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Synthesis, Characterization, and Inelastic Neutron Scattering Study of Hydrogen Insertion Compounds of VO_2(Rutile)

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Hydrogen insertion compounds, H_xVO_2 (rutile) ($0 < x < 0.37$), have been prepared at ambient temperatures both chemically, by hydrogen spillover, and electrochemically, with subsequent characterization by powder X-ray diffraction and chemical analysis. For H_xVO_2 ($0.16 < x < 0.37$), distortion of the monoclinic parent oxide occurs to give an orthorhombic rutile-related structure with lattice parameters similar to those of $VO_{2-x}(OH)_x$ formed by the high-pressure, high-temperature decomposition of ammonium metavanadate, reported previously. The vibrational spectrum of $H_{0.3}VO_2$ has been measured using inelastic neutron scattering spectroscopy. The spectrum and the corresponding vibrational analysis further confirm that the hydrogen insertion compound can be formulated as an oxyhydroxide. © 1991 Academic Press, Inc.

Introduction

Vanadium dioxide exists as a number of polymorphs; three of which, VO_2 (rutile) (*1*), VO_2 (A) (*2*), and VO_2 (B) (*3*), have been well characterized. The most stable form, VO_2 (rutile), has the ideal tetragonal rutile structure at temperatures above 340 K and exhibits metallic conductivity. Below this temperature, however, it distorts to a semiconducting monoclinic form which contains V–V pairs. To date, compounds of the form H_xVO_2 ($0 < x < 1$) with rutile-related structures have been prepared only under high-temperature and/or high-pressure conditions. For example, one polymorph of stoichiometric VOOH, which is isostructural with InOOH and β-CrOOH, can be prepared hydrothermally from V_2O_3 at 80 kbar and 873 K (*4*). A second polymorph, which has the diaspore (α-AlOOH) structure, in which double rutile chains share vertices, occurs naturally as the mineral montroseite and can also be synthesized under hydrothermal conditions by hydrolysis of $NaVO_3$ previously reduced under hydrogen (*5*). More recently, a nonstoichiometric phase, $VO_{2-x}(OH)_x$ ($0.13 < x < 0.37$), with the $CaCl_2$-distorted variant of the rutile structure, has been reported by Range and Zintl as one of the products of high-pressure, high-temperature decomposition of ammonium metavanadate at >20 kbar and 973–1073 K (*6*, *7*).

In the present work, we describe the ambient-temperature synthesis, characterization, and inelastic neutron scattering spectrum of hydrogen insertion compounds of VO_2 (rutile), H_xVO_2 ($0 < x < 0.37$).

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I. Preparation and Characterization of H_xVO_2

(i) *Preparation and Characterization of VO_2*

Powder X-ray diffraction data, recorded using a Stöe–Guinier focusing camera with Cu$K\alpha$ radiation (λ = 1.54178 Å), were used both for phase identification and as an indication of the purity of all the compounds prepared. The mean oxidation state of vanadium in each sample was determined by the reducing-power method of Choain and Marion (*8*). The parent oxide VO_2 was prepared by heating a stoichiometric mixture of V_2O_5 and V_2O_3 in an evacuated silica tube at 1173 K for 1 week. Reducing-power analysis gave the composition as $VO_{2.01\pm0.01}$, and comparison of the X-ray data with those of Longo and Kierkegaard (*9*) further confirmed that the product was monoclinic VO_2.

TABLE I

POWDER X-RAY DATA FOR $H_{0.37}VO_2$

Intensity	2θ	d_{obs} (Å)	d_{calc} (Å)	h	k	l
s	27.379	3.257	3.254	1	1	0
m	36.475	2.463	2.460	0	1	1
m	37.001	2.429	2.428	1	0	1
vw	38.178	2.357	2.356	0	2	0
m	41.837	2.159	2.158	1	1	1
w	43.340	2.088	2.087	1	2	0
vvw	44.636	2.030	2.031	2	1	0
mw	54.240	1.691	1.691	1	2	1
m	55.392	1.659	1.660	2	1	1
mw	56.595	1.626	1.627	2	2	0
wm	64.663	1.441	1.442	0	0	2
w	67.946	1.380	1.379	0	3	1
w	70.978	1.328	1.330	3	0	1
w	71.579	1.318	1.318	1	1	2

Note. Refined orthorhombic lattice parameters (Å): a = 4.499(1), b = 4.712(1), and c = 2.883(1); cf. $VO_{1.63}(OH)_{0.37}$ (*6*): a = 4.502, b = 4.649, c = 2.870 Å.

