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Preparation and Properties of the System $Fe_{1-x}V_xNbO_4$

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Members of the system $Fe_{1-x}V_xNbO_4$ were prepared and their crystallographic, electrical, and magnetic properties were determined. The wolframite structure is formed for $x \le 0.2$, but for $x \ge 0.4$, a phase transformation to the rutile structure takes place. Magnetic studies established the formal valencies of the elements for members crystallizing with the wolframite phase. However, similar analyses of compounds with the rutile structure did not provide a unique assignment of the formal valencies.

Introduction

The substitution of 10 at.% of chromium for iron in $FeNbO_4$ resulted in a significant lowering of the band gap (*1*). This is in good agreement with the reported decrease in the optical band gap of α-Fe_2O_3 for a similar percentage substitution of chromium (*2*). This observed lowering of the band gap was attributed to the formation of $Cr^{3+}(3d^3)$ energy levels within the optical band gap of $FeNbO_4$.

Whereas in the system $Fe_{1-x}Cr_xNbO_4$, the only possible valence assignment for the transition metals was Cr^{3+}, Fe^{3+}, and Nb^{5+}, the substitution of vanadium for iron in $Fe_{1-x}V_xNbO_4$ can give rise to multiple valence assignments. The measurement of the electrical and magnetic properties of a number of compositions in this system is useful in assigning appropriate valencies.

Experimental

Synthesis

All materials were prepared from the solid state reaction between Fe_2O_3 (Johnson–Matthey, spec. pure), Nb_2O_5 (Kawecki Berylco Industries, spectroscopic grade) and V_2O_3 which was formed by the reduction of V_2O_5 (Johnson–Matthey) under a 15% hydrogen–85% argon gas mixture. The vanadium-substituted iron niobate samples were made at 1000°C in evacuated silica tubes to avoid any contact with air. Each product was X-rayed, ground, and reheated until a single phase was obtained. A Philips Norelco diffractometer, with Cu$K\alpha$ radiation (1.5405 Å) at a 2θ scan rate of 0.25° min^{-1}, was used to carry out the X-ray analysis.

Disks were formed by pressing aliquots of approximately 150 mg at 90,000 psi; the pressed disks were placed in a sealed silica tube and heated at a rate of 85°C/hr to 1000°C, and maintained at that temperature

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TABLE I

Precision Lattice Constants for the System $Fe_{1-x}V_xNbO_4$

Compound	a (Å)	b (Å)	c (Å)	β (deg)
$FeNbO_4$	4.997(2)	5.619(2)	4.651(2)	90
$Fe_{0.9}V_{0.1}NbO_4$	4.998(2)	5.613(2)	4.646(2)	90
$Fe_{0.8}V_{0.2}NbO_4$	5.007(2)	5.613(2)	4.646(2)	89.87
$Fe_{0.6}V_{0.4}NbO_4$	4.685(2)	—	3.037(2)	—
$Fe_{0.4}V_{0.6}NbO_4$	4.684(2)	—	3.034(2)	—
$VNbO_4$	4.677(2)	—	3.034(2)	—

for 24 hr. After the sintering process, the disks were cooled at the same rate.

X-Ray diffraction patterns of the sintered disks showed, at the limit of detection, the presence of the strongest line of α-Fe_2O_3, which is consistent with the formation of a solid solution of $FeNb_2O_6$ in $FeNbO_4$ under the sintering conditions. Essentially identical resistivities were measured before and after abrading these disks to one-half their original thickness, which established their homogeneity.

Magnetic Measurements

Magnetic susceptibilities were measured using a Faraday balance (*3*) over the range from liquid-nitrogen to room temperature at a field strength of 10.4 kOe. Honda–Owen (field dependency) plots were also made to determine the presence or absence of ferromagnetic impurities. The data were then corrected for core diamagnetism (*4*).

Electrical Measurements

The resistivities of the samples were measured using the Van der Pauw technique (*5*). Contacts were made by the ultrasonic soldering of indium directly onto the samples, and their ohmic behavior was established by measuring their current–voltage characteristics.

