

## A Study on the NiVO<sub>3</sub> System

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The reaction of NiO and VO<sub>2</sub> at high pressure yielded a distorted ilmenite phase, NiVO<sub>3</sub>(I). The black crystalline product was characterized by crystallographic, electrical, and magnetic properties. This new phase was found to be a semiconductor and possess antiferromagnetic properties. The Neel temperature is 153°K and the moment corresponds to the valence states Ni<sup>2+</sup>V<sup>4+</sup>O<sub>3</sub>. The properties of NiVO<sub>3</sub> are quite similar to those reported for the isostructural CoVO<sub>3</sub>. A model is proposed which is consistent with the structural and magnetic properties.

### Introduction

The characterization of CoVO<sub>3</sub> and CuVO<sub>3</sub> derivatives has recently been reported (1). These compounds, prepared at high pressure, were found to have the ilmenite or distorted ilmenite structure from single-crystal studies. Previous attempts (2) to prepare the NiVO<sub>3</sub> derivative were unsuccessful.

In this paper, we wish to report the preparation, crystallographic, magnetic, and electrical properties of the distorted ilmenite composition NiVO<sub>3</sub>(I), which is isostructural with CoVO<sub>3</sub>(I) and CuVO<sub>3</sub>(I).

### Experimental

Vanadium dioxide V<sub>2</sub>O<sub>4</sub>, was prepared by the solid-state reaction of V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> at 1000°C in an evacuated, fused-silica tube for 24 hr. Sub-micron nickel oxide powder (average particle size—0.02μ) obtained from Vitro Laboratories was used as the main source of reactive nickel oxide. The reactants were mixed in an agate mortar and pestle, pelleted, and heated in an evacuated, fused silica tube at 1000°C for 26 hr to yield a highly sintered black crystalline mass. The X-ray powder pattern was suitably indexed on an orthorhombic basis:  $a = 8.240$ ,  $b = 11.331$ , and  $c = 5.688\text{Å}$ . The elemental analyses gave:

Calcd. for NiVO<sub>3</sub>: V, 32.31; O, 30.45; V oxid. state, 4.00;

Found: V, 32.42; O, 30.5, 31.1; V oxid. state, 3.97 ± .02.

This product was reground and heated at 60–65 kbars in a tetrahedral anvil (3) to 1400°C for 2 hr then quenched. Small black crystals of the distorted ilmenite NiVO<sub>3</sub>(I) were obtained.

The Faraday magnetic data were obtained on a Cahn microbalance in the temperature region 77–298°K. The instrument was calibrated with HgCo(CNS)<sub>4</sub> as the standard. The observed susceptibilities were corrected for atomic diamagnetism. Four-probe electrical resistivity data were obtained on a single crystal from 77 to 298°K. The activation energy was derived from the slope in the log resistivity versus reciprocal temperature plot. The X-ray data were obtained with a Guinier powder camera using CuKα<sub>1</sub> radiation and a KCl internal standard.

### Results

Single-crystal precession data approximated rhombohedral symmetry and the ilmenite space group,  $R\bar{3}$ . The powder diffraction data, however, indicated lower symmetry than that of rhombohedral. Further examination of the single-crystal photographs showed triclinic symmetry with the possible space groups  $P1$  or  $P\bar{1}$ . The Guinier powder diffraction data was suitably indexed with the triclinic lattice dimensions:  $a = 4.935 \pm 1$ ,  $b = 5.377 \pm 1$ ,  $c = 4.903 \pm 1\text{Å}$ ,  $\alpha = 90.72 \pm 1$ ,  $\beta = 119.13 \pm 1$ , and  $\gamma = 63.00 \pm 1^\circ$ . The unit cell volume was  $97.56 \pm 5\text{Å}^3$ . The indexed powder data obtained on NiVO<sub>3</sub>(I) is given in Table I. A slight trace of

TABLE I  
POWDER DIFFRACTION DATA OF NiVO<sub>3</sub> (I)

<i>h k l</i>	<i>l</i>	<i>d</i> <sub>obsd</sub>	<i>d</i> <sub>calcd</sub>
1 0 0	25	3.7007	3.7005
1 1 -1	70	3.6271	3.6264
0 1 1	45	3.5922	3.5913
0 1 -1	60	2.7342	2.7338
-1 1 1	100	2.6732	2.6739
1 2 0	85	2.6674	2.6663
1 1 1	70	2.4893	2.4902
2 1 -1	75	2.4667	2.4668
1 0 -2	60	2.4507	2.4508
0 2 0	15	2.3076	2.3080
1 1 -2	45	2.1844	2.1840
2 2 -1	25	2.1652	2.1659
1 2 1	30	2.1620	2.1623
-1 1 2	10	2.1469	2.1457
2 2 0	10	2.0427	2.0427
-2 0 0	20	1.8499	1.8502
2 2 -2	35	1.8132	1.8132
0 2 2	20	1.7961	1.7957
-1 1 -1	10	1.7220	1.7210
0 1 -2	20	1.7196	1.7197
1 2 -2	30	1.6983	1.6984
-2 1 1	30	1.6942	1.6946
2 3 -1	45	1.6765	1.6763
1 3 1	30	1.6657	1.6659
-1 2 2	35	1.6633	1.6626

unreacted NiO was detected in some of the powder patterns. The two structures, triclinic NiVO<sub>3</sub> and rhombohedral, ilmenite-type NiTiO<sub>3</sub>, appear to be quite closely related. The two structural types were observed in the CuVO<sub>3</sub> system (I).

