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by

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ABSTRACT

Electron microscope specimens of vanadium, thinned by a technique known to add hydrogen, showed evidence for ordering in β -vanadium hydride. Extra half-order reflections were observed and concluded to be due to scattering from hydrogen. The transformation between the ordered and disordered phases occurs reversibly at a specific temperature in the range 160 to 190°C depending on the specimen. The reciprocal lattice as determined by electron diffraction was shown to be in the monoclinic Laue group. Indirect evidence places the composition of the ordered phase in the vicinity of V_2H . The possible monoclinic structures consistent with observations place the hydrogens in tetrahedral sites on alternate $(101)_{b.c.t.}$ planes.

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Introduction:

A partial phase diagram for the vanadium-hydrogen system as determined by Maeland⁽¹⁾ using X-ray techniques and extended to VH_2 by Reilly and Wiswall⁽²⁾ is shown in Fig. 1. The α -phase is an interstitial solid solution of hydrogen in body-centered cubic V; the β -hydride has a body-centered tetragonal structure and the γ -hydride has a face-centered cubic structure.

Several authors have discussed the possibility of ordering of hydrogen in the group Vb transition metals (Vanadium, Niobium, Tantalum)⁽⁴⁻⁹⁾. Roberts⁽⁴⁾ studied a powder sample of vanadium deuteride near the composition V_4D_3 using neutron diffraction and at room temperature observed a single diffraction peak at the 110 b.c.t. position. For this case the intensity is almost entirely due to the deuterium since vanadium has a very low coherent cross section for neutrons. For X-rays just the reverse is true, the vanadium scatters very strongly and the deuterium scatters very weakly. At liquid nitrogen temperature many more reflections were observed which Roberts indexed on the basis of a primitive cubic cell with a_0 equal to $6.30\text{\AA}$, or twice the b.c.c lattice parameter determined by X-rays. An order-disorder transformation was reported to occur at $207 \pm 10^\circ \text{K}$.

From a neutron study of powder specimens of NbD and TaD Somenkov et al.⁽⁵⁾ deduced an ordered structure best described on the basis of a 2 atom body-centered tetragonal niobium unit cell. On this basis, the unit cell has dimensions $2a$ by $2c$ by a where a and c are the parameters of the b.c.t. cell. The deuterium atoms occupy tetrahedral sites in the b.c.t. cell. Somenkov et al chose a unit cell consistent with the orthorhombic space group P_{nnn} of dimensions $a \approx b \approx a_0 \sqrt{2}$, $c = a_0$ where a_0 is the parameter of the disordered body-centered cubic cell. The Nb atoms are in the $f(000, 0\frac{11}{22}, \frac{1}{2}0\frac{1}{2}, \frac{11}{22}0)$ positions and the deuterium atoms are in the $a(\frac{1}{4} \frac{1}{4} \frac{1}{4}, \frac{3}{4} \frac{3}{4} \frac{3}{4})$ and $b(\frac{3}{4} \frac{1}{4} \frac{1}{4}, \frac{1}{4} \frac{3}{4} \frac{3}{4})$ positions.

An electron microscopy study by Hull and Wynne⁽⁷⁾ on the Ta-H system showed the presence of domain walls and extra diffraction spots corresponding to a planar spacing twice that of the normal b.c.c. 110 spacing. These results were interpreted in terms of ordering of hydrogen atoms. Similar evidence for ordering was reported by Westlake⁽⁸⁾ in the V-H system, but neither of these studies was very extensive.

Further resistometric studies by Westlake⁽⁹⁾ indicate that tetragonal β -vanadium hydride undergoes a transformation below 224°K and also two more in the vicinity of 450°K . These observations were suggested to indicate increasing disorder of interstitial hydrogen with increasing temperature.

As part of a larger study of hydrogen in vanadium a single crystal structure analysis was performed using the electron microscope, the results of which are reported in this paper.

Experimental Procedure:

Specimens were obtained from single crystals of vanadium containing a few atomic percent hydrogen. 250 μm thick sections were cut with a string saw and then ground down to 75 μm with wet 600 grit silicon carbide powder on glass. These samples were then chemically polished in a cooled solution ($<10^\circ\text{C}$) of 2 parts HF and 1 part HNO_3 . This method has been shown (8,10) to considerably increase the hydrogen content of vanadium. The electron diffraction patterns showed that the specimens were in the single phase β region. It should be pointed out that the same thinning procedure on polycrystalline vanadium strip resulted in specimens which contained primarily α phase with a small amount of β phase. All observations were made at 200 KV on a JEM 200 electron microscope equipped with either a 30° goniometer or goniometer-hot stage.