(ii) *Preparation of H_xVO_2 by Hydrogen Spillover*

A series of hydrogen insertion compounds, H_xVO_2, was prepared by hydrogen spillover at room temperature and at 365 K using a finely dispersed platinum catalyst as described previously (*10, 11*). The uptake of hydrogen at room temperature was extremely slow and the maximum composition achieved was $H_{0.08\pm0.02}VO_2$. The powder X-ray diffraction pattern of this product closely resembled that of the parent oxide. The hydrogen insertion reaction proceeded much more rapidly at 363 K and the maximum composition obtained at this temperature was $H_{0.37\pm0.01}VO_2$. The product was shown to be inhomogeneous as the X-ray diffraction pattern contained two series of lines, one of which could be indexed on the basis of the monoclinic VO_2 unit cell and the other on a VO_2-related orthorhombic unit cell. Heating the sample at 423 K in an evacuated, sealed Pyrex tube for 2 months produced a homogenous, monophasic product, with X-ray lines indexable on the orthorhombic unit cell alone (Table I). Two further single-phase compounds, H_xVO_2 of intermediate composition (x = 0.16, 0.30), were also prepared by spillover at 363 K, followed by several weeks' equilibration. These also show an orthorhombic distortion and their lattice parameters are given in Table II. The three high-hydrogen-content compounds were not air-sensitive; their reducing power remained constant over a number of months. However, the low-hydrogen-content phase was readily oxidized in air to VO_2.

Two phases of H_xVO_2 can thus be identified from their powder X-ray diffraction patterns. For small values of x ($0 < x < 0.08$), H_xVO_2 retains the monoclinic VO_2 (rutile) structure, while over the composition range ($0.16 < x < 0.37$), distortion of the rutile-type structure occurs to give an orthorhombic unit cell. The orthorhombic distortion appears as a splitting of the (hkl) reflections with $h \neq k$, and the extent of the splitting increases with increasing hydrogen content. The lattice parameters of this phase are in close agreement with those

TABLE II

LATTICE PARAMETERS FOR H_xVO_2

x	Structure type	a (Å)	b (Å)	c (Å)	
0.0	VO_2 tetragonal[a]	4.554	4.554	2.847	
0.08	VO_2 monoclinic	5.759(3)	4.533(3)	5.372(3)	122.49(1)
0.16	Orthorhombic	4.525(2)	4.609(2)	2.863(3)	
0.30	Orthorhombic	4.505(3)	4.633(4)	2.869(1)	
0.37	Orthorhombic	4.499(1)	4.712(1)	2.883(2)	
1.00	Orthorhombic	4.446	4.862	2.962	(4)

[a] Extrapolated values for tetragonal lattice parameters at 298 K (6).

of $VO_{2-x}(OH)_x$ ($0.13 < x < 0.37$) prepared by Range and Zintl (6) by the high-pressure, high-temperature decomposition of ammonium metavanadate.

(iii) Electrochemistry

The electrochemical behavior of VO_2 in acidic media was also investigated. VO_2 was intimately mixed with PTFE and graphite (~10% by weight each) and pressed onto a platinum grid to form the cathode of a conventional three-compartment cell (12). Platinum foil was used as the anode, and the reference electrode was a saturated calomel electrode. A Princeton constant-current controller was used to monitor the galvanostatic discharge curves.

