TUFTS UNIVERSITY

DEPARTMENT OF CHEMISTRY

PART I

Line broadening in the X-ray diffraction patterns of the vanadium hydrogen system.

A Thesis

by

John H. MacMillan

LINE BROADENING IN X-RAY DIFFRACTION PATTERNS OF THE VANADIUM-HYDROGEN SYSTEM

- Introduction -

When Hydrogen was taken up by body-centered cubic Vanadium metal, an anisotropic expansion to a body-centered tetragonal lattice has been reported. (1)

(1) Arnulf J. Maeland -J. Phys. Chem. 68 ,2197 ,(1964)

It is difficult to account for the observed expansion if hydrogen occupies only tetrahedral interstices and there is no convincing evidence that octahedral interstices are involved. (2)

(2) T.R.P.Gibb Jr. "Advances in Chemistry" 39, 99, (1963).

The problem could be resolved by neutron-diffraction but experimental observations by Hardcastle,(3)

(3) K. Hardcastle, unpublished results

and a study of the possibly comparable TaH_2 by Wallace (4)

(4) W.E.Wallace - J.Chem.Phys. 35, 6, 2156-2164 (1961)

have not let to useful results, partly because of the complexity of the diffraction patterns and partly because of

the assumption that octahedral sites are not occupied.

Objectives

It was desired to investigate the breadths of the tetragonally distorted cubic phase X-ray diffraction lines of various vanadium hydrides and to compare these with the corresponding lines of the pure metal. Then one could ascertain whether certain lines corresponding to certain planes in the crystal, were broadened more than others, and it was also hoped that from these observations some idea of the positions of the hydrogen in the tetragonally distorted body centered cubic lattice could be obtained. Also it was hoped initially that accurate quantitative measurements of the line broadening could be carried out.

A.J. Maeland (1) investigated the change in lattice parameters with hydrogen content in nonstoichiometric hydrides of vanadium via X-ray diffraction using the powder method with a Straumanis 3 mm cylindrical camera. His collection of films from his study were left with Dr. T.R.P. Gibb of Tufts University and these films were used in my observations. Maeland observed that between stoichiometries $VH_{.05}$ and $VH_{.46}$ a b.c.c. cubic phase and a b.c.t. phase exist together and that at room temperature the cubic phase disappears at $VH_{.46}$. At higher temperatures the cubic phase appears at stoichiometries up to $\sim VH_{.9}$. Accordingly, on some films the breadths of body centered

cubic diffraction planes were measured and compared with the breadths of the pure metal, while on some high H content films at room temperature b.c.t. planes are compared to corresponding planes in the body centered cubic pure vanadium lattice.

Experimental Methods

Initially a photometer available in the laboratory was used to record the widths of the lines, but it was found that the machine gave variable results for the same line on different days and took much time to measure one film. Therefore this procedure was abandoned and recourse was made to visually measuring the breadths of the seven cubic phase lines for many different films. To accomplish this, a box with a white glass illuminated field was employed with a movable steel support for the film and a rider on the support with magnifying glass and measuring device.

Since it was necessary to measure the line breadths visually only an approximate value for the breadths was obtained. There can be errors of measurement and with some faint lines it is extremely difficult for the eye to judge where the line ends and the field begins. However, the majority of lines were measured to $\pm$ .01 mm. Over the average of a large number of films, however, any trends should become apparent.

Sources of Line Broadening

Line broadening can be caused by either extremely

small particle size or stress or disorder in the metal. (5)

- - - - - - - - - - - - -

(5) N. F. Mott and H.Jones "The Theory of the Properties of Metals and Alloys" Clarendon Press, Oxford 1936.

- - - - - - - - - - - - -

Since particle size causes broadening only for particle diameters below 1000 A° and the particles in the V metal used are coarse according to Maeland's article (1), line broadening in these films should then be due to stress and disorder in the metal. Any mechanical stress in the metal should be annealed out upon heating to form the hydride, therefore any broadening observed in the hydrides diffraction lines must be due to stress and disorder caused by hydrogen atoms slightly distorting the lattice. A plane in the crystal greatly distorted by hydrogen atoms should be substantially broadened.

Experimental Results

The results of the measurements are tabulated in the figures. Each cubic phase line is numbered and the Miller indices of the plane it represents are given. It is seen that lines 3, 2 and 1 often were obscured due to scattered radiation darkening the front reflection region of the films. Therefore results from these lines are less reliable. It is seen that that there is no general trend of increased broadening with increasing hydrogen content but that broadening does occur in most lines with respect to vanadium metal lines.

Also temperature differences have little effect on the breadth of the lines. Rough percentage broadenings of the lines relative to vanadium are given on the third data page.

From these data the most noticeable trend is that line 5, the 211 plane, is substantially more broadened than all the others. Lines four and one are less broadened than the others but these results are less certain due to many obscured lines. The single most consistent feature of the data is the greater broadening of the line corresponding to the 211 plane.

BREADTHS FOR VANADIUM HYDRIDES DIFFRACTION LINES COMPARED TO PURE VANADIUM. BREADTHS IN MM.

Films from A. Maeland
O = line obscured
F = Faint. V.F. = Very Faint.

Diffraction Plane:

Compound	T° C	7 110	6 200	5 211	4 220	3 310	2 222	1 321
V powder	Room	.04	.04	.06	.06	.09	.08 F	est. .16
"	158	.04	.04	.05	.07	.07	0	.17
"	305	.04	.04	.05	.07	.07	0	.17
V-H.15	81°	.04	.06	.08	.08	~.13	0	~ .23
"	135°	.04	.04	.07	.07 F	.08	0	.17
"	308	.04	.04	.06	0	.07	.05 F	.18
V-H.26	Room	.05	.05	.09	.07 F	~.12	0	~.2
"	"	.07	.06	.09	~.08 F	~.12	0	0
"	200° C	~.1	~.1	~.15	~.15 F	0	0	0
V-H.30	169°	.06	.07	.07	.06	~.1	0	~.2
"	311°	.04	.06	.06	.07	.08	0	.17
V-H.37	Room	.04	.04	.08	0	0	0	0
"	163°	.04	.04	.07	0 ~	.12	0	F but > V line
"	320°	.04	.04	.06	.06? best	.07	0	.17
V-H.43	Room	.05	.05	.08	0	~.1 F	0	~.22 F
"	144°	.06	.05	.07	0	0	0	> V line
"	300°	.05	.05 F	.06	.06 F	.08 F	0	.17
V-H.59	Room	.05	.05	.06	0	0	0	0
"	164°	.05	~.09 VF	~.1	0	F but > V	0	0
"	311°	.04	.04	.06	.07 ~	.09	.06 F	.17
V-H.69	152°	.06	.05 F	.07	0	> V	0	> "
"	300°	.06	.07 F	.08	.07F	~.1 F	0	~.18
V-H.76	Room	.05	~.07	~.1	0	0	0	0
"	167°	.05	~.1	~.12	0	> V	0	0

(Cont'd) -2-

BREADTHS FOR VANADIUM HYDRIDES DIFFRACTION LINES COMPARED TO PURE VANADIUM. BREADTHS IN MM.

Films from A.Maeland
0 = line obscured
F = Faint. V.F.= Very Faint.

Compound	T°C	Diffraction Plane: 7 110	6 200	5 211	4 220	3 310	2 222	1 321
V-H.76	270°	.06	.06	.08	0	0	0	0
V-H.80	Room	.05	.05	.09	~.1 F	.09	.12 VF	0
"	"	.05	.06	.08	.08	~.1	0	0
"	200°	.08	.06	.07	0	0	0	0
"	158°	.05	.06	.07	.07	~.1 F	0	0

ROUGH PERCENTAGE BROADENING IN VANADIUM HYDRIDE CRYSTAL PLANES DIFFRACTION LINES COMPARED TO PURE VANADIUM AT COMPARABLE TEMPERATURES.

The 222 plane is omitted since lines from it are nearly always obscured.

Compound	T°C	Diffraction Plane: 7 110	6 200	5 211	4 220	3 310	1 321
V-H.15	81°	0%	50%	60%	15%	65%	44%
"	135°	0%	0%	40%	0%	14%	0%
"	308°	0%	0%	20%	—	0%	6%
V H.26	Room	25%	25%	80%	0%	73%	25%
"	"	75%	50%	80%	11%	53%	—
"	200°	150%	175%	200%	110%	—	—
V H.30	169°	50%	75%	16%	0%	57%	25%
"	311°	0%	50%	20%	0%	14%	0%
V H.57	Room	0%	0%	60%	—	—	—
"	163°	0%	0%	40%	—	70%	10%
"	320°	0%	0%	20%	0%	0%	0%
V H.43	Room	25%	25%	60%	—	43%	40%
"	144°	50%	25%	40%	—	—	10%
"	300°	25%	25%	20%	0%	11%	0%
V H.59	Room	25%	25%	20%	—	—	—
"	164°	25%	—	100%	—	25%	—
"	311°	0%	0%	20%	0%	28%	0%
V.H.69	152°	50%	25%	40 %	—	25%	10%
"	300°	50%	75%	60%	0%	43%	5%
V-H.76	Room	25%	75%	100%	—	—	0
"	167°	25%	150%	240%	—	25%	—
"	270°	50%	50%	60%	—	—	—
V-H.80	Room	25%	25%	80%	43%	30%	—
"	Room	25%	50%	60%	14 %	10%	—
"	200°	100%	50%	40%	—	—	—
"	158°	25%	50%	40%	0%	10%	—
Average		32%	43%	60%	14%	30%	12.5%

Conclusions

The greater broadening of the 211 plane relative to the others leads us to speculate about the positions of the hydrogen atoms in the lattice. In a body centered cubic lattice the hydrogen atoms can occupy either octahedral or tetrahedral sites. In a b.c.c. unit cell there are 24 tetrahedral and 18 octahedral sites. (6) (See diagram one).

- - - - - - - - - - - - - - -

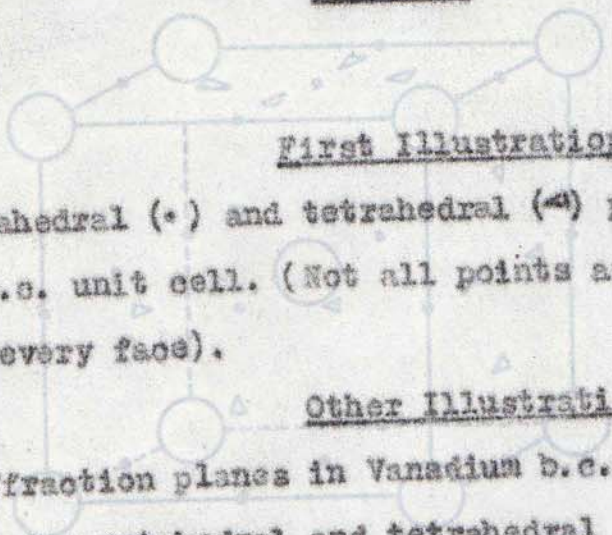
(6) T.R.P. Gibb Jr.-J.Phys.Chem. 68, 1096,(1964).

- - - - - - - - - - - - - - -

A great broadening would seem to indicate that hydrogens are in certain octahedral or tetrahedral sites. Let us now tabulate the octahedral and tetrahedral points for the various planes in one unit cell. (See diagrams).

Plane	No. Octahedral	No. Tetrahedral
211	11	0
110	4	0
222	3	0
321	1	0
310	1	0
200	8	8
220	6	4

FIGURE I

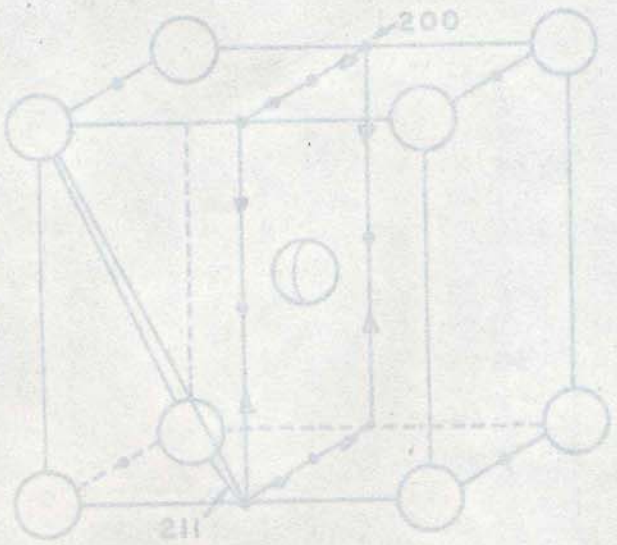


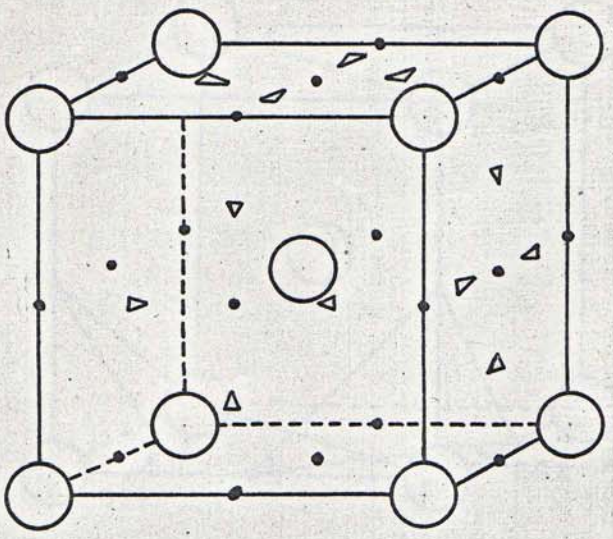
First Illustration:

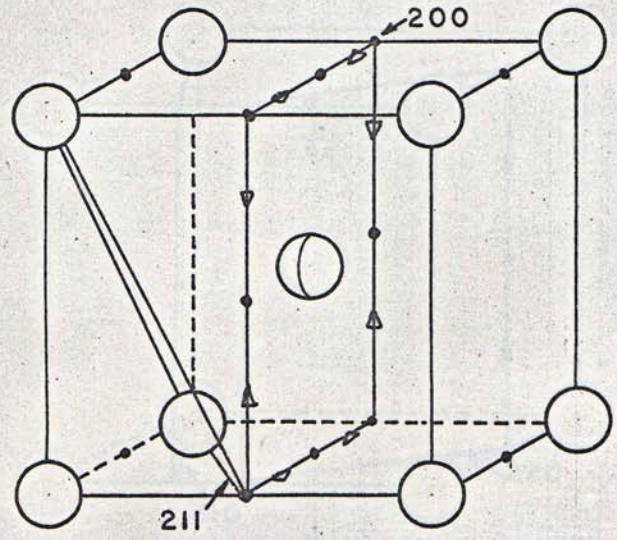
Octahedral (•) and tetrahedral (△) points in b.c.c. unit cell. (Not all points are shown on every face).

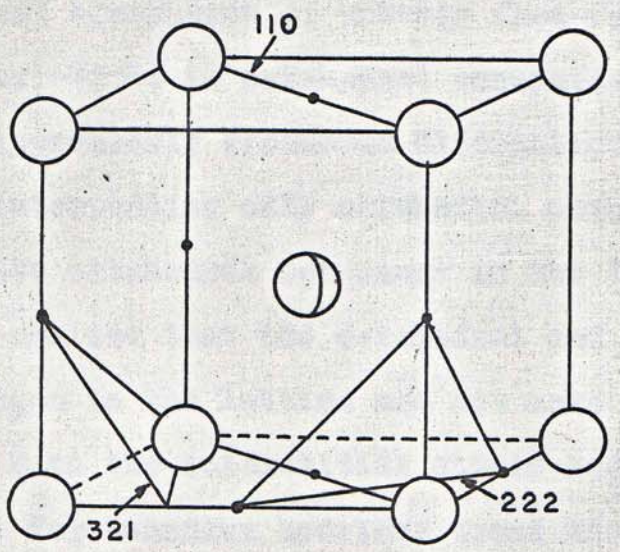
Other Illustrations:

