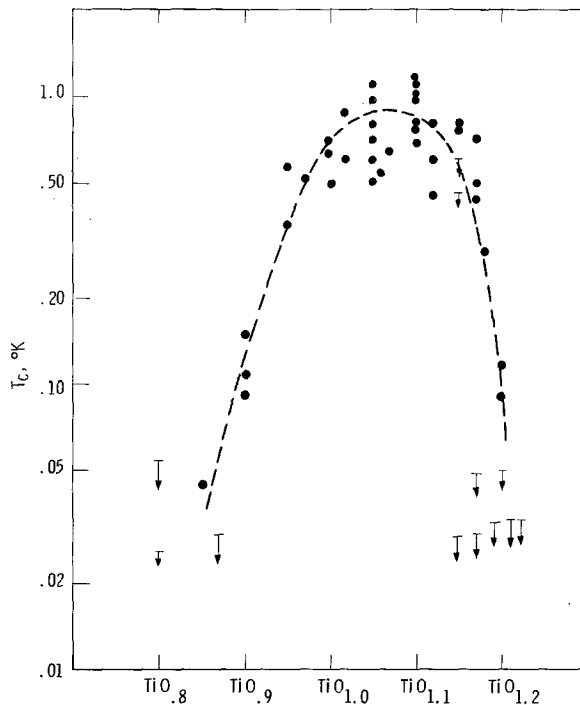


Fig. 6. Superconducting critical temperature vs. composition, titanium monoxide (points). Each horizontal bar with an arrow below it represents a sample which was normal down to the temperature shown by the bar.

titanium ratio, but rather the average vacancy content. Because this is so large in TiO, about 15%, we suspected that fluctuations in this number might be affecting T_c .

To test the above hypothesis, an effort was made to deliberately vary the vacancy content of TiO by the application of high pressures. With pressures up to 90 kbar and temperatures up to 1650°C, it was found¹⁶ that stable TiO samples could be produced with vacancy contents all the way down from 15% to zero. As the vacancy population declined, T_c increased, reaching an ultimate value of 2.3 K for zero vacancy material at the stoichiometric composition. The variation of T_c with vacancy concentration proved to be highly nonlinear, with the steepest slope at the highest concentrations, around 15%. In this region a change of about 1% in the total vacancy content produces a 100% change in T_c . We suggest that such a change is possible as a random fluctuation during normal preparation procedure, and explains the large spread of T_c values at the maximum of Fig. 6.

In view of the dependence of the electrical resistivity of TiO_x on the exact details of heat treatment, attempts were made to detect similar effects on T_c . For specimens annealed for 72 h at 800°C, no substantial change of T_c could be detected relative to the data of Fig. 6. Normal specimens remained normal, and only small shifts in T_c were detected for the superconducting cases. Curiously, these shifts were most noticeable in the vicinity of the T_c maximum. This was probably due to a small reduction of vacancy content associated with the annealing process. We conclude that the ordering of vacancies produced by annealing does not have a substantial effect on T_c .

In an effort to obtain some insight into the nature of the electronic density of states for TiO_x , some critical magnetic field data were obtained. For these measurements the samples were cooled below the critical temperature and a constant longitudinal dc magnetic field was applied to the mutual inductance coil system surrounding the sample. Both χ' and χ'' , the in-phase and out-of-phase components of the complex ac magnetic susceptibility, were then measured as functions of temperature as the sample warmed due to the natural heat leak of the system. Data thus obtained in zero applied field and in a field of 655 Oe are shown in Fig. 7.

The appearance of a maximum in the χ'' data obtained for zero applied magnetic field indicates that the sample trapped some of the magnetic flux associated with the ac measuring field. For samples which exhibit such nonideal magnetic behavior, the determination of the upper critical magnetic field is somewhat uncertain. However, in the present work we have assumed that the midpoint of the χ' transition curve is a good measure of $H_{c2}(T)$, the upper critical magnetic field. Data obtained for several applied-field values between zero and 655 Oe were used to obtain estimates of the initial slope, $[dH_{c2}/dT]_{T_c}$, presented in Table II.