In conventional aqueous acid electrolytes such as 0.05 *M* H_2SO_4, VO_2 proved to be a very unstable cathode material as both the parent oxide and the insertion products dissolved before the discharge was complete. However, a galvanostatic discharge curve was obtained at 298 K under nonaqueous conditions, using an electrolyte of deoxygenated 0.099 *M* toluene(IV) sulphonic acid monohydrate in dry EtOH (13) at a current of 5 μA (Fig. 1). The initial voltage (vs the standard hydrogen electrode) was 630 mV with a small plateau at 220 mV ($0.02 \leq x < 0.04$). Hydrogen insertion proceeded only to a value of $x = 0.06$ before the voltage fell to zero. This is in reasonable agreement with the maximum value of $x = 0.08$ achieved by hydrogen spillover at room temperature. Similar behavior was observed for the insertion of hydrogen into CrO_2 (14). The maximum achieved electrochemically at room temperature is $H_{0.1}CrO_2$, which retains the rutile structure, while spillover at 423 K gives orthorhombic $H_{0.8}CrO_2$ (14).

II. Vibrational Study of $H_{0.3}VO_2$

(i) Inelastic Neutron Scattering Spectrum of $H_{0.3}VO_2$

The metallic nature of H_xVO_2 makes optical spectroscopic measurements difficult. The vibrational spectrum was therefore measured using inelastic neutron scattering (INS) spectroscopy. This technique has proved useful in the past for investigating the nature of the hydrogen attachment in insertion compounds, e.g., H_xWO_3 (15), H_xMoO_3 (16), and $H_xV_2O_5$ (17), since the large incoherent scattering cross section of hydrogen results in their INS spectra being dominated by vibrational modes involving hydrogen displacements.

The spectrum of $H_{0.3}VO_2$ was recorded at 80 K over the range 250–2000 cm^{-1} using the IN1 BeF spectrometer at the ILL, Grenoble. Nine grams of $H_{0.3}VO_2$, prepared by hydrogen spillover and characterized as above, was loaded under nitrogen into a

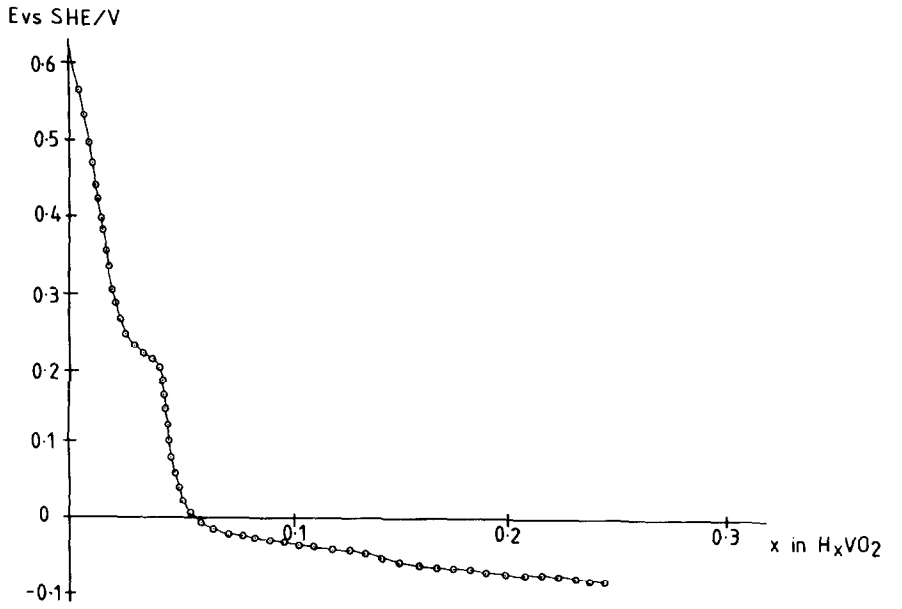

FIG. 1. Galvanostatic discharge curve of H_xVO_2 at 5 μA in 0.1 *M* toluene(IV) sulphonic acid at 298 K.

