Magnetic, Electrical and Thermal Studies of $V_{1-x}Ti_xO_2$ ($0 \leq x \leq 0.06$)

T. HÖRLIN, T. NIKLEWSKI and M. NYGREN

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

The metal-insulator transition in the $V_{1-x}Ti_xO_2$ system has been studied by NMR, DTA, X-ray diffraction, magnetic susceptibility, and electrical conductivity measurements over extended regions of temperature. Three phases have been shown to exist. A semiconducting VO_2 phase of the M_1 structure exists below a temperature which decreases with increasing Ti content. At temperatures below the transition to the metallic high temperature rutile phase (R) an intermediary phase area exists. This phase is semiconducting and has an almost temperature-independent paramagnetism: it possesses the M_2 type of structure known from the $(V,Cr)O_2$ system. The observed properties of the insulating phases are discussed in terms of a model in which the $3d$ electrons are assumed to be localized on the vanadium atoms, with a Heisenberg exchange coupling between neighbours.

The metal-insulator transition in VO_2 at about 340 K has been subject to considerable interest. The high temperature form is metallic and possesses the rutile structure,[1] named R below. The structure of the low temperature form (hereafter called M_1) is of MoO_2 type,[2] which can be regarded as a monoclinic distortion of the rutile-type structure. In the M_1 structure the V atoms occur in pairs which are tilted somewhat from the c_R axis in such a way that zig-zag chains with alternating shorter and longer $V-V$ distances are formed.

During recent years numerous papers have been published concerning the metal-insulator transition in pure VO_2 and VO_2 doped with various transition elements. Especially the studies of the effects of various dopants have been fertile.

The phase diagrams of the $V_{1-x}Me_xO_2$ systems with Me = W,[3] Mo,[4] Nb,[5] and Re[6] exhibit strong similarities. These metals cause a linear decrease of the $M_1 \rightarrow R$ transition temperature with increasing x value.

Cr, Al and Fe belong to a second class of dopants.[7-10] A partial substitution of any of these metals for V gives rise to a rather complex phase diagram. Besides the R and M_1 phases it displays two more insulating phases; one with a triclinic (T) and one with a monoclinic (M_2) symmetry.

The M_2 structure[7] resembles M_1 in that half of the V atoms form pairs along the c_R direction of the rutile subcell; they are not tilted, however, as in the M_1 phase. The other half of the metal atoms are accommodated in zig-zag chains of equally spaced atoms also running parallel with the c_R direction.

The triclinic phase T might be regarded as a transitional phase between M_1 and M_2.[7] Close to the T/M_1 phase boundary the T phase is nearly isostructural with M_1 phase, while near the T/M_2 transition temperature the metal positions in the T phase are close to those in the M_2 phase.

This article reports on X-ray, DTA, NMR, magnetic susceptibility and electrical conductivity studies of the $V_{1-x}Ti_xO_2$ system with $0 \leq x \leq 0.06$. Three phases are observed, namely the M_1 and R phases at low and high temperatures, respectively, and at intermediary temperatures an M_2 phase. In this paper particular attention is paid to the physical properties of M_1 and M_2 phases. The phase relations in and magnetic properties of the entire $VO_2 - TiO_2$ system are presented in a subsequent paper.[11]

EXPERIMENTAL AND RESULTS

Preparation. The starting materials were V_2O_5 (Fisher, Sc.Co., *p.a.*) and TiO_2 (Baker,

T　　　　$V_{1-x}Ti_xO_2$
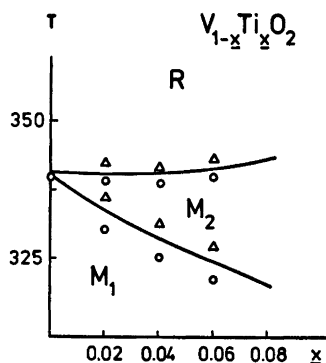
R

350 ─

M$_2$

325 ─

M$_1$

0.02　0.04　0.06　0.08　x

Fig. 1. Transition temperatures plotted *versus* x in $V_{1-x}Ti_xO_2$. The △ and ○ corresponds to data from the heating and cooling, respectively, part of a complete DTA run.

