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THE ORDERING OF HYDROGEN IN β -TANTALUM HYDRIDE[†]

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In a recent paper we presented the results of an investigation into the ordering of hydrogen in β -vanadium hydride⁽¹⁾. The symmetry of the reciprocal lattice as determined by electron diffraction placed the ordered structure in the monoclinic Laue group. Because of the similarity of the V-H and Ta-H systems⁽²⁾ we studied with the same technique the structure of the β -tantalum hydride phase. We show in this note that β -tantalum hydride with a composition estimated to be in the vicinity of Ta_2H , has an ordered structure quite similar to that of V_2H .

An electron microscopy study by Hull and Wynne⁽³⁾ 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 the ordering of hydrogen atoms.

From a powder neutron study Somenkov et al⁽⁴⁾ obtained an ordered structure for TaD based on a unit cell consistent with the orthorhombic space group P_{nnn} , with $a = b = \sqrt{2}a_0$, $c = a_0$, where a_0 is the lattice parameter of the disordered b.c.c. structure. The Ta atoms are in the $f(000, 0\frac{1}{2}\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0)$ positions and the D 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.

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Using Wallace's neutron results⁽⁵⁾ and the TaD unit cell, Somenkov et al proposed a structure for Ta₂D where the D atoms are in positions $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ and $(\frac{1}{4}\frac{3}{4}\frac{3}{4})$. This structure belongs to space group B2 and is one of the three structures suggested for V₂H by Wanagel et al. Further neutron studies by Petrunin et al⁽⁶⁾ on the β phase precipitated out in the α phase corroborated the suggested structure for Ta₂D.

250 μ m thick sections were spark cut from Ta single crystals and then charged with a few atomic percent hydrogen by a standard technique⁽⁷⁾. The specimens were chemically polished in a cooled solution (<10°C) of 2 parts HF and one part HNO₃. This type of treatment has been shown to considerably increase the hydrogen content of Ta⁽⁸⁾, as with V.

Using selected area diffraction in conjunction with dark field microscopy it was possible to obtain several reciprocal lattice sections from a single domain as shown in Fig. 1. The starting [010]_{b.c.t.} orientation is the central pattern*. Since the c/a ratio is nearly unity in β -tantalum hydride it was not possible to distinguish between the [100] and [001] reciprocal lattice sections as was done for β -vanadium hydride. Nevertheless it was possible to unambiguously determine the reciprocal lattice of a single domain using several different starting orientations such as [010], [100], [001], [101] and [10 $\bar{1}$]. The resulting reciprocal lattice symmetry is exactly the same as obtained for β -

* The symbol [010] represents the reciprocal lattice plane perpendicular to the [010] direction. For convenience the reciprocal lattice planes and directions are indexed in terms of the b.c.t. arrangement of Ta atoms.

vanadium hydride by Wanagel et al. The maximum point group symmetry is $2/m$ which places the hydride structure in the monoclinic Laue group.

The method of preparation of the microscope samples leads to uncertainty in the final H concentration. Some of the samples contained both the α and β phases and in these cases the diffraction pattern from the β phase was the same as from samples entirely in the β field. At room temperature the two phase region $\alpha+\beta$ exists over the range of H/Ta from 0.22 to 0.53⁽²⁾. Thus, this observation suggests that the ideal composition of the ordered structure can be taken as Ta_2H . If this is so, and noting that the reciprocal lattice is the same as for V_2H , then much of the discussion concerning V_2H also pertains to Ta_2H .

Using either tetrahedral or octahedral sites to construct models for Ta_2H , there is, as with V_2H , only one relative arrangement of H atoms consistent with the observed reciprocal lattice, and this is shown in Fig. 2. This arrangement can be placed in the voids in the body centered array of Ta atoms in several possible ways. Without intensity measurements on the full order reflections it is not possible to distinguish between the various possibilities. One such structure using tetrahedral sites for the D atoms (based on Wallace's neutron data on Ta_2D) has been suggested by Somenkov et al, and was discussed above. Since this structure is in agreement with the reciprocal lattice determined in this paper as well as with neutron intensity measurements it is reasonable to conclude that it is the most likely structure for both Ta_2D and Ta_2H .

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FIGURE CAPTIONS

Fig. 1: Some reciprocal lattice sections which are within 30° of the $[010]$ starting orientation. Extra half order reflections are present in the $[131]$, $[010]$ and $[\bar{1}3\bar{1}]$ planes. The $\frac{1}{2}0\frac{1}{2}$ reflection is indicated in the $[010]$ plane.

Fig. 2: The relative arrangement of hydrogen atoms consistent with the observed reciprocal lattice and a composition of Ta_2H . The dimensions in terms of the b.c.t. Ta unit cell are $2a \times a \times 2c$.

Figure 1.

○ $H (Z=0)$

□ $H (Z=1/2)$

Figure 2.