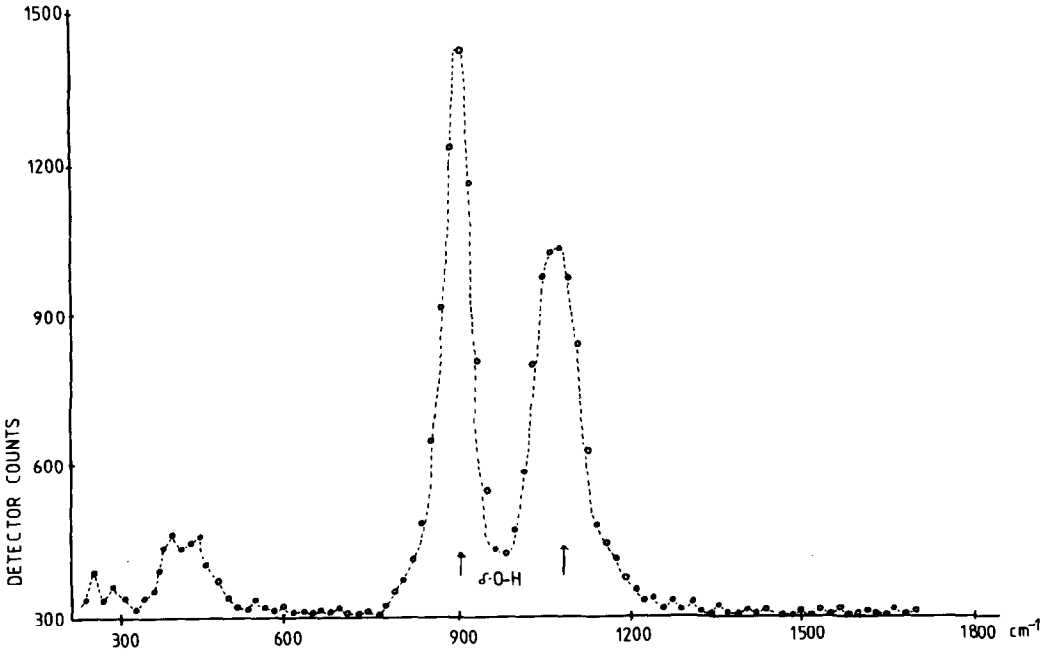

FIG. 2. Inelastic neutron scattering spectrum of $H_{0.3}VO_2$ at 80 K.

TABLE III

ATOM PARAMETERS FOR $H_4V_2O_4$

Space Group *Pnnm* (No. 58 in the International Tables) Unit cell dimensions (Å): a = 4.5113, b = 4.6303, c = 2.8652 Cell content: $H_4V_2O_4$[a]
4O and 4H in (g): $(x,y,0)$, $(-x,-y,0)$, $(-x+\frac{1}{2},y+\frac{1}{2},\frac{1}{2})$, $(x+\frac{1}{2},\frac{1}{2}-y,\frac{1}{2})$
2V in (a): $(0,0,0)$, $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$

	x/a	y/b	z/c
V	0	0	0
O	0.286	0.312	0
H[b]	0.1202	0.433	0

[a] No provision for partial occupancy of sites can be made in this program, and H's accordingly are placed on all 4(g) sites.

[b] H atoms were not located in (*6*) and by analogy with the isostructural β-$HCrO_2$ (*19*), H atoms are placed at 1 Å from the nearest O atom.

number of high-purity silica tubes (approximately 3-mm internal diameter) to a depth of 5 cm. The tubes were evacuated and sealed. They were then arranged in a drilled aluminium block, designed to present the maximum sample volume to the neutron beam, mounted on a sample stick, and loaded into an ILL orange cryostat on the sample table. Previous experiments have shown that the scattering from the silica tubes produces little contribution to the background spectrum and can be ignored (*15*).

The INS spectrum of $H_{0.3}VO_2$ shows two intense peaks at 1083 and 909 cm^{-1} and two smaller ones at 476 and 431 cm^{-1}. (Fig. 2). Assignment to vibrational modes is discussed below.