Experimental Results:

In addition to the reflections characteristic of a body-centered tetragonal structure, many half order reflections were observed in the electron diffraction

patterns as shown in the (010)b.c.t. reciprocal lattice section in Fig. 2a. Using the dark-field technique, the half order reflections were shown to come from definite domains as illustrated in Figs. 2b,c. The full-order (to be referred to as matrix) reflections are formed from both domains. Upon heating, the half-order array of spots disappear at a specific temperature in the range from 160 to 190°C depending upon the specimen. At or near this temperature, the matrix reflections changed from a b.c.t. to a b.c.c. array. Upon cooling, the half-order and the b.c.t. reflections reappeared at approximately the same temperature. When the specimen was heated to above 385°C and then cooled to room temperature in the microscope, no half-order reflections reappeared and the diffraction pattern was b.c.c. This observation indicates that the half-order spots most likely result from the presence of hydrogen, since no other interstitial atoms can be removed from vanadium by vacuum annealing at such low temperatures. (11)

Using selected area diffraction in conjunction with dark field microscopy, it was possible to obtain several reciprocal lattice sections from one domain as shown in Fig. 3. In this case the starting orientation was (010) b.c.t. Using several different starting orientations [e.g. (001), (012), (100) and (010)] the complete reciprocal lattice of a single domain was determined. It was not possible to perform this study

on the same domain, since the goniometer stage limited tilts to 30° from the starting orientation. It was possible to get overlap between the observations obtained from the different starting orientations and this allowed the unambiguous determination of the reciprocal lattice from one domain as shown in Figs. 4a,b. Fig. 4a shows the reciprocal lattice indexed with reference to the b.c.t. hydride structure and a convenient unit cell is outlined in Fig. 4b. The reciprocal lattice basis vectors A^* , B^* , C^* have been chosen such that $H=h+1$, $K=h-1$, and $L=k$ where HKL are the indices referred to the new cell and hkl the indices referred to the b.c.t. cell. The maximum point group symmetry for this reciprocal lattice is $2/m$ which places it in the monoclinic Laue group. The observed reflections are seen to satisfy the extinction condition ⁽¹²⁾ for a B-face centered Bravais lattice (i.e. $H+L$ is even). With these restrictions there are only five possible space groups: $B2$, Bm , $B2/m$, Bb , and $B2/b$. The last two have the extra restriction on $HK0$ reflections such that K is even ⁽¹²⁾, and since 010 , 210 , etc. reflections exist the space groups Bb and $B2/b$ are eliminated. The reciprocal lattice is therefore consistent with the three monoclinic space groups $B2$, Bm and $B2/m$ and at this point it is not possible to distinguish between the three due to the centrosymmetric nature of the diffraction patterns.

Discussion:

It is reasonable to assume that the extra reflections are due to the interstitial ordering of hydrogen in the β hydride since chemical thinning has been shown to greatly increase the hydrogen content of vanadium (8,10,13) and heating above 385°C permanently removes the effect. The solubility of hydrogen decreases with increasing temperature (14) and vacuum degassing of carbon, nitrogen, or oxygen is not expected at this low temperature (11).

Although one might at first expect hydrogen scattering by electrons to be quite small, the ratio of vanadium to hydrogen electron atomic scattering factors (15) is the order of 11 for $\frac{\sin \theta}{\lambda} \approx 0.1$ as compared to about 25 in the X-ray case.

Atom models were constructed based on the ordering of hydrogen in tetrahedral sites for a composition V_2H in order to find an array of hydrogen atoms consistent with the extra half-order reflections. Tetrahedral sites are larger than octahedral sites for b.c.c. structures and Beshers (16) has shown that for small interstitials the tetrahedral sites are energetically more stable and this choice is supported by NMR studies on $VH_{0.5}$. (17)

An inherent difficulty related to the method of preparation of the microscope samples is the uncertainty in the final hydrogen concentration. Due to the small size of the electron microscope sample this concentration

could not be measured directly. For a sample in which only the β hydride is observed the composition limits of $VH_{0.45}$ to $VH_{0.9}$ can be inferred from the phase diagram in Fig. 1. Another means of determining the composition would be the c/a ratio in the β field. This ratio varies from 1.10 for composition $VH_{0.45}$ to 1.13 for $VH_{0.9}$. Our measurements give a value of 1.10 ± 0.01 , which at best places our specimens in the low hydrogen end of the β -field.