Chem.Co., *p.a.*). VO_2 was prepared by reduction of V_2O_5 at 1275 K. The oxygen equilibrium pressure over V_2O_5 at this temperature is of the order 10^{-3} atmosphere and therefore the

reduction proceeded easily as the oxygen was pumped off by an ordinary rotary vacuum-pump. The product was characterized by its X-ray powder pattern and DTA thermogram (see below).

Powder samples of $V_{1-x}Ti_xO_2$ $(0 \leq x \leq 0.06)$ were prepared from appropriate mixtures of VO_2 and TiO_2, heated in evacuated silica tubes at 900 °C for 6 days. We observed that slightly oxygen-deficient samples exhibit irregularities of one kind or the other in their DTA thermograms, X-ray patterns and susceptibility curves (see also Refs. 4, 12). The stoichiometry could be reproducibly controlled by addition of a small amount (< 0.5 wt. %) of V_2O_5 to the dioxide mixtures. After the firing, traces of V_2O_5 were found on the walls of the silica tubes. Thus the stoichiometry of the samples should be at the oxygen rich extreme of the dioxide phase area. The accurate position of this phase boundary is not known; however, it is assumed to be close to the true dioxide.

Crystals of Ti-doped VO_2 were prepared by chemical transport reaction techniques using $TeCl_4$ as transporting agent. The method applied has previously been described.[3,4] The transported materials consisted of crystals

Table 1. A summary of experimental results.

x in $V_{1-x}Ti_xO_2$		0.00	0.02	0.04	0.06
Cell parameters at 298 K					
	a (Å)	5.751(±1)	5.759(±1)	5.767(±1)	5.775(±1)
	b (Å)	4.526(±1)	4.527(±1)	4.526(±1)	4.528(±1)
	c (Å)	5.382(±1)	5.381(±1)	5.384(±1)	5.385(±1)
	β (degrees)	122.60(±1)	122.63(±1)	122.62(±1)	122.66(±1)
Transition temperature (K)	$M_1 \rightarrow M_2$	340 ($M_1 \rightarrow R$)	336	331	326
	$M_2 \rightarrow R$		342	343	344
Latent heat (cal/mol)	$M_1 \rightarrow M_2$	1020 [a] ($M_1 \rightarrow R$)	130	126	116
	$M_2 \rightarrow R$		938	886	832
Activation energy just below the transition temp. (eV)	$M_1 \rightarrow M_2$	0.45 ($M_1 \rightarrow R$)	0.38	0.36	
	$M_2 \rightarrow R$		~ 0.4	~ 0.4	
Magnetic properties $T < 70$	C_{obs} in eqn. (1)	0	0.78×10^{-2}	1.45×10^{-2}	1.73×10^{-2}
	μ_{eff} per Ti atom	–	1.77	1.71	1.52
$T = 338$	$\delta\chi_M$ (emu/mol)	–	1.26×10^{-4}	1.31×10^{-4}	1.17×10^{-4}
Spin exchange coupling constant J (K)		–	410	400	440
ΔH_M (cal/mol)		–	110	110	95

[a] From Ref. 16.

shaped either as octahedra or rectangular rods. The compositions of the crystals were obtained from their cell parameters and also from the transition temperatures. As the DTA thermograms of the starting and transported material and the residue in the hot zone were identical, the DTA measurements on powder samples, which will be described in the following, served to establish the phase diagram necessary for converting a measured transition temperature to a crystal composition.

Phase analysis. DTA studies were performed in the temperature region 100 – 400 K with an equipment, designed and built at this Institute, which permits simultaneous analysis of five samples.[13]

While pure VO_2 exhibits one DTA peak at 340 K, the Ti substituted material was found to give two peaks. The observed transition temperatures are plotted versus x in $V_{1-x}Ti_xO_2$ in Fig. 1. The DTA curves indicate three phases to be present which can be transformed into one another when the temperature is cycled between 300 and 400 K. The hysteresis was approximately 2 degrees for the transitions at the higher temperature but considerably larger for those at the lower transition temperature, as indicated in the figure.