The magnetic and electrical resistivity results are given in Table II.

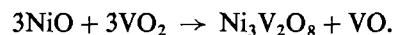
### Discussion

The reaction of NiO and VO<sub>2</sub> at autogenous pressure and 1000°C in a sealed, evacuated system yields a heterogeneous phase which retains the

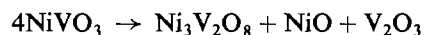
TABLE II  
ELECTRICAL AND MAGNETIC PROPERTIES OF NiVO<sub>3</sub>(I)

Electrical properties	Magnetic properties
$\rho_{298^\circ\text{K}} = 9.0 \Omega\text{cm}$	$\mu_{\text{eff}} = 3.36 \mu\text{B}$
$E_g = 0.20 \text{ eV}$	$\theta = -129.5^\circ\text{K}$
	$T_N = 153 \pm 5^\circ\text{K}$

overall proper stoichiometry and valence state for the composition Ni<sup>2+</sup>V<sup>4+</sup>O<sub>3</sub>. X-ray studies show, however, that the principal crystalline phase is Ni<sub>3</sub>V<sub>2</sub>O<sub>8</sub> or Ni<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>. This compound has previously been reported (4, 5). Structural investigations on Ni<sub>3</sub>V<sub>2</sub>O<sub>8</sub> were performed by Durif and Bertaut (6). The nickel vanadium oxide product isolated in this study is presumably formed through a redox reaction.



The overall nickel to vanadium ratio is retained and the average vanadium oxidation state in the combined product is  $\{[(2 \times 5) + 2]/3 = 4.0\}$ . The VO phase, possibly present as 15 wt % impurity, may have been formed in a subdivided or amorphous state and was, therefore, not detected in the diffraction pattern. Rüdorff et al. (2) noted that this autogenous pressure reaction yielded an unknown phase having some common lines with NiO and V<sub>2</sub>O<sub>3</sub>. In this study we did not detect the presence of V<sub>2</sub>O<sub>3</sub> or NiO in our autogenous pressure product but we noticed that the thermal decomposition of NiVO<sub>3</sub>(I) proceeds according to the following disproportionation reaction.



The X-ray diffraction pattern of the DTA residue (heated to 1000°C in dry nitrogen) was found to contain the orthorhombic Ni<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, NiO, and V<sub>2</sub>O<sub>3</sub> phases in approximately equal amounts. No weight change was observed during the thermal treatment and decomposition stages.

The electrical properties of NiVO<sub>3</sub>(I) indicate semiconducting behavior similar to that observed (I) for the triclinic CoVO<sub>3</sub>(I) product. A slight change in slope appears at the Néel temperature and the activation energy below  $T_N$  is 0.10 eV.

The magnetic data show definite antiferromagnetic behavior with a minima in the reciprocal susceptibility vs  $T$  plot at 153°K, corresponding to the Néel temperature. Above this temperature the material obeys the Curie-Weiss law, having a Weiss constant of -130°K and a  $\mu_{\text{eff}}$  of 3.36 $\mu\text{B}$ . The calculated free-spin moment for Ni<sup>2+</sup>V<sup>4+</sup>O<sub>3</sub> is 3.32 $\mu\text{B}$ , assuming a "g factor" of 2.00 for both Ni<sup>2+</sup>( $d^8$ ) and V<sup>4+</sup>( $d^1$ ). The magnetic properties of related Co and Ni compounds are summarized in Table III.

It should be noted that in the series NiMO<sub>3</sub>, where M<sup>4+</sup> = Ti( $d^0$ ), V( $d^1$ ), and Mn( $d^3$ ), there is an increase in the two sublattice interactions giving rise to an increasing  $T_N$ ,  $\theta$ , and the ratio of  $\theta$  to  $T_N$ .

A suitable model for NiVO<sub>3</sub>(I) can be derived by

TABLE III  
MAGNETIC PROPERTIES OF NiMO<sub>3</sub> AND CoMO<sub>3</sub> COMPOSITIONS

Compounds	Structure		$T_N(^{\circ}\text{K})$	$\theta(^{\circ}\text{K})$	$-\theta/T_N$	Reference
	cryst <sup>a</sup>	mag <sup>b</sup>				
NiTiO <sub>3</sub>	ilm.	AF	23	-13	0.56	7, 8
NiVO <sub>3</sub> (I)	d.-ilm.	AF	153	-130	0.87	This work
NiCrO <sub>3</sub>	cor.	AF	250	-870	3.5	9
NiMnO <sub>3</sub>	ilm.	Fi	437	—	—	10
CoTiO <sub>3</sub>	ilm.	AF	38	-3	0.08	8
CoVO <sub>3</sub> (I)	d.-ilm.	AF	142	-22 <sup>c</sup>	0.15	1
CoMnO <sub>3</sub>	ilm.	Fi	391	—	—	10

<sup>a</sup> Crystal structure: ilm. = ilmenite; d.-ilm. = distorted-ilmenite; cor. = corundum.