(*ii*) *Calculation of the Vibrational Spectrum of* $H_{0.3}VO_2$

Fundamental vibrational frequencies and corresponding atomic displacements were calculated using the program SOTONVIB (*18*). A simple valence force field (SVFF),

$$2V = \sum_i k_{r_i} \Delta r_i^2 + \sum_j k_{\theta_j} \Delta\theta_j^2,$$

involving bond stretches, Δr_i and angle deformation, $\Delta\theta_j$ was chosen. The SOTONVIB input requirement is for atomic masses, Cartesian coordinates of all atoms in the unit cell, definition of enough internal coordinates to cover all vibrational degrees of freedom, and chosen values for the force constants k_{r_i} and k_{θ_j}. The complete input file used for this purpose may be obtained on request to the authors; essential data involved are summarized in Table III.

Atomic parameters. A plan of the unit cell is shown in Fig. 3; also shown are the positions of neighboring atoms needed to complete the specification of all the internal coordinates used, which are based on changes in V–O and O–H bond lengths and VOV, OVO, and VOH bond angles.

Force constants. V–O stretching force constants were chosen by scaling, according to length, the force constants of the V–O stretch in the V_3O unit in V_2O_5 (*20*). The VOV and OVO deformation force constants were taken to be the same as those of the corresponding bends in the V_3O unit of V_2O_5. The remaining force constants were chosen to fall within the range of previously published values for similar motions. Chosen values are given in Table IV (with atom numbering as in Fig. 3).

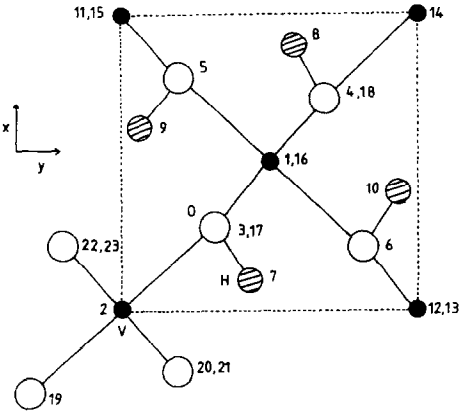

FIG. 3. Unit cell of $H_4V_2O_4$.

TABLE IV

FORCE CONSTANTS FOR $H_4V_2O_4$

Bond stretch	k_r (mdyn Å^{-1})	Angle bend	k_θ (mdyn Å rad^{-2})
V(1)–O(4)	1.14	VOV(all)	0.23
V(1)–O(5)	1.14	OVO(all)	0.30
O–H	6.43	V(1)O(6)H(10)	0.35
		V(1)O(3)H(7)	0.40

Calculated vibrations. For $H_4V_2O_5$, 27 optic modes are predicted belonging to the representation

$$4A_g + 4B_{1g} + 2B_{2g} + 2B_{3g} + 3A_u + 2B_{1u} + 5B_{2u} + 5B_{3u}.$$

The calculated frequencies and their assignments (based on calculated atomic displacements) are shown in Table V.

The main features of the calculated modes can be shown by a consideration of the atomic displacements about one of the four V_3OH units (Fig. 4). The O–H stretch calculated at approximately 3400 cm^{-1} lies outside the range of the IN1 spectrometer. The two main peaks found in the measured spectrum at 1083 and 909 cm^{-1} coincide nicely with the calculated orthogonal δ-VOH bending modes (one set in the xy plane, the other in the z direction). The high intensities observed for these peaks in the spectrum of $H_{0.3}VO_2$ confirm that they correspond to modes involving large hydrogen displacements. The vibrations, calculated at approximately 580 cm^{-1} and below, involve principally V–O stretching and bending modes which carry hydrogen along with the oxygen displacement and this accounts for their prominent appearance in the INS spectrum. The assignments made at 476 and 431 cm^{-1} agree well with Beattie's previous analysis of the motions of almost-planar M_3O units in compounds such as V_2O_5, MoO_3, and TiO_2 (rutile and anatase) where in-plane modes occur in the region 830–470 cm^{-1} and out-of-plane modes in the region 360–120 cm^{-1} (*21*).