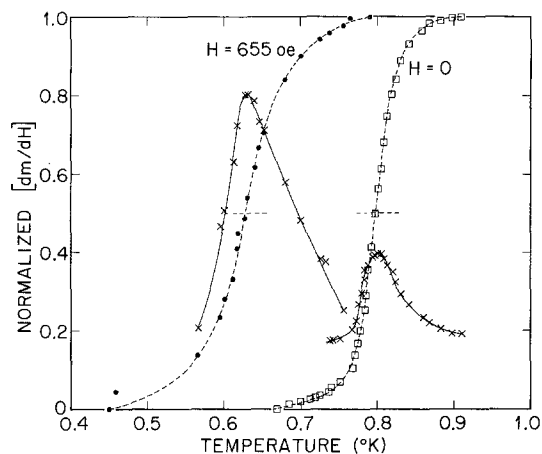


Fig. 7. Real and imaginary components of the ac magnetic susceptibility of TiO as a function of temperature, for dc applied fields of zero and 655 Oe (unannealed sample, $\text{TiO}_{0.95}$).

3.2. Vanadium Monoxide

Since vanadium and titanium are neighboring elements in the periodic system, oxides of the same crystal structure may be expected to resemble each other in properties. One point of resemblance has already been noted, that is, the unusually wide phase region of both monoxides, extending for at least 20 at. % above and below the stoichiometric compound. Similarly, both materials have a remarkable concentration of vacancies on both lattice sites. It is not surprising that there are similarities in the electrical properties, which can be seen by comparing Figs. 2 and 8. Figure 8 contains our resistivity data for four representative single-phase samples of VO_x measured between 100°C and 1 K.

The room-temperature resistivity of VO_x is high by metallic standards, falling between 400 and 1300 $\mu\Omega\text{-cm}$ for the samples of Fig. 8. This is probably attributable to scattering of carriers by vacancies, as was the case for TiO_x . VO_x also exhibits a negative temperature coefficient of resistivity, which

TABLE II

Composition	T_c , K	$-(dH_{c2}/dT)_{T_c}$, kOe/deg	V , cm^3/mole	ρ_0 , $\mu\Omega\text{-cm}$	γ , $\text{mJ}/\text{mole-deg}^{-2}$	λ
$\text{TiO}_{0.95}$	0.80	3.7	12.8	100	0.89	0.41
$\text{TiO}_{1.00}$	0.64	3.4	13.0	140	0.60	0.38
$\text{TiO}_{1.06}$	0.54	4.4	13.4	210	0.52	0.37

becomes more pronounced as the oxygen content rises. Departure from metallic behavior seems to be somewhat more noticeable in the case of VO_x than in TiO_x .

Kawano *et al.*¹³ studied the electrical resistivity of VO_x from room temperature down to 100 K and concluded that the material is semiconductive in this temperature region, with an energy gap characteristic of each composition. At high temperatures the data of Fig. 8 are in good agreement with the results of Kawano *et al.* and may be interpreted similarly. However, it is not possible to extend this interpretation to cover the entire temperature range of Fig. 8. In other words, a plot of the logarithm of resistivity vs. $1/T$ does not yield a straight line for each composition. One obtains, instead, a curve which indicates a gradually decreasing energy gap with decreasing temperature. An exception to this is the $\text{VO}_{0.80}$ sample, for which there is a changeover to a positive temperature coefficient of resistivity below about 10 K. It is also interesting to note that for the $\text{VO}_{1.10}$ sample, the resistivity is essentially proportional to $1/T^{1.43}$ over the entire range of measurement.

All of the samples of Fig. 8 were tested for superconductivity. No evidence of a superconducting transition was found down to 0.063 K in the case of the $\text{VO}_{1.0}$ sample and down to 0.07 K for the other three samples. In view of the fact that VO_x is somewhat less metallic in character than TiO_x , this result was not entirely surprising. However, since the isomorphous VN compound is superconducting at 8.5 K it seems desirable to test lower resistivity samples such as $\text{VO}_{0.80}$ down to lower temperatures.

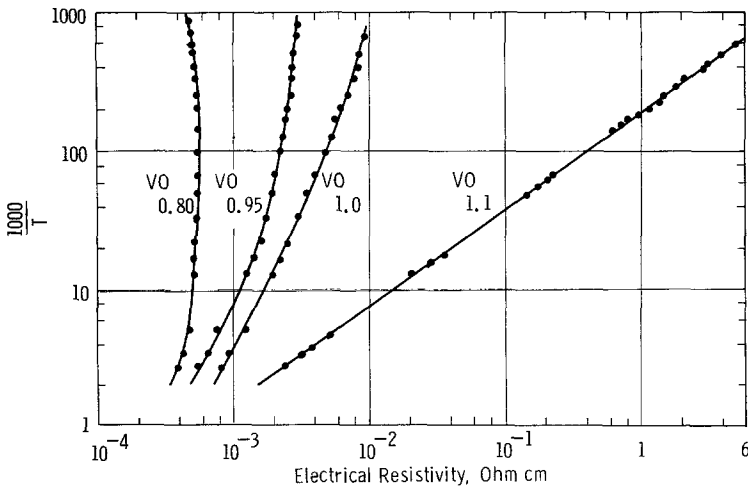


Fig. 8. Electrical resistivity vs. temperature for as-cast, single-phase samples of vanadium monoxide; various compositions.

