

Crystal structure and hydrogen occupation in $H_xV_2O_5$ ($x=0.0-3.9$)

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Changes in the crystal structure and the lattice constants of powdered crystalline V_2O_5 after absorption of hydrogen were measured, as a function of the concentration, by X-ray diffractometry. The diffraction spectra obtained showed that three kinds of phases, α ($x < 0.4$ in $H_xV_2O_5$), β (co-existing with either terminal phase in the range of $0.4 \leq x < 3.2$) and γ ($3.2 \leq x \leq 3.9$), appear up to $x=3.9$, which was found to be the upper limit of the absorption at 70°C under a hydrogen pressure of 5 MPa. The crystal system of the three phases was determined to be orthorhombic, although the lattice constants differed. The diffraction lines were broadened, and the background of the X-ray spectra grew with hydrogenation, especially in the γ -region, which indicates the growth of the lattice distortion and a quasi-amorphous state. The occupation of hydrogen atoms in each phase is discussed on the basis of the experimental results.

1. Introduction

It is well-known that crystalline V_2O_5 has an orthorhombic crystal structure with columnar spaces extending two-dimensionally along the b - and c -axes, and that it can accommodate various kinds of metallic elements, such as alkali metals, in these spaces.

Tinet *et al.* [1] first reported that V_2O_5 is capable of absorbing large amounts of hydrogen at ambient temperatures. Since then, several measurements on the change in the crystal structure or the phase on doping with hydrogen have been carried out using X-ray diffractometry [2, 3] and an electrochemical method [4]. But the crystallographic change has not been so systematically investigated, especially as a function of the concentration of hydrogen, and the following problems have been left unresolved. (i) Is there no solid solution region, as Tinet *et al.* [4] supposed from their measurements of the electrochemical potential? (ii) What phases of hydrides appear, and at what values of x , in $H_xV_2O_5$? (iii) What are the crystal structures? (iv) What is the occupation of hydrogen atoms in each phase?

We have measured X-ray diffraction (XRD) of $H_xV_2O_5$ during doping of hydrogen up to the absorption limit. In the present paper, we report the changes in the lattice structure and in the lattice constants as a function of x , together with the broadening of the diffraction lines. The occupation of hydrogen atoms in each phase is discussed on the basis of the results of the anisotropic expansion and the distortion of the lattice.

2. Experimental procedure

The introduction of hydrogen into crystalline V_2O_5 of CERAC co. powder (with a purity better than 99.5%, sieved within #200 mesh) was performed by the spillover

technique [5]. The powdered V_2O_5 was first impregnated with a 0.2 M H_2PtCl_6 solution. After drying, the sample was outgassed under a vacuum for 1 h at 100°C , and then kept for 20 min at 200°C ; by these treatments the sample of V_2O_5 was coated with Pt particles, which act as a catalyser and accelerate the dissociation of H_2 molecules. The temperature was then lowered to 70°C as the sample was kept under the vacuum; the sample was repeatedly exposed to pure hydrogen gas (99.99999%) at pressures from 0 to 5 MPa until a given amount of the dopant was obtained. The value of x in $H_xV_2O_5$ was determined from the drop in the hydrogen pressure due to the absorption. Specimens doped with hydrogen for levels of the concentration up to $x=3.9$ were prepared by this manner. The concentration of $x=3.9$ was found to be the upper limit under the conditions of 70°C and 5 MPa.

To investigate the crystallographic change during the absorption of hydrogen, XRD measurements were carried out at room temperature using CuK_α radiation with a RIGAKU X-ray diffractometer.

3. Results

Fig. 1 shows some typical XRD patterns obtained for samples with different amounts of hydrogen. The formation of two hydride phases, together with a solid-solution phase, was confirmed by the analysis of the spectra. These three phases will be denoted as α , β and γ , they are in order of increasing concentration of hydrogen.

For specimens containing hydrogen between $0.0 < x < 0.4$, which corresponds to the α -phase region, all the diffraction lines obtained were indexed to be orthorhombic, similar to those of V_2O_5 . The lattice constants were calculated by least-squares fitting. The

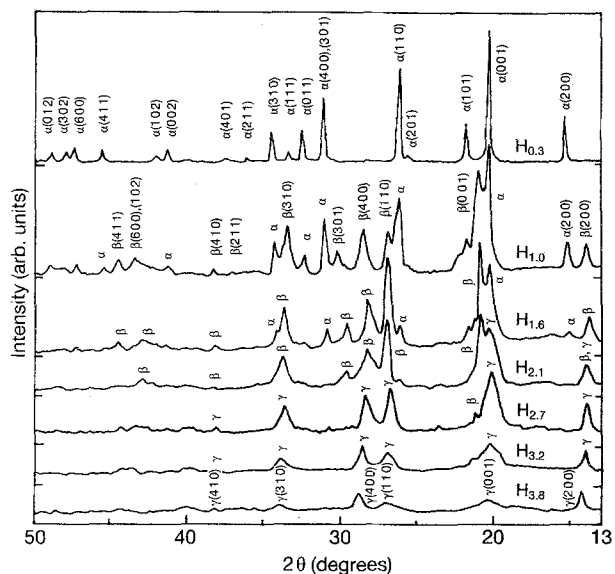


Figure 1 Typical diffraction spectra of $H_xV_2O_5$ for $x = 0.3, 1.0, 1.6, 2.1, 2.7, 3.2$ and 3.8 .

results are shown as a function of x in Fig. 2a, together with results for the β - and the γ -phase. The volume of the unit cell consisting of two molecular units of V_2O_5 was calculated from the lattice constants obtained and the changes against x are shown in Fig. 2b. The volume expansion due to a hydrogen atom is estimated to be $\sim 2.5 \times 10^{-3} \text{ nm}^3/V_2O_5/H$ from Fig. 2b when averaged from $x = 0.0$ to 0.4 . This value is almost the same as that for metal hydrides [6].

As can be seen in Fig. 2a, the lattice constants of the α -phase changed monotonically with x within the experimental errors. The changes are characterized by a large extension over the a -axis. When heating at 70°C for 16 h under a vacuum, the lattice constants of $H_{0.2}V_2O_5$ returned to the values for V_2O_5 . The continuous extension of the lattice constants with x from those of V_2O_5 , and their recovery, indicate that hydrogen atoms really are dissolved in the solid-solution state, in contradiction to the supposition of Tinet *et al.* which was mentioned in Section 1. The β -phase appeared in the range $0.4 \leq x < 3.2$ and was, in our measurements, observed only in co-existence with either the α - or the γ -phase. The crystal structure was found to be orthorhombic. The γ -phase, ranging from $x = 3.2$ to 3.9 , was also orthorhombic, with its lattice constants different from those of the α - and the β -phase. Our spectra for the γ -range coincided with those obtained for $H_{3.8}V_2O_5$ by Marcq *et al.* [7].

The half-amplitude widths of lines (200), (400), (110) and (001) were measured, and the changes with x are shown in Fig. 3, in the range $x < 0.4$ for the lines of the α -phase, in $1.0 \leq x \leq 2.7$ for those of the β -phase, and in $x \geq 3.2$ for those of the γ -phase. As can be seen in Fig. 1, the background of the diffraction spectra increased with increasing x , especially in the γ -phase. The enormous broadening of the diffraction lines, and the growth of the background, indicate the progress of amorphization of the lattice. In fact, Marcq *et al.* [7] also reported from their measurements of XRD that $H_xV_2O_5$ became quasi-amorphous for values of x greater than 3.0.