<sup>b</sup> Magnetic structure: AF = antiferromagnetic; Fi=ferrimagnetic.

<sup>c</sup>  $\chi_M$  was reevaluated and corrected for atomic diamagnetism, new  $\mu_{\text{eff}} = 5.53\mu_B$  and the calculated  $g_{\text{Co}^{2+}} = 2.71$  assuming the "g factor" for V<sup>4+</sup> is 2.00.

considering the various magnetic interactions in other NiMO<sub>3</sub> compositions. This same model should be applicable to the isostructural CoVO<sub>3</sub>(I) system. The spin structure of NiVO<sub>3</sub> must necessarily be different from that of NiTiO<sub>3</sub> and NiMnO<sub>3</sub> since the former has only one paramagnetic ion in two antiferromagnetic sublattices and the latter, with two paramagnetic sublattices, is observed to possess ferrimagnetic interactions between the two different layer sequences.

The cation order in hexagonal closed packed ABO<sub>3</sub> structures is shown in Fig. 1. The structural and magnetic model proposed for the antiferromagnetic NiVO<sub>3</sub>(I) system is shown in Fig. 2.

Each layer contains Ni<sup>2+</sup> and V<sup>4+</sup> ions (two sublattices) which order ferrimagnetically at the Néel temperature. A co-operative antiferromagnetic

effect between layers also arises at  $T_N$  and one observes only the overall antiferromagnetic spin ordering at this temperature. A similar magnetic model was proposed by J. B. Goodenough (12, 13) and G. Shirane *et al.* (14) for MTiO<sub>3</sub> compounds but was never actually observed in any of the systems investigated.

The triclinic distortion of the ilmenite could reasonably arise from V<sup>4+</sup>-V<sup>4+</sup> coupling in alternate layers removing rhombohedral symmetry. A similar coupling is presumed to be responsible for the monoclinic distortion of the tetragonal rutile structure in vanadium dioxide below 65°C.

A complete structural determination of NiVO<sub>3</sub>(I), CoVO<sub>3</sub>(I), or CuVO<sub>3</sub>(I) would be necessary to confirm the actual atom positions and the proposed coupling of alternate layers by homopolar V-V

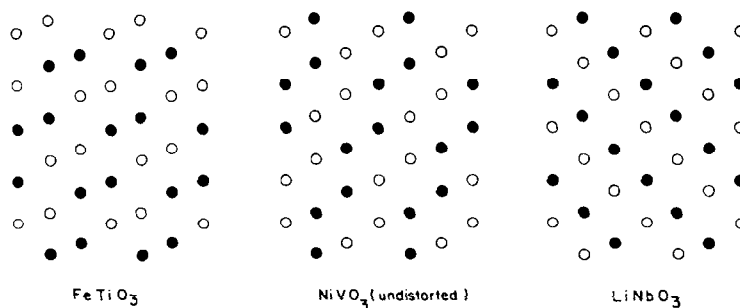


FIG. 1. Three types of cation order found in ABO<sub>3</sub> compositions.

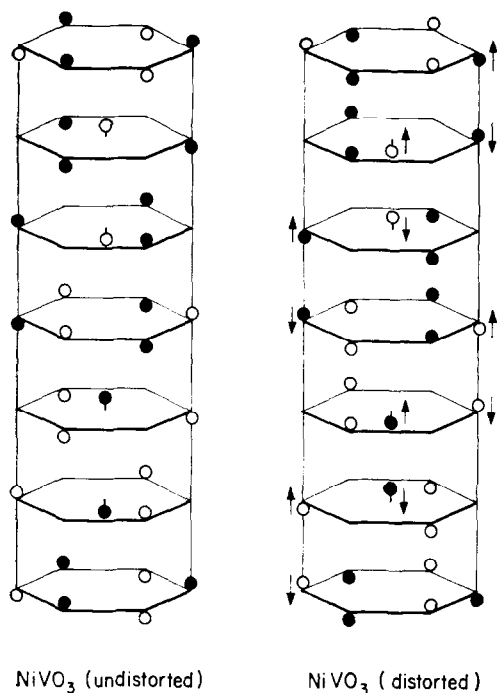


FIG. 2. Hexagonal representation of the proposed distorted and undistorted models for the transition metal ions and spin states in  $\text{NiVO}_3(\text{I})$ . Black circles represent  $\text{Ni}^{2+}$  ions while the white circles represent  $\text{V}^{4+}$  ions. The spin directions for a few ions are represented by arrows. The distortion in the structure arises from homopolar  $\text{V}^{4+} - \text{V}^{4+}$  bonds along the  $c$  axis of the hexagonal unit cell.

bonds, but all the observed properties are presently consistent with the proposed model. Syono, *et al.* (15) report the isolation of a similar high pressure, triclinic  $\text{MnVO}_3$  phase which is ferromagnetic below  $70^\circ\text{K}$ .

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