

## Semiconductor-Metal Transitions in $\text{NbO}_2$ and $\text{Nb}_{1-x}\text{V}_x\text{O}_2$

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$\text{NbO}_2$ ,  $\text{Nb}_{0.98}\text{V}_{0.02}\text{O}_2$ , and  $\text{Nb}_{0.95}\text{V}_{0.05}\text{O}_2$  transform from semiconducting to metallic state at temperatures higher than the DTA phase-transition temperatures. Vibrational mode softening and *c*-axis Nb-Nb pairing appear to be important factors in the mechanism of these transitions. In the solid solutions, *c/a* ratio is maximum at  $x = 0.5$  since the metal-metal interaction along the *c* axis becomes minimum; conductivity is minimum at this composition since there are no mobile electrons.

### Introduction

The heat content, coefficient of thermal expansion and electrical conductivity of  $\text{NbO}_2$ , were reported by Kusenko and Geld (1) over a decade ago. Since then, a few other workers have examined various properties of  $\text{NbO}_2$  (2-6) as well as of solid solutions of  $\text{NbO}_2$  with  $\text{VO}_2$  (7-9).  $\text{NbO}_2$  has a distorted rutile structure at room temperature and it transforms at high temperatures ( $T_i' \approx 1125$  K) to the basic rutile structure (3-5). In the low-temperature phase,  $\text{NbO}_2$  has a pairing of Nb ions along the *c* axis to give alternate short and long Nb-Nb bonds. At  $T_i'$ , the superstructure lines of the distorted rutile structure disappear. In the solid solutions,  $\text{Nb}_{1-x}\text{V}_x\text{O}_2$  with  $x \geq 0.95$ , transitions akin to the  $\text{VO}_2$  transition (at  $\sim 340$  K) are observed (9); when  $0.5 < x < 0.95$ , however, the  $\text{VO}_2$  transition is not seen and the solid solutions possess the basic rutile structure even at room temperature (9, 10). We have presently examined the nature of the phase transitions and conductivity anomalies in pure  $\text{NbO}_2$  and its solid solutions with vanadium,  $\text{Nb}_{1-x}\text{V}_x\text{O}_2$  with  $0.0 < x < 0.5$ . It was of particular interest to find out whether  $\text{NbO}_2$  exhibits a semiconductor-metal transition around  $T_i'$ .

### Experimental

$\text{NbO}_2$  was prepared by melting stoichiometric quantities of  $\text{Nb}_2\text{O}_5$  (>99.995% purity) and Nb metal (>99.995% purity) in an arc in argon

atmosphere (11) or by the vacuum sintering (6) of stoichiometric quantities of NbO (12) and  $\text{Nb}_2\text{O}_5$ . The solid solutions,  $\text{Nb}_{1-x}\text{V}_x\text{O}_2$ , were prepared by melting stoichiometric quantities of  $\text{NbO}_2$  and  $\text{VO}_2$  or by vacuum sintering of appropriate mixtures of  $\text{NbO}_2$ ,  $\text{V}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$ . All the samples were analyzed by combustion to higher oxides.

X-Ray diffraction studies were carried out with a GE recording diffractometer and differential thermal analysis with an Aminco or duPont thermoanalyzer. Four-probe electrical conductivity and Seebeck coefficient measurements were carried out on pressed pellets employing the apparatus fabricated in this laboratory (9, 13, 14).

### Results and Discussion

DTA studies (Fig. 1) show a transition at 1073 K ( $=T_i''$ ) in pure  $\text{NbO}_2$  with a small thermal hysteresis ( $\Delta T = 8$  K) and with an enthalpy change,  $\Delta H$ , of  $\sim 600$  cal/mole. Obviously, the transition is of first order just like in  $\text{VO}_2$ . At  $T_i''$ , the thermal expansion coefficient is known to show a discontinuity (3). It is significant that the transition temperature,  $T_i''$ , is lower than  $T_i'$  corresponding to the structural changes seen by X-ray diffraction (4). In the solid solutions with  $x = 0.02$  and  $0.05$ , the DTA transitions (Fig. 1) are found around 1040 and 965 K, respectively, indicating a decrease in the transition temperature with increase in  $x$ . The  $\Delta H$  of the transition in

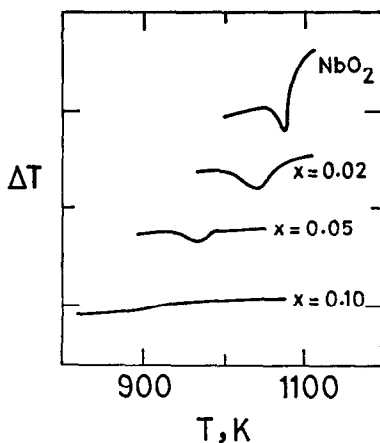


FIG. 1. Differential thermal analysis curves (heating rate 16 K min<sup>-1</sup>) of NbO<sub>2</sub> and Nb<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub>.