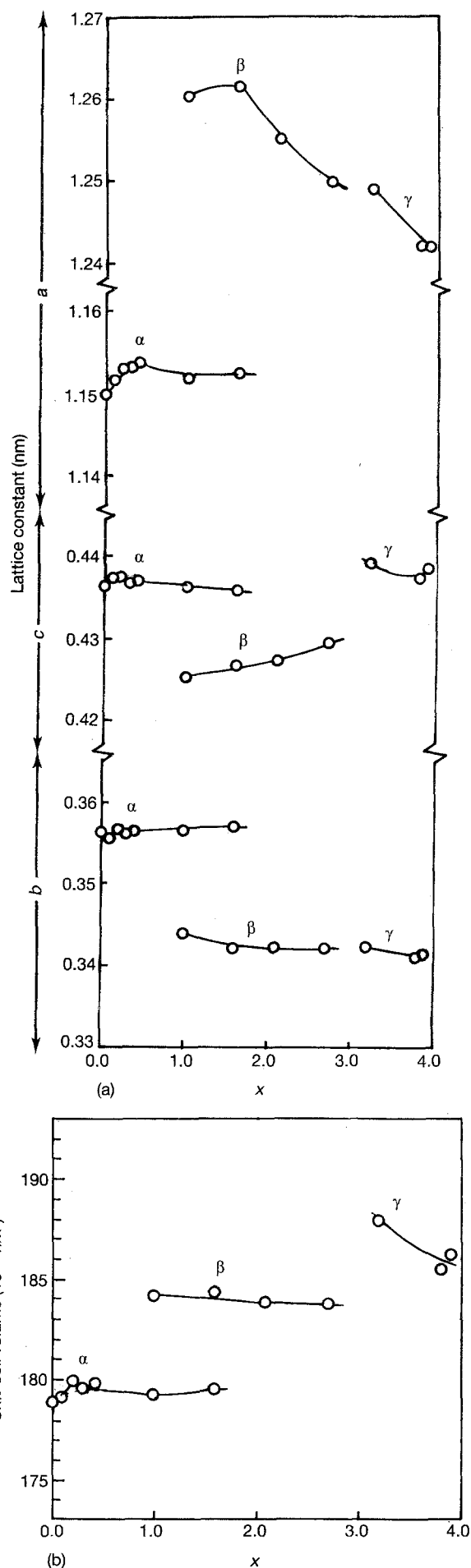


Figure 2 (a) Changes in the lattice constants of the α -, β -, and γ -phases as functions of x in $H_xV_2O_5$; and (b) changes in the volume of the unit cell of $H_xV_2O_5$.

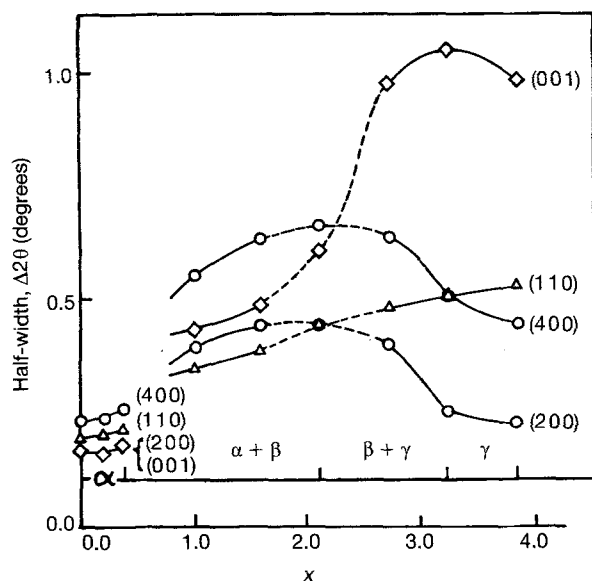


Figure 3 Changes in the half-amplitude widths of XRD lines with x in $H_xV_2O_5$. The values which are shown in the $\alpha + \beta$ and $\beta + \gamma$ regions are the values for the β -phase.