3.3. Niobium Monoxide

According to Elliott,¹⁷ single-phase NbO is formed in a very narrow range of composition close to the stoichiometric formula. Measurements on NbO in the present work tend to confirm this picture. A series of samples were prepared with the oxygen/niobium ratio changing from 0.5 to 1.5. X-ray studies on these indicated that composition deviation by as little as 0.5 at. % on either side of stoichiometric NbO produces a mixed-phase sample. Resistivity and critical temperature data for our samples are shown in Fig. 9.

Single-phase NbO itself is a metal, with an electrical resistivity of $21 \mu\Omega\text{-cm}$ at 298 K. The resistivity decreases with decreasing temperature, reaching the value $1.8 \mu\Omega\text{-cm}$ at 4.2 K. There is no evidence of negative-temperature-coefficient behavior of the type observed in TiO and VO. NbO also becomes superconducting at about 1.38 K.

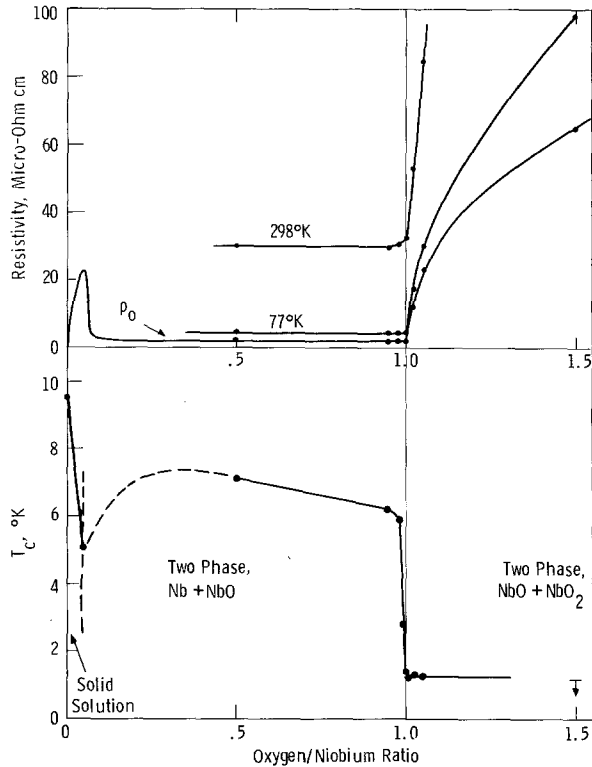


Fig. 9. Electrical resistivity and superconducting critical temperature as a function of composition; as-cast alloys of niobium and oxygen.

The electrical behavior of the two-phase systems on each side of NbO (Fig. 9) is more or less in keeping with the phase diagram. Considering first the niobium-rich side, the steep rise in critical temperature is consistent with the addition of free niobium metal, which has a much higher critical temperature than NbO. From the mode of preparation this free metal should contain dissolved oxygen, which tends to depress the critical temperature below 9.5 K.¹⁸ In the present case, T_c values between 6 and 7 K were observed, consistent with the presence of 1–2% of dissolved oxygen. According to the work of Desorbo,¹⁸ the residual resistivity of such material should lie around 10 $\mu\Omega\text{-cm}$. Thus, it is not surprising that the two-phase mixture exhibits a residual resistivity close to that of the low-resistivity component, NbO itself.

On the oxygen-rich side of the phase diagram, the addition of NbO₂ to NbO produces a steep rise of resistivity. Presumably this is due to the presence of high-resistivity NbO₂ in intergranular form. At the same time T_c is essentially unaffected by the presence of NbO₂, since the latter is not a superconductor.