Nb<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub> decreases with increase in  $x$  (Table I) while the thermal hysteresis of the transition increases ( $\Delta T = 25$  K for  $x = 0.05$ ). Similar lowering of the transition temperature and  $\Delta H$  in such solid solutions has been observed with respect to the VO<sub>2</sub> transition (9).

All the Nb<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub> solid solutions were indexed on the basis of the rutile structure, although they possess a distorted rutile structure when  $x < 0.1$  (or  $x > 0.9$ ). The lattice parameters of the various solid solutions are shown in Table I along with the  $c/a$  ratios. The  $c/a$  ratio shows a maximum at  $x = 0.5$  (Fig. 2) and the results generally agree with those reported earlier by Rüdorff and Märklin (7). On the VO<sub>2</sub>-rich side,

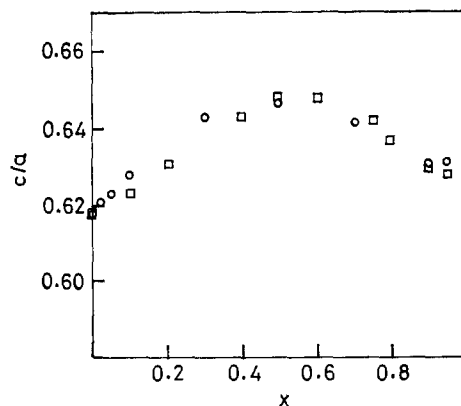


FIG. 2. Variation of  $c/a$  ratio of Nb<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub> with  $x$ : circles, present data and from Ref. (10); square, data from Ref. (7).

the extrapolated value of the  $c/a$  ratio at  $x = 1$  corresponds to the value (9) found in the rutile phase at 340 K. The rutile phase of Nb<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub> solid solutions is undoubtedly composed of two mixed-oxide phases (7, 15): (Nb<sub>1-x</sub><sup>5+</sup>V<sub>x</sub><sup>4+</sup>V<sub>2x-1</sub><sup>3+</sup>)O<sub>2</sub> for  $0.5 < x < 1.0$  and (Nb<sub>1-2x</sub><sup>4+</sup>Nb<sub>2x</sub><sup>5+</sup>V<sub>x</sub><sup>3+</sup>)O<sub>2</sub> for  $0 < x < 0.5$ . Since the  $c/a$  ratio is determined by the metal-metal interactions along the  $c$  axis, we would expect minimum bonding between unlike ions particularly if one of these has no  $d$  electrons<sup>1</sup> (as in Nb<sub>0.5</sub><sup>5+</sup>V<sub>0.5</sub><sup>3+</sup>O<sub>2</sub> when  $x = 0.5$ ).

<sup>1</sup> An examination of the crystallographic data on the V<sub>1-x</sub>Ti<sub>x</sub>O<sub>2</sub> system obtained in this laboratory (9, 10) shows that the  $c/a$  ratio increases up to  $x = 0.5$  in this system as well.

TABLE I  
CRYSTAL STRUCTURE, DTA AND ELECTRICAL CONDUCTIVITY DATA ON Nb<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub>

$x$	Lattice parameters			DTA		Electrical conductivity		
	$a$ (Å)	$c$ (Å)	$c/a$	$T_i''$ (K) <sup>a</sup>	$\Delta H$ (cal/mole)	$T_a$ (K) <sup>c</sup>	$E_a$ (eV)	
							$T < T_a$	$T > T_a$
0.00	4.822	2.981	0.618	1073 (1120)	600	580	0.28	0.45
0.02	4.807	2.985	0.621	1040 (1090) <sup>b</sup>	400	460	0.26	0.43
0.05	4.786	2.979	0.623	965 (1080) <sup>b</sup>	100	400	0.17	0.41
0.10	4.793	3.009	0.628	—	—	530	0.28	0.50
0.30	4.726	3.040	0.643	—	—	550	0.23	0.47
0.50	4.685	3.032	0.647	—	—	480	0.39	0.50

<sup>a</sup>  $T_i''$  is from DTA data: values in parenthesis refer to  $T_i'$ .

<sup>b</sup>  $T_i'$  is taken to be the temperature where conductivity jump is abrupt.

<sup>c</sup> Temperature at which there is a change in the activation energy:  $T_a < T_i'' < T_i'$ .