In one instance a sample was prepared from a single crystal initially containing no hydrogen. After thinning, this sample was found to contain $\alpha + \beta$. The diffraction pattern from the β phase in this case was the same as for the samples entirely in the β -field. In another instance a sample was prepared which was in the $\beta + \gamma$ field.[†] The diffraction pattern from the β phase in this case was again similar to the patterns from samples entirely in the β -field, with the important difference that the extra half-order reflections were substantially weaker. These facts suggest that the composition of our samples which were only in the β -field are near V_2H . These considerations tend to support our choice of the composition V_2H for the structural models.

[†] This sample was thinned without cooling the chemical solution.

Initially a cell with twice the b.c.t.[†] hydride dimensions (i.e. 2a by 2a by 2c) was chosen. Since there are no extra reflections in the (001) reciprocal lattice plane, the projection of the hydrogen atom positions onto the (001) plane must have the same relative arrangement as the projection of the vanadium atoms. This fixes the relative x,y coordinates of the hydrogen atoms. Similarly, the (100) reciprocal lattice plane shows no extra reflections thus determining the relative y,z coordinates. Both these observations are consistent with a translation vector between hydrogens of the form $\frac{1}{2} \frac{1}{2} \frac{1}{2}$. Using only tetrahedral sites, there is only one relative arrangement of the hydrogen atoms consistent with the observed reciprocal lattice. With this arrangement the assumed cell can now be reduced to a cell size 2a by a by 2c and is shown in Fig. 5a. The same result could have been obtained using only octahedral sites since these sites are also related by $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ translations. The twelve tetrahedral sites per b.c.c. cell are broken up by a tetragonal distortion into an equivalent set of eight larger and four smaller sites.⁽⁶⁾ The larger sites are at $\frac{1}{2} \frac{1}{4} 0$, $\frac{1}{2} \frac{3}{4} 0$, $\frac{1}{4} \frac{1}{2} 0$, $\frac{3}{4} \frac{1}{2} 0$, plus $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ translations. The smaller sites are at $0 \frac{1}{2} \frac{1}{4}$, $\frac{1}{2} 0 \frac{1}{4}$ plus $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ translations.

[†] Though the results of this paper show that β vanadium hydride is most probably monoclinic and not b.c.t., for clarity in the discussion the vanadium atom arrangement will be referred to as b.c.t.

Using the eight larger sites as the origin for the hydrogen array in Fig. 5a, it can be shown that only three distinguishable structures are produced (Figs. 5b-d). A smaller monoclinic unit cell (twice the primitive) is outlined in Figs. 5b-d and the A and B axes are labeled consistent with the indexing chosen for the reciprocal lattice in Fig. 4b. The model in Fig. 5b has a mirror plane and therefore belongs to the monoclinic space group Bm. The models in Figs. 5c,d are mirror images (enantiomorphs) of each other and possess a 2-fold axis, thus belonging to the monoclinic space group B2. Whereas the monoclinic Laue group has symmetry $2/m$, the above arrangements are not centrosymmetric and therefore have lower symmetry. Unfortunately without intensity measurements it is not possible to distinguish between the three structures since they all give the same extra reflections.[†] It is interesting to note that the structure suggested for Ta_2D by Somenkov et al⁽⁵⁾ to explain Wallace's neutron data is the structure in Fig. 5d. They arrived at this by an interesting argument based on their observed TaD structure. In TaD tetrahedral sites in both the a and b sublattices are occupied and the symmetry is orthorhombic.

[†] An attempt was made to determine the relative structure factors from the thickness fringes. The results were inconsistent with expected structure factors of H versus V. We feel that the origin of this discrepancy is related to n-beam dynamical effects.

For Ta_2D they argue that the deuterium atoms prefer to order with one atom in each sublattice seeking the pair of sites such that the two deuterium atoms are as far apart as possible. This is indeed the situation we arrive at in seeking consistency with the observed reciprocal lattice. In fact, all three structures in Figs, 5b,c,d have the same relative positions of the deuterium atoms.

It could be argued that the extra reflections are due to a periodic distortion of the vanadium atoms caused by the ordering of the hydrogens. This should produce in the X-ray patterns half-order reflections whose intensity relative to the matrix reflections would be approximately the same as for electron diffraction. This suggestion is contrary to experimental observations and the absence of the half-order spots in x-ray studies further supports the contention that the additional spots observed by electron diffraction are indeed due to hydrogen scattering.

The hot stage results indicate that the hydrogen atoms in the hydride structure disorder in the temperature interval 160 to 190°C. From the results thus far obtained it is not completely certain that at the precise temperature where the half-order spots disappear the matrix spots are in an exact b.c.c. array. We must conclude that the β hydride phase has a monoclinic structure and it is very likely that the tetragonal hydride structure does not exist, or if it does, only over a very small

temperature interval.