The X-ray patterns of the powder samples were recorded in a Guinier-Hägg focusing camera, with $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å) and KCl as internal standard ($a = 6.2919$ Å). The recording was performed at room temperature and the obtained patterns could be indexed on the basis of the monoclinic unit cell of the M_1 structure. The lattice parameters are given in Table 1. The major effect observed is a slight increase of the a_{M1} axis with increasing content of Ti.

X-Ray powder diffractograms were taken at 355 K of the same samples and the high temperature modification was found to be of the rutile type, R.

The DTA studies indicated that for $x > 0$ in $V_{1-x}Ti_xO_2$ the $M_1 \rightarrow R$ transition takes place *via* an intermediary phase. The X-ray powder diffractogram of the latter phase with $x = 0.06$ could be indexed assuming an orthogonal cell with $a = 12.643$ (± 3) Å, $b = 12.971$ (± 3) Å and $c = 5.807$ (± 1) Å. The NMR data and the magnetic and electrical properties described below suggest that this phase possesses the M_2 type of structure previously found in the $(V,Cr)O_2$ system (see above). (The cell parameters of the monoclinic unit cell are $a = 9.043$ (± 3) Å, $b = 5.801$ (± 1) Å, $c = 4.542$ (± 1) Å and $\beta = 91.44$ (± 3).)

Experimental evidence for the occurrence of an intermediary phase in the $V_{1-x}Ti_xO_2$ system has previously been presented by Umeda *et al.*[14] and by Mitsuishi.[15] They suggested this phase to be triclinic.

The latent heat evolved at the $M_1 \rightarrow R$ transition in VO_2 is 1020 cal/mol.[16] If the DTA peak area is assumed to be proportional to the

latent heat, one observed for the $M_2 \rightarrow R$ transition a decrease of the latent heat of the order 36 cal per mol and atomic percent Ti. The latent heats associated with the $M_1 \rightarrow M_2$ transition temperature were found to be about 14 % of the corresponding ones at the higher temperature (see Table 1).

NMR Data. ^{51}V NMR measurements were performed in the temperature interval 100 – 400 K at the Laboratoire des Physique des Solides, Université Paris-Sud by one of us (M.N.) using a set-up described elsewhere.[7]

The ^{51}V NMR spectra of powder samples of pure VO_2 and of Ti substituted material possessing the M_1 type of structure contained, besides the central line due to the $1/2 \rightarrow -1/2$ transition, the quadrupole satellites due to the $\pm 3/2 \rightarrow \pm 1/2$ transitions of the two principal axes with smallest electrical field gradients, *i.e.* V_{yy} and V_{xx}. Taking $V_{zz} = V_{yy} + V_{xx}$ the following experimental values for the composition $V_{0.96}Ti_{0.04}O_2$ were obtained at room temperature.

$V_{yy} = 121 \pm 3$ kHz $k_y = 0.27 \pm 0.03$ %
$V_{xx} = 365 \pm 4$ kHz $k_x = 0.35 \pm 0.03$ %
$V_{zz} = 486 \pm 5$ kHz

giving a quadrupole frequency $\nu_q = 486$ kHz and anisotropy parameter $\eta = 0.50 \pm 0.02$. K_y and K_x are the Knight shifts in the directions of the respective principal axes. The experimental values given above did not vary with temperature or composition inside the M_1 phase area. Our findings are in agreement with previous NMR results for pure VO_2 [7,14] and for Cr-doped VO_2 possessing the M_1 structure.[7]

As one approaches the $M_1 \rightarrow M_2$ transition temperature the central line starts to broaden. A few degrees below the transition temperature the shape of the central line suggests it to be composed of one narrow line almost unshifted in comparison with its position in M_1 and one negatively shifted, very broad line.