4. DISCUSSION

The three compounds TiO, VO, and NbO resemble each other in having the same structure and an unusually high concentration of lattice vacancies. Electrically, however, we have found marked differences between these three compounds. At one extreme NbO behaves as a pure metal with a low residual resistivity, which suggests the possibility of natural ordering of the vacancies. At the other extreme, VO has an unusually high residual resistivity and a strong negative temperature coefficient of resistance reminiscent of nonmetallic behavior. The high resistivity is probably in part due to scattering of charge carriers by disordered vacancies. Possibly the carrier density is on the low side for this material. In between these two extremes lies TiO, with a moderately high residual resistivity, also attributable to disordered vacancies. However, for TiO the vacancies can be ordered by heat treatment, particularly at low oxygen contents, and the resistivity behavior then becomes more like that of NbO.

Against this background, our failure to detect superconductivity in VO is not particularly surprising. At the stoichiometric compositions TiO and NbO are both superconductors with not too dissimilar critical temperatures. The difference between them is simply that we are unable to vary the oxygen/metal ratio appreciably in the NbO case, whereas for TiO, as we have seen, a very wide variation is possible, with dramatic effect on T_c .

What is the origin of the striking maximum of T_c vs. x for TiO _{x} , as shown in Fig. 6? This is not a question that can be satisfactorily answered at the

present time, but some comments are appropriate. In the first place we note that the phenomenon is not completely unique to TiO_x . It was demonstrated earlier by Giorgi and coworkers¹⁹ that the compound NbC_x and TaC_x both show a sharp decline of T_c when the carbon content is reduced below 1.0. This occurs with a steep slope, not too dissimilar from that found on the low oxygen side of the maximum in Fig. 6. However, it should be noted that the carbide behavior was monotonic, that is, no evidence was found for a drop off of T_c at high carbon contents. Perhaps this is merely due to the fact that the carbon content cannot appreciably exceed 1.0.

Critical temperature maxima are found in many solid-solution alloy systems,²⁰ and can be explained largely on the basis of variations of the electronic density of states γ using BCS theory. In Table II γ values have been calculated for three annealed samples of TiO_x , using the equation²¹

$$\gamma/V = [(1.88 \times 10^{-4})/\rho_0](dH_{c2}/dT)_{T_c} \quad (3)$$

where ρ_0 is the normal state residual resistivity in $\Omega\text{-cm}$, and V is the molar volume.

Table II suggests that γ declines appreciably with increasing oxygen content. This result is qualitatively consistent with earlier work on the magnetic susceptibility of TiO_x , which also declines noticeably as x increases.¹² Such a decrease in density of states may perhaps be responsible for the disappearance of T_c on the high side of the maximum (Fig. 6), but obviously does not explain the drop off at low x values.

It is interesting to compare the results of Table II with some theoretical estimates of the density of states. Ern and Switendick²² estimated that $N(0)$ for both spin directions in vacancy-free TiO is essentially one state per primitive cell per electron volt. The resulting γ value, unrenormalized,²³ is approximately $3.4 \text{ mJ}\cdot\text{mole}^{-1}\cdot\text{deg}^{-2}$. Schoen and Denker²⁴ have shown that if vacancies are taken into account, γ is reduced from 3.4 to $0.97 \text{ mJ}\cdot\text{mole}^{-1}\cdot\text{deg}^{-2}$ for 15% vacancies on both lattice sites. The agreement between the theoretical value and the results of Table II is not impressive.

It would be premature to attribute the experimental observations on the critical temperature of TiO_x to variations in $N(0)$ alone since we cannot rule out variations in V^{BCS} . Ern and Switendick's²² APW calculation of the band structure suggests that the Fermi level of stoichiometric, vacancy-free TiO lies in an overlapping $3d-4s$ band, not too far from a rather wide $2p$ band. With the introduction of 15% vacancies plus variations of the O/Ti ratio, large shifts of these bands relative to each other can be anticipated. It is known that the BCS interaction parameter is radically different for s -band conduction as opposed to d -band conduction,²⁵ and is doubtless different again for the p -band case. Our present suggestion is that the T_c maximum of TiO_x is due to a combination of two effects, first a shift between different conduction

bands, and second, a decrease in $N(0)$ as the O/Ti ratio is increased. Possibly the $2p$, $3d$, and $4s$ bands are involved in this shift, but in what order we are unable to state at present. It may also be that the band shift is not monotonic in a rigid-band sense, so that possibly only the $3d$ and $4s$ bands are involved, with a shift occurring from one to the other and then back to the first as x is steadily increased. More detailed electronic structure studies will be necessary to go from these speculative remarks to a satisfactory model.

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