The characteristic features of the changes in the lattice constants, which are shown in Fig. 2a, are as follows. (i) In the α -region for $x < 0.4$, the lattice constant a markedly increased with increasing x , but b and c only increased a little. (ii) At the transition from the α - to the β -phase, a increased discontinuously by a significant amount, while b and c decreased. In the two-phase region of $\alpha + \beta$, the lattice constant a in the β -phase increased with x at first and then it steeply decreased, but c monotonically increased and b was almost constant except for a small decrease at the beginning. (iii) At the transition from the β - to the γ -phase, c increased discontinuously, but a and b hardly changed. Fig. 2a shows a remarkable decrease with x for a , and a small decrease for b and c in the γ -region ($3.2 \leq x \leq 3.9$), resulting in a decrease in the volume of the unit cell, as seen in Fig. 2b. This decrease must be apparent, because it is likely in such heavily hydrogen-doped V_2O_5 that some of the oxygen atoms composing the skeleton of the lattice are released from the lattice. The details will be discussed in the next section.

The characteristic features of the changes in the line width (Fig. 3) are as follows. (i) The line broadening observed for all the diffraction lines of the β -phase was much larger than that in the α -phase. (ii) In the early stage of the β -phase, the width of the diffraction lines (400) and (200) increased rapidly with x , whereas the increases in (110) and (001) were rather gradual. In the later stage, the widths of (400) and (200) tended to decrease after saturation. (iii) The width of these two lines sharply decreased on the appearance of the γ -phase and then gradually decreased with increasing x . The width of (110) continued to increase gradually with increasing x through the β - and the γ -region. (iv) The line width of (001) increased steeply at the later stage of β and saturated in the early stage of γ -formation. It is noticeable that the broadening was more than twice as large as that for the other diffraction lines.

4. Discussion

In this section, we will discuss the occupation of the hydrogen atoms in each phase on the basis of the characteristic features which are shown in Figs 2 and 3.

The atomic arrangement of the V_2O_5 crystal is shown in Fig. 4. Fig. 4a is a projection onto the (a - c)-plane and Fig. 4b is a projection onto the (a - b)-plane. Fig. 4 shows two kinds of tunnel-like spaces extending along the b - and the c -axes. The interstice located at the intersection of these two kinds of tunnels is as large as $0.36 \times 0.36 \times 0.44 \text{ nm}^3$ per molecular V_2O_5 . Since a large vacant space induces less distortion when doped, it is very likely that hydrogen atoms are accommodated in this kind of interstice. In fact, it has been clarified in alkali- or noble-metal-atom-doped V_2O_5 that these dopants occupy essentially the same kind of sites as those located at the tunnel-like space in the lattice of V_2O_5 [8-15]. Figs 5 and 6 show the atomic arrangements around the interstice located at the intersection of the two kinds of tunnel-like space; Figs 5 and 6 are extracted from Fig. 4a and b, respectively. By analogy with metal-vanadium bronzes, we assume in the following discussion that the sites which hydrogen atoms occupy in $H_xV_2O_5$ are either the sites denoted by \oplus in Fig. 5 or by \otimes in Fig. 6.

It is preferable that hydrogen atoms in the α -phase randomly occupy either of the sites denoted by \oplus in Fig. 5. This is because such an occupation produces a large expansion along the a -axis than for the other axes, which is in agreement with the experimental results. The occupancy of the sites in the α -range will be less than 0.2 per site on average taking account of the fact that the solubility limit is smaller than 0.4. In the β -phase, each interstice marked with \oplus will accommodate two hydrogen atoms lining up in a paired manner in the direction of the a -axis, as shown in Fig. 5. This occupation will cause a local lattice distortion from the full lines to the dashed lines, as indicated in Fig. 5, which corresponds to a discontinuous extension along the a -axis and to a discontinuous contraction along the b - and the c -axes. Since the occupation of the \otimes sites will cause some reduction in a and some