In the region of stability of the M_2 phase the spectrum consists of one central line with nearly the same position as that in M_1 phase and quadrupole satellites with smaller width than observed for the M_1 structure. The intensity of the central line is one half of that observed in the M_1 phase. The following data, representative for all compositions studied, were obtained:

$V_{yy} = 57 \pm 2$ kHz $K_y = 0.29 \pm 0.03$ %
$V_{xx} = 294 \pm 3$ kHz $K_x = 0.35 \pm 0.03$ %
$V_{zz} = 351 \pm 4$ kHz

with $\nu_q = 351$ kHz and $\eta = 0.68 \pm 0.02$, which compares favourably with previous findings for the M_2 phase.[7,14,17]

The NMR spectrum of an M_2 phase should in principle contain two central lines, *viz.* one associated with the vanadium atoms which are paired, the other with the vanadium atoms
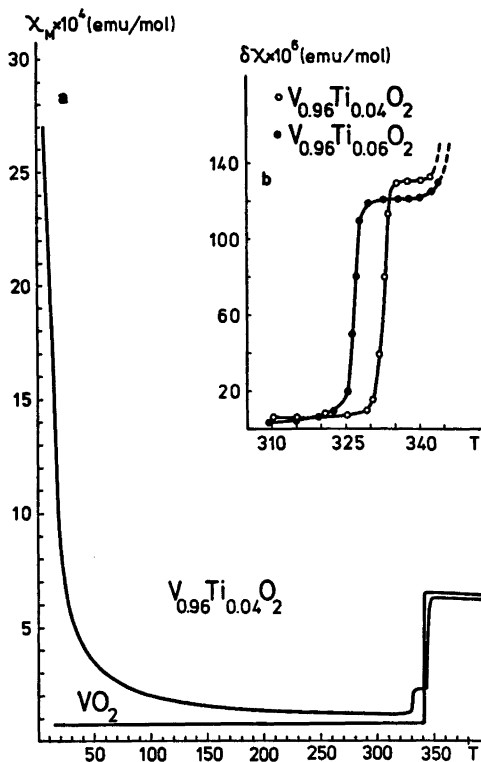
Fig. 2. (a) The molar magnetic susceptibility of VO_2 and Ti-doped VO_2 plotted *versus* the temperature. (b) The remaining susceptibility $\delta\chi_M$, defined according to eqn. 2, plotted *versus* the temperature.

located in the zig-zag chains. Pouget *et al.*[7] report that the latter central line is rather broad for small x values and broadens further for increasing x. The absence of such a line in our spectrum of the M_2 phase is most certainly due to the relatively high Ti content in our samples. The only indication of such a central line is seen close to the $M_1 \rightarrow M_2$ transition temperature.

The intensity of the central line is proportional to the number of V atoms contributing to the NMR line. In the M_1 structure all V atoms are crystallographically equivalent and thus contribute to the intensity of the observed central line. As mentioned above, the observed central line in the M_2 phase area exhibits features very similar to that of the M_1 phase, except that its intensity is only one half of that of the low temperature phase. This agrees with the fact that only half of the number of the V atoms available are paired.

Magnetic susceptibility. Magnetic susceptibility measurements were performed according to the Faraday method in the temperature

interval 80 – 400 K. The measurements in the 5 – 100 K region were carried out at the University of Bordeaux by one of us (M.N.).

The molar magnetic susceptibilities of pure VO_2 and of $V_{0.76}Ti_{0.04}O_2$ are given as functions of the temperature in Fig. 2a. The χ_M values are not corrected for the underlying diamagnetism. The monoclinic modification of pure VO_2 is temperature independent paramagnetic ($\chi_M = 65 \times 10^{-6}$ emu/mol). The transition to the rutile structure gives rise to an abrupt increase of the susceptibility to about 10 times the low-temperature value. For $x > 0$ the susceptibility increases with decreasing temperature and at low temperatures ($T < 70$ K) varies according to:

$$\chi_M = \frac{C_{obs}}{T} + \chi_0 \qquad (1)$$

where χ_0 is the susceptibility plateau of pure VO_2. The C_{obs} and corresponding μ_{eff} values are given in Table 1.