Results and Discussion

The influence of $V^{3+}(3d^2)$ on the phase transition of $FeNbO_4$ bears a striking resemblance to that of $Cr^{3+}(3d^3)$ (*1*). The system $Fe_{1-x}V_xNbO_4$ forms a solid solution over the range of $0 \leq x \leq 0.2$ which crystallizes with the wolframite $FeNbO_4$ structure (space group $P2/c$) shown in Fig. 2. At values of $x \geq 0.4$, a phase transformation to the rutile structure (space group $P4_2/mnm$) shown in Fig. 2 takes place. The crystallographic data for this system are summarized in Table I. However, in contrast to the chromium-substituted system, the electrical and magnetic behavior cannot be explained in terms of a simple localized model.

The results of the magnetic measure-

TABLE II

Electrical and Magnetic Data for the System $Fe_{1-x}V_xNbO_4$

	Structure[a]	ρ (ohm-cm)	C_M(exp.)	C_M(theor.)[b]	Formal valence assignment
$FeNbO_4$	W	40(1)	4.18	4.35	Fe^{3+}, Nb^{5+}
$Fe_{0.9}V_{0.1}NbO_4$	W	84(1)	3.70	3.68	$Fe^{3+}_{0.8}$, $Fe^{2+}_{0.1}$, $V^{4+}_{0.1}$
$Fe_{0.8}V_{0.2}NbO_4$	W	115(2)	3.06	3.17	$Fe^{3+}_{0.6}$, $Fe^{2+}_{0.2}$, $V^{4+}_{0.2}$
$Fe_{0.6}V_{0.4}NbO_4$	R	1520(11)	—	—	—
$Fe_{0.4}V_{0.6}NbO_4$	R	1900(29)	—	—	—
$VNbO_4$	R	$>10^4$	1.10	1.0	V^{3+}, Nb^{5+}

[a] W = Wolframite; R = Rutile.

[b] Corrected for $C_M(Fe^{3+}) = 4.18$.

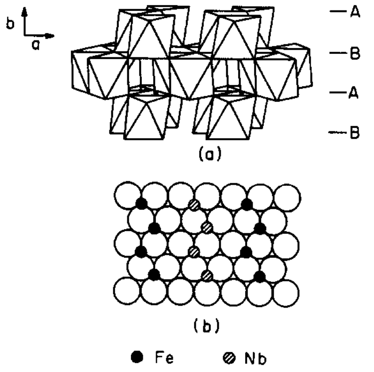

FIG. 1. Structure of FeNbO$_4$: (a) packing of MO$_6$ octahedra; (b) closest-packed layer of oxygen around Fe and Nb atoms.

ments are summarized in Table II. In the region $0 \leq x \leq 0.2$, the compounds show a Curie–Weiss behavior. The experimental Curie constants of 3.70 and 3.06 for the compositions $x = 0.1$ and $x = 0.2$ (wolframite structure) can only be accounted for if an assignment of V^{4+}($3d^1$) is made for the formal valence of vanadium. An equivalent amount of Fe^{2+}($3d^6$) is assumed for the formal valence of iron, with the remainder of the iron present as Fe^{3+}($3d^5$). Hence, the formula for the wolframite members may be represented by $\mathrm{Fe}^{3+}_{1-2x}\mathrm{Fe}^{2+}_{x}\mathrm{V}^{4+}_{x}\mathrm{Nb}^{5+}\mathrm{O}_4$. The resistivity values reported for sintered disks of compositions having this structure indicate that these phases show considerable conductivity. It can be seen from an examination of the wolframite structure (Fig. 1) that one-half of the zig-zag chains along the c direction contain Nb^{5+}, whereas the other chains have Fe^{2+}, Fe^{3+}, as well as V^{4+}. Conductivity undoubtedly results from the mixed valence states present in these chains.

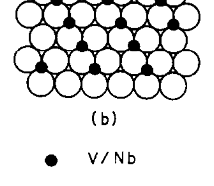

FIG. 2. Structure of rutile: (a) packing of MO$_6$ octahedra; (b) closest-packed layer of oxygen around V and Nb atoms.