Since X-rays are insensitive to hydrogen scattering, X-ray measurements would only be sensitive to the metal atom arrangement. Therefore the lower symmetry monoclinic structure could be detected by the departure of the axial ratios and the angles between axes from that expected for the tetragonal system. This would be expected because the ordering of hydrogen on alternate (101) planes would in principle cause the a_1 and a_2 axes (see Fig. 5) to be unequal and the angle between c and the plane containing a_1 and a_2 to not be equal to 90° . From our measurements this splitting and the change in angle would be very small and not readily detected.

Neutron measurements, on the other hand, are sensitive to the hydrogen atom arrangement. However, since neutron diffraction experiments on this system deal with powders the lower symmetry monoclinic system would not be readily apparent if the departure of the axial ratios from tetragonality is small. The integrated intensity on the other hand, will be sensitive to the lower symmetry crystal structure and in fact this is the case as Somenkov et al.⁽⁶⁾ have shown for their Ta_2D structure based on Wallace's experimental data. Even in the case of single crystal neutron diffraction the lower symmetry structure would most probably be masked by many differently oriented domains of the monoclinic structure.

The distinct advantage of the electron microscope approach is that the use of the dark-field technique in conjunction with selected area diffraction allows the unambiguous determination of the reciprocal lattice of a single domain. This immediately identifies the symmetry as being lower than tetragonal as we have shown in this paper.

Conclusions:

Specimens of vanadium, thinned by a technique known to add hydrogen, showed evidence for ordering in β -vanadium hydride. It was concluded that the extra half-order reflections are due to scattering from hydrogen. The transformation between the ordered and disordered phases occurs reversibly at a specific temperature in the range 160 to 190°C depending on the specimen. The reciprocal lattice as determined by electron diffraction was shown to be in the monoclinic Laue group. Indirect evidence indicated that the composition of the ordered structure is close to V_2H . Assuming this composition and that the hydrogen atoms go into favored tetrahedral sites in the b.c.t. array of vanadium atoms, one relative arrangement of hydrogen atoms was shown to be consistent with the observed reciprocal lattice. When this arrangement, which involved alternate $(101)_{b.c.t.}$ planes of hydrogen atoms, was placed in the b.c.t. vanadium structure, the possible monoclinic space groups for the

ordered hydride were shown to be either B2 or Bm. From the point of view of the vanadium atoms alone, the structure is very nearly b.c.t. Thus any diffraction technique which is not sensitive to hydrogen atoms would lead to the erroneous conclusion that the structure of the β -phase was tetragonal. Our results indicate that the β hydride structure is most probably monoclinic.

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Figure Captions

Fig. 1 A partial phase diagram for the V-H system. The α -phase is an interstitial solid solution of hydrogen in b.c.c. vanadium, the β -hydride is a b.c.t. structure, and the γ -hydride is f.c.c. ● Maeland,⁽¹⁾ ▲ Reilly and Wiswall,⁽²⁾ ○ Zanowick and Wallace⁽³⁾.

Fig. 2 (a) An $(010)_{\text{b.c.t.}}$ electron diffraction pattern of β -vanadium hydride. The weaker spots are additional half order reflections. (b) A dark-field micrograph using the half order spot $\frac{1}{2}0\frac{1}{2}$ labeled A in Fig. 2a. (c) A similar micrograph using the half order spot labeled B in Fig. 2a. The micrographs are oriented correctly relative to the diffraction pattern.

Fig. 3 Some reciprocal lattice sections which are within 30° of the $(010)_{\text{b.c.t.}}$ starting orientation. Extra reflections are present in the (131) , (010) , and $(\bar{1}3\bar{1})$ planes. The various orientations were obtained by tilting about directions lying in the (010) section which is the center photograph in the composite.

Fig. 4 (a) shows the reciprocal lattice indexed with reference to the b.c.t. hydride structure and a convenient unit cell is outlined in (b).

● matrix reflections; ○ half order reflections

Fig. 5 (a) A relative arrangement of hydrogen atoms consistent with the observed reciprocal lattice.

(b-d) The three distinguishable structures which can be produced by using preferred tetrahedral sites. The corresponding space groups are Bm, B2 and B2 respectively. All structures in this figure are consistent with the reciprocal lattice shown in Fig. 4. The a_2 axis is normal to the plane of the diagram.

Fig. 1

a

b

c

Fig. 2

Fig. 3

(a)

(b)

(a)

(b)

- $V(z=0)$
- $V(z=1/2)$
- $H(z=0)$
- $H(z=1/2)$

(c)

(d)

- $V(z=0)$
- $V(z=1/2)$
- $H(z=1/4)$
- $H(z=3/4)$