Goodenough (16) has recently identified two distinguishable mechanisms of the monoclinic-tetragonal transition in  $\text{VO}_2$ : an antiferroelectric-paraelectric transition at a temperature  $T_i^a$  and a change from homopolar to metallic V-V bonding at a temperature  $T_i^b$ . In pure  $\text{VO}_2$ , the two transitions occur at the same temperature ( $\sim 340$  K). The two transitions can, however, be separated out ( $T_i^b < T_i^a$ ) by atomic substitutions, the intermediate structure (between  $T_i^b$  and  $T_i^a$ ) being different. In principle, a similar situation could exist in  $\text{NbO}_2$ , an antiferroelectric metal-anion bonding tilting the  $c$  axis Nb-Nb pairs (17). While  $T_i^b$  and  $T_i^a$  appear to be identical in pure  $\text{NbO}_2$ , we have not found any evidence for the separation of the two components in the  $\text{Nb}_{1-x}\text{V}_x\text{O}_2$  ( $x \leq 0.05$ ) solid solutions as well.<sup>2</sup>

The results of our electrical conductivity measurements on  $\text{NbO}_2$  are shown in Fig. 3 along with the literature data (1-3, 6). We see that there are differences in the conductivity data of different workers.<sup>3</sup> There appears to be

<sup>2</sup> In the vanadium-rich end of these solid solutions with  $x \geq 0.95$ , we have found that the two components of the  $\text{VO}_2$  transition are separated. We are presently investigating these systems.

<sup>3</sup> The actual magnitude of the conductivity as well as some of the features in the  $\log \sigma - 1/T$  curve vary with sample preparation. Our low temperature conductivity data below  $T_i''$  show a behaviour similar to Roberson and Rapp's (6) and Janninck and Whitmore's (2).

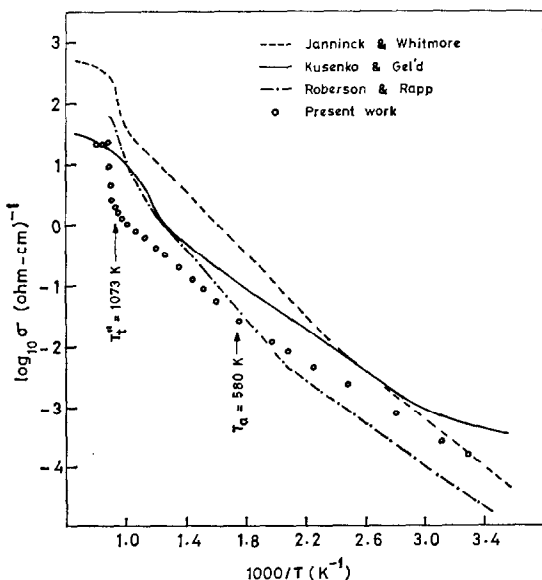


FIG. 3. Four-probe conductivity data on  $\text{NbO}_2$ . Results from earlier literature are shown for purpose of comparison.

little doubt, however, that a tenfold increase in conductivity occurs around the transition temperature. Our measurements show the conductivity jump to be sharp as in semiconductor-metal transitions (18). We find that at  $T_i''$  corresponding to the DTA transition temperature ( $=1073$  K), conductivity starts increasing (Fig. 3), but the tenfold increase in conductivity seems to occur only around  $T_i' \approx 1120$  K. Crystallographic studies of Sakata and coworkers (3) show that the superstructure lines in the X-ray pattern of the low-temperature distorted rutile phase of  $\text{NbO}_2$  disappear at  $T_i'$  ( $\sim 50$  K above  $T_i''$ ). Since the low-temperature structure appears to have  $90^\circ$  rotations of some of the octahedral sites (19), the observations regarding the phase transition can be interpreted following the arguments of Goodenough (15). Nb-Nb pairing along the  $c$  axis occurs only below  $T_i''$  while the octahedral site rotations occur below  $T_i'$ . This implies that vibrational-mode softening is an important precondition for the initiation of distortion.