The magnetic properties of the members of the system crystallizing with the rutile structure indicate more complex behavior. VNbO$_4$, itself, shows Curie–Weiss behavior (Fig. 3). Its Curie constant of 1.1 given in Table II is consistent with d^2 vanadium (V^{3+}), and there is no apparent contribution from Nb^{5+} ($\mu_{\mathrm{eff}} = 0$). However, for other members of the vanadium-substituted system crystallizing with the rutile structure ($0.4 \leq x \leq 1$), deviations from Curie–Weiss behavior are observed which increase with decreasing values of x. The marked deviation shown in Fig. 3 for $x = 0.4$ precludes the evaluation of a reliable Curie constant. Results of field dependency shown in Fig. 4 indicate the existence of a ferromagnetic component for $x = 0.4$. Hence, the susceptibility data cannot be used reliably for the assignment of formal valencies for members of the system Fe$_{1-x}$V$_x$NbO$_4$ crystallizing with the rutile structure.

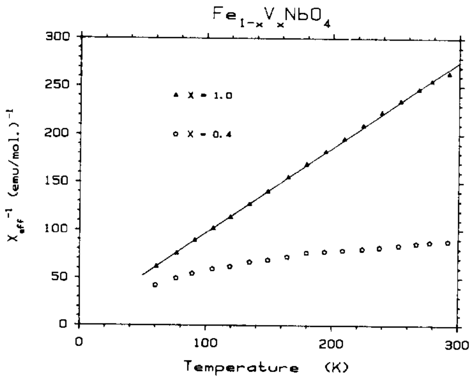

FIG. 3. Thermal variation of the inverse magnetic susceptibility for VNbO$_4$ and Fe$_{0.6}$V$_{0.4}$NbO$_4$.

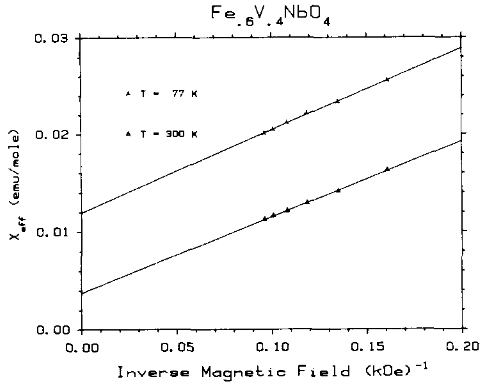

FIG. 4. Variation of χ_{eff} with inverse applied field for $Fe_{0.6}V_{0.4}NbO_4$ at 77 and 300 K.

Rüdorff and Märklin (6) have reported, and Villeneuve *et al.* (*7*) have confirmed that for the system $V_{1-x}Nb_xO_2$, the electrical resistivity increases with increased niobium concentration. Rüdorff indicated that the rutile phase was composed of two mixed oxide phases $(V^{4+}_{1-x}V^{3+}_xNb^{5+}_x)O_2$ with $0 < x < 0.5$, and $(V^{3+}_{1-x}Nb^{5+}_{1-x}Nb^{4+}_{2x-1})O_2$ with $0.5 < x < 1.0$. In addition, for $V^{3+}Nb^{5+}O_4$, the resistivity was a maximum. The presence of two valence states for either the niobium or vanadium was responsible for the higher conductivity of the other members of the system.

Similarly, in this study, electrical and magnetic measurements obtained on the end member $VNbO_4$ support the presence of V^{3+}, Nb^{5+}. However, the introduction of iron results in the formation of mixed valencies of vanadium and, possibly, also niobium. This would be consistent with the relatively high conductivity values given in Table II for the rutile members of the series; since otherwise, a random occupation of 50% of the cation sites by Nb^{5+} would block any possible conductivity.

These considerations, together with the complex magnetic behavior observed for the composition $x = 0.4$, preclude any attempt to assign formal valencies.

Acknowledgments

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