ESR studies of Ti-doped VO_2 indicate that the electrons are localized at the V atoms.[18] The agreement between the observed μ_{eff} values and the spin only value of 1.73 μ_B per substituted Ti atom shows that the Ti atoms are not clustered but dispersed.

When one approaches the $M_1 \rightarrow M_2$ transition temperature the temperature dependence of the susceptibility starts to deviate from that given by eqn. 1. The remaining susceptibility, $\delta\chi_M$, defined as

$$\delta\chi_M = \chi_M - \frac{C_{obs}}{T} - \chi_0 \qquad (2)$$

is plotted *versus* the temperature in Fig. 2b. At the $M_1 \rightarrow M_2$ transition temperature $\delta\chi_M$ increases rapidly. In the region of stability of the M_2 phase the $\delta\chi_M$ term is of the order 1.2×10^{-4} emu per mol, approximately independent of temperature and composition (see also Table 1). Our data are in good agreement with previous findings for the M_2 phase in the $(V,Cr)O_2$ and $(V,Al)O_2$ systems.[7,20]

Electrical properties. The conductivity measurements were performed with the four probe technique on rectangular rod-shaped crystals. The logarithm of the conductivity parallel to the c_R direction was continously recorded as a function of the inverse temperature in the temperature range 100 – 400 K.

In Fig. 3 the logarithm of the conductivity is plotted *versus* T^{-1} for pure VO_2 and $V_{0.96}Ti_{0.02}O_2$. The observed data for VO_2 are in good agreement with previous findings.[3,4] The M_1 modification of Ti substituted material exhibits semiconducting properties. Close to the $M_1 \rightarrow M_2$ transition temperature an activation energy of about 0.38 eV for $x = 0.02$ and 0.04 is found compared with 0.45 eV for $x = 0$. The activation energies for both undoped and Ti-doped samples decrease with decreasing
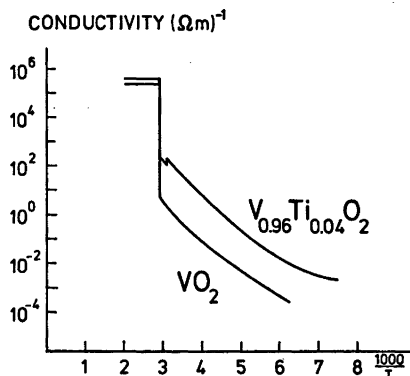
CONDUCTIVITY $(\Omega m)^{-1}$

Fig. 3. The logarithm of the conductivity of VO_2 and Ti-doped VO_2 plotted *versus* the inverse temperature.

temperature and more rapidly so for higher x values. This behaviour indicates that impurity conduction dominates at low temperatures, which is in agreement with the findings by Kabashima *et al.*[21]

The conductivity of the M_2 phase is about a factor 0.5 times that of the M_1 phase, while the activation energy appears to be unchanged as seen in Table 1 and Fig. 4. The same figure also illustrates the hysteresis in the $M_1 \rightarrow M_2$ and $M_2 \rightarrow R$ transition temperatures. The crystals showed a tendency to crack when passing the transition temperatures, but the
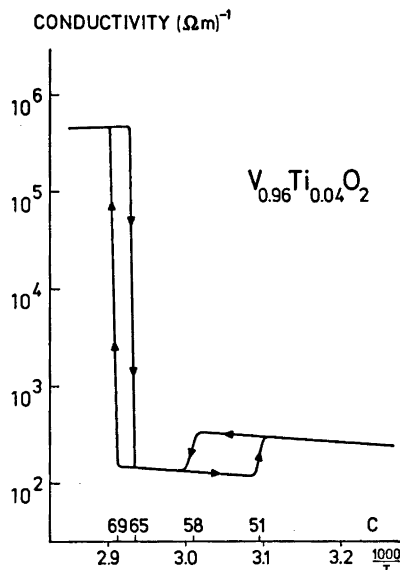
CONDUCTIVITY $(\Omega m)^{-1}$

Fig. 4. The logarithm of the conductivity of Ti-doped VO_2 plotted *versus* the inverse temperature close to the $M_1 \rightarrow M_2 \rightarrow R$ transition temperatures.

data presented are from crystals which passed through a complete cycle of heating and cooling without cracking.