Use of a more sophisticated force field would allow greater "fine-tuning" to measured frequencies but the present analysis serves to account for most of the main features of the observed spectrum. The marked splitting observed for the δM–OH vibration here is also found for a number of other oxyhydroxides containing M_3OH groups such as α-AlO(OH) (diaspore) (*22*), GaO(OH) (*23*), and β-CrO(OH) (*24*). In the last example, the bending modes, observed

TABLE V

FREQUENCIES AND ASSIGNMENTS OF GENERATED VIBRATIONAL MODES OF H_xVO_2

Calculated frequency (cm^{-1})	Observed frequency (cm^{-1})	Assignment	Mode
3407 (×4)		B_{1g} B_{3u} B_{2u} A_g	ν(O–H)
1098 1095	1083	B_{2u} B_{3u} B_{1g} A_g	δ(O–H) in xy plane
1093 1092			
918 916 914	909	B_{1u} A_u B_{3g} B_{2g}	δ(O–H) out of xy plane
914			
587 583 553	476 431	B_{3u} B_{2u} B_{1u} A_g	
517 515 493		B_{1g} A_u B_{3g} B_{2g}	Lattice modes
414 414 342		B_{2u} B_{1g} B_{3u}	
342 341 322		B_{3u} B_{2u} A_u A_g	
292 267 212			
177			

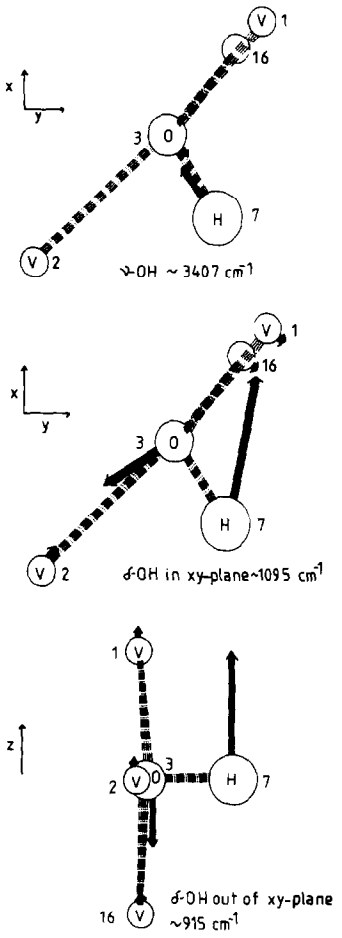

FIG. 4. Generated atomic displacements of V_3OH unit.

in both IR and INS spectra (*24*), occur at higher frequencies than in $H_{0.3}VO_2$, i.e., at 1391 and 1215 cm^{-1}, reflecting the greater strength of hydrogen bonding in this compound. The O–O distance is 2.46 Å in β-CrO(OH) compared with 3.11 Å in $VO_{1.7}(OH)_{0.3}$ (*6*).

III. Conclusions

Two phases of H_xVO_2 ($0 < x < 0.37$) have been prepared and characterized. The low-hydrogen-content phase ($0 < x < 0.08$), prepared at room temperature electrochemically and by hydrogen spillover, is monoclinic and has lattice parameters little changed from those of the parent oxide VO_2. The small tunnels in the VO_2 structure and the highly crystalline nature of the oxide, which was prepared at a high temperature, may restrict the mobility of the hydrogen through the bulk of the solid. Structural distortions occur upon the formation of the higher-hydrogen-content phase of H_xVO_2 ($0.16 < x < 0.37$) and this is only readily achieved by spillover at temperatures above the VO_2 monoclinic–tetragonal transition temperature. H_xVO_2 ($0.16 < x < 0.37$) is orthorhombic and has been shown by INS to contain -OH groups. It is thus clearly identifiable with $VO_{2-x}(OH)_x$ ($0.13 < x < 0.37$) prepared previously by high-temperature–high-pressure decomposition of ammonium metavanadate (*6*). Thus, what was formerly regarded as a high-pressure phase of H_xVO_2 has been prepared under ambient conditions in the present investigations by the reaction of VO_2 and atomic hydrogen.

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