In the low-temperature region (below  $T_i''$ ),  $\text{NbO}_2$  is an  $n$ -type semiconductor with an apparent activation energy,  $E_a$ , of about 0.23 eV, which increases to 0.45 eV beyond a temperature,  $T_a$  ( $\approx 575$  K) and up to  $T_i'$  or  $T_i''$ . The conductivity essentially remains constant above  $T_i'$ ; we do not see semiconducting behavior above  $T_i'$  which seems to be apparent in the data of Janninck and Whitmore (2) and Sakata (5). The material is undoubtedly metallic above  $T_i'$  as evidenced by Seebeck coefficient data (Fig. 4). The Seebeck coefficient  $\alpha$  decreases from 500 K and becomes

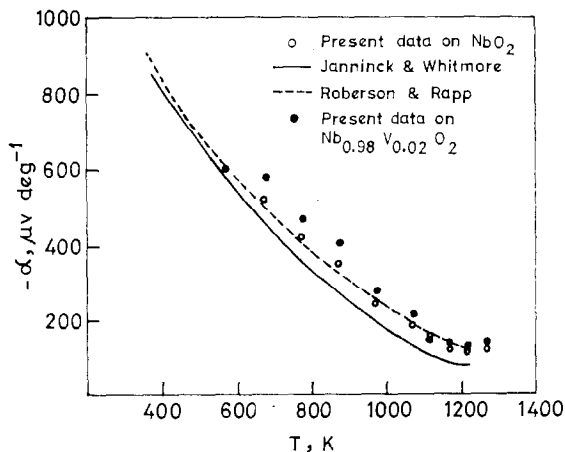


FIG. 4. Seebeck coefficient data on  $\text{NbO}_2$  and  $\text{Nb}_{0.98}\text{V}_{0.02}\text{O}_2$ . Literature data on  $\text{NbO}_2$  are shown for purpose of comparison.

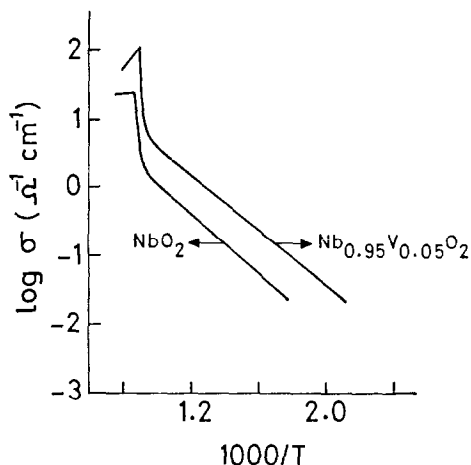


FIG. 5. Four-probe conductivity data on Nb<sub>0.95</sub>V<sub>0.05</sub>O<sub>2</sub>. The data on NbO<sub>2</sub> are shown for purpose of comparison.

constant around 1200 K which is close to  $T_i'$  (Fig. 4). This is in accordance with the earlier conclusions regarding the transition. Our data on  $\alpha$  are in good agreement with the literature reports (2, 6). All these observations on the transport properties indicate that the transition in NbO<sub>2</sub> is associated with a change from semiconducting to metallic behavior.

Conductivity data on the solid solutions Nb<sub>1-x</sub>V<sub>x</sub>O<sub>2</sub>, with  $x = 0.02$  and  $0.05$  show features similar to pure NbO<sub>2</sub> (Fig. 5) except that the solid solutions clearly exhibit metallic conductivity after the tenfold jump in conductivity occurs. The slope of the conductivity curve in the metallic region is marked in these doped samples because of the disorder effects due to the foreign atoms. Taking the temperature at which the conductivity jump occurs to be  $T_i'$ , we see that  $T_i' > T_i''$  in both the solid solutions (Table I). The Seebeck coefficient of Nb<sub>0.98</sub>V<sub>0.02</sub>O<sub>2</sub> also becomes constant above  $T_i'$  (Fig. 4). Below  $T_i''$ , the conductivity data are similar to those of NbO<sub>2</sub> with a change in activation energy at  $T_a$  (Table I). The fairly large difference between  $T_i'$  and  $T_i''$  in the two solid solutions is again suggestive of the importance of vibration mode softening and Nb-Nb pairing in the semiconductor-to-metal transitions of these systems.

The conductivity data on other solid solutions with  $0.10 \leq x \leq 0.50$  show no evidence for any transition, but show a change in activation energy at  $T_a$  (Table I). We find that the conductivity of the solid solutions shows a minimum at  $x = 0.5$  in agreement with the earlier observation

by Rüdorff and Märklin (7); at this composition, we also see a maximum in the  $c/a$  ratio. At  $x = 0.5$  where the composition is likely to be Nb<sub>0.5</sub><sup>5+</sup>V<sub>0.5</sub><sup>3+</sup>O<sub>2</sub>, there would be no mobile electrons for conduction and hence the minimum in conductivity.<sup>4</sup>

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<sup>4</sup> It is interesting that the conductivity is minimum at  $x = 0.5$  in the V<sub>1-x</sub>Ti<sub>x</sub>O<sub>2</sub> system also (9, 10); at this composition we do not see the transition of VO<sub>2</sub> either.