Chase[22] has found similar temperature dependence of the conductivity for samples with compositions: $V_{1-x}Ti_xO_2$ with $x = 0.05$, 0.10, 0.15 and 0.20. The reported semiconductor to semiconductor transition temperatures are, however, appreciably higher than ours, while the transition temperatures to the metallic phase are essentially the same.

DISCUSSION

The DTA and X-ray studies of the $V_{1-x}Ti_xO_2$ system presented above revealed a temperature *versus* composition diagram which, besides the M_1 and R phase areas, contained an intermediary phase area. The X-ray powder diffractogram of the latter phase exhibits strong similarities with that of the M_2 phase previously found in the $V_{1-x}Cr_xO_2$, $V_{1-x}Al_xO_2$ and $V_{1-x}Fe_xO_2$ systems.[7-10] Furthermore, a comparison of the magnetic and electrical properties of the intermediary phase of Ti-doped VO_2 with corresponding data for the M_2 phase shows that the two phases most probably are isostructural. The mechanism by which a particular substituent stabilizes the various alternative phases of VO_2 is at present not known. Anyhow, the physical properties of the T and M_2 phases have to be incorporated in any model intended to explain the character of the metal-insulator transition in VO_2.

Several authors have interpreted the $M_1 \rightarrow R$ transition in pure and doped VO_2 in terms of a band model.[23-25] The electrical and magnetic properties of Ti-doped VO_2 possessing the M_1 type of structure reported above might also be elucidated within the framework of such a model.

The NMR data, the magnetic properties and the structural features of M_2 phase of Ti-doped VO_2 suggest the presence of localized $3d$ electrons, and so do the ESR spectra.[19] Since the chains of the paired V atoms are essentially non-magnetic the observed $\delta\chi_M$ values originate from the magnetic moments associated with the equidistant V atoms. The magnitude of the $\delta\chi_M$ values indicates, however, that magnetic interactions between these V atoms have to be present. Following Pouget *et al.*[7] we thus treat these zig-zag chains as a set of noninteracting antiferromagnetic Heisenberg chains with $S = 1/2$.

Bonner and Fisher [27] have calculated the magnetic susceptibility of such a chain. We have determined the spin exchange coupling constants, J, given in Table 1 by fitting our $\delta\chi_M$ values to their data. The magnetic entropy of the M_1 phase is negligible while the magnetic entropy, S_M, of the M_2 phase can be estimated from the calculations by Bonner and Fisher, using the J values given in Table 1. The change in magnetic enthalpy ΔH_M ($= TS_M$) at the $M_1 \rightarrow M_2$ transition is also given in Table 1.

The change in the lattice latent heat at the $M_1 \rightarrow M_2$ transition, defined as $\Delta H_L = \Delta H_{exp} - \Delta H_M$, is in our case of the same magnitude as that observed for the $T \rightarrow M_2$ transition in the $(V,Cr)O_2$ system.[7] However, in view of the uncertainties in the procedure for obtaining $\delta\chi_M$ and ΔH_M, the only significant conclusion might be that the ΔH_{exp} values do not preclude the possibility of treating the zig-zag chains as antiferromagnetic Heisenberg chains.

The electrical conductivity measurements of Ti-doped VO_2 showed that the activation energies are almost the same in the M_1 and M_2 phases. The insulating M_1, T, and M_2 phases of Cr and Al-doped VO_2 have activation energies of the same order of magnitude.[27] This indicates that the band gap does not originate from the crystal structures of the phases concerned but arises from electron-electron correlation effects.

The magnetic and electrical properties of Ti-doped VO_2 thus support the model proposed by Pouget et al.[7] and by Zylbersztejn and Mott [28] which states: (i) Pure and doped VO_2 possessing the M_1 type of structure is a borderline case for classical band transport description, and (ii) the properties of the M_2 phase cannot be properly described without taking into account the interatomic correlation energy.

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