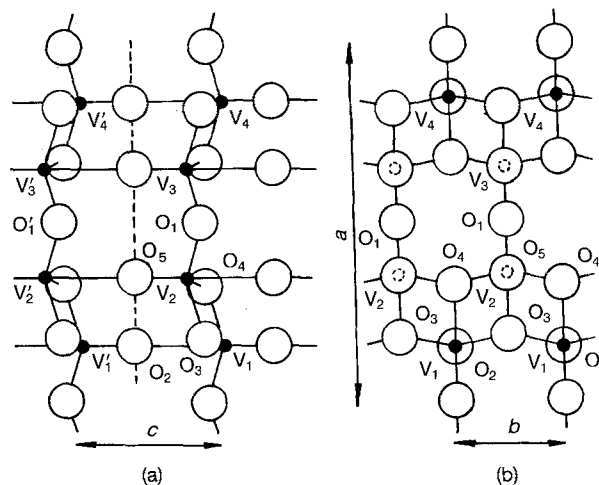


Figure 4 Atomic arrangements of the V_2O_5 lattice: (a) a projection onto the (a - c)-plane, (b) a projection onto the (a - b)-plane. a , b and c are the lattice constants. (○) O atom, and (●) V atom.

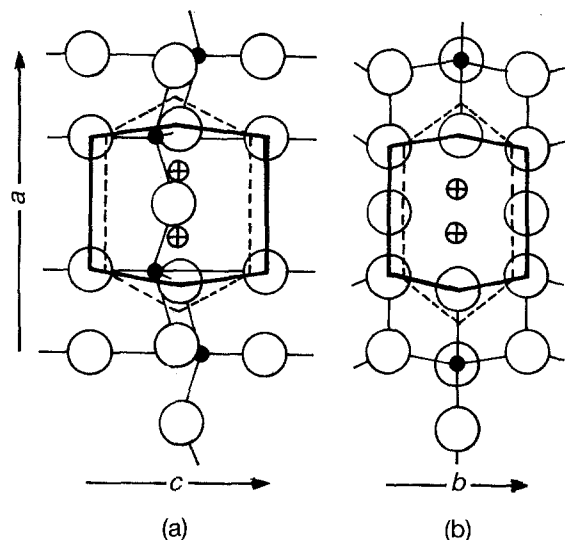


Figure 5 Positions of the sites, \oplus , at which hydrogen atoms are expected to partially occupy in the α - and β -phases and to fully occupy in the γ -phase.

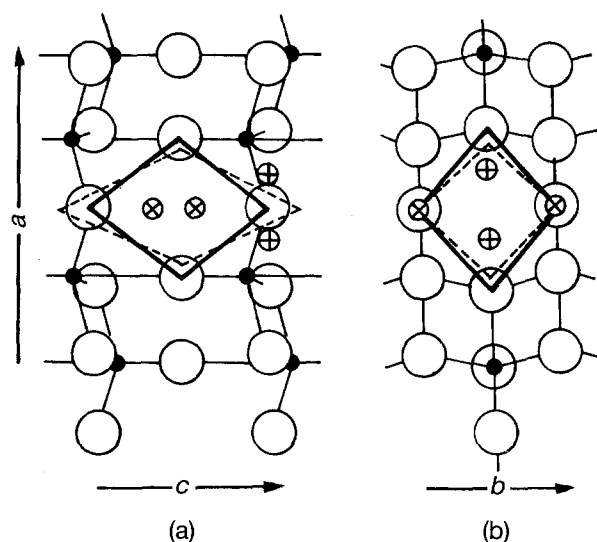


Figure 6 Positions of the sites, \otimes , at which hydrogen atoms are expected to occupy partially in the γ -phase in addition to their full occupation of the sites denoted by \oplus .

extension in c , as shown in Fig. 6, partial and random occupation of either site shown by \otimes in Fig. 6, after the full accommodation of the site \oplus , can explain the changes in the lattice constants in the β -phase with $x \geq 2.0$ which are shown in Fig. 2a. In the γ -phase, the accommodation of hydrogen atoms lining up in a paired manner with the c -axis (Fig. 6) will progressively be accomplished with increasing x , in addition to the occupation of the sites \oplus which were already fully accommodated in the β -phase. This occupation in the γ -phase will result in a discontinuous increase in c , and little change in a and b .

When the hydrogen occupation is as described above, the diffraction lines should broaden in the following manner. The occupation of the \oplus sites by hydrogen atoms in a paired manner in the β -phase will cause a distortion along the c -axis and will produce a broadening of the diffraction lines relating to the

a -axis, for example, the (400) and (200) reflections. Furthermore, the progress of amorphization must reflect the displacement to a distorted position of the matrix atoms neighbouring dopant atoms. Partial and random occupation of the \otimes sites, which will occur at the heavily doped stage of the β -region ($x \geq 2.0$) and will cause the reduction in a , possibly reduces the broadening of the diffraction lines ($h00$), because such occupation will reduce the local displacement of the matrix atoms in the direction of the a -axis. This occupation will cause the steep decrease in the width of (400) and (200) for the later stage of the β -phase.

In the γ -region, an additional accommodation of hydrogen atoms at the \otimes sites in a paired manner is expected to occur, and this will be accompanied by the broadening of (001) lines, as well as by an abrupt increase in the lattice-constant c . The large increase, more than twice that in the other lines, in the width of the line (001) is thought to originate from the weak bonding in the direction of the c -axis, which is attributed to the crystal structure of V_2O_5 . Oxygen atoms aligned along the dashed line shown in Fig. 4a are weakly bound by a Van der Waals-like force, with the neighbouring vanadium atoms, in the direction of the c -axis. When hydrogen atoms occupy the \otimes sites, a local large disturbance along the c -axis is likely to occur, resulting in a large broadening of the (001) reflection. The disturbance will be much larger in the early stage of the occupation of the \otimes sites; that is, in the later β - or in the early γ -region. The accommodation of hydrogen at this kind of site will destroy the cohesion of the lattice around the occupied sites and continue the progress of amorphization of the crystal, as observed in heavily hydrogenated specimens, especially in the γ -phase.

Another effect that is possibly caused by the occupation of hydrogen atoms at the \otimes sites in a paired manner is the growing importance of O-H bonding between the H and the O_1 atoms which neighbour each other in the direction of the pairing. The growth of this bonding possibly reflects a reduction in the strength of V-O bonding between O_1 and neighbouring V_3 or V_2 atoms (shown in Fig. 4). In fact, Hirata and Yagisawa [16] observed in their infrared measurements that the vanadyl stretching vibration became broad and less intense with doping of H in the γ -region. The reduction of binding between O_1 and V_3 (or V_2) atoms will facilitate growth of O-H(-H) species liberated from the V_2O_5 lattice and will enhance amorphization. The removal of O_1 atoms from the skeleton of the lattice will reduce the lattice-constant a and cause a reduction in the volume of the unit cell with increasing x , which was observed in the γ -region in Fig. 2b.

5. Conclusions

The following results were obtained from XRD measurements for hydrogen-doped $H_xV_2O_5$.

1. Three phases, α , β and γ appear during the doping up to $x = 3.9$. α : $0 < x < 0.4$, solid solution. Hydrogen atoms introduced into V_2O_5 in this range of x exist in

a solid solution state. β ; $0.4 \leq x < 3.2$, compound, but co-existing with either terminal phase. γ ; $3.2 \leq x \leq 3.9$, compound, but quasi-amorphous state.

2. The crystal structures of the α -, β -, and γ -phases are all orthorhombic, but with different lattice constants.

3. The upper limit of the absorption of hydrogen is $x = 3.9$ under a temperature of 70 °C and a hydrogen pressure of 5 MPa.

4. The likely positions of the occupation of H in V_2O_5 are the two types of sites, \oplus and \otimes , both of which locate at the intersection of the two kinds of tunnel-like columnar spaces shown in Figs 5 and 6. The occupation in the α -phase is random occupation of the \oplus sites. A random and partial occupation of the \otimes sites is preferred for the β -phase in addition to a partial to full occupation of the \oplus sites in a paired manner. In the γ -phase, a partial to full occupation of the \otimes sites in a paired manner is suggested, in addition to full occupation of the \oplus sites in the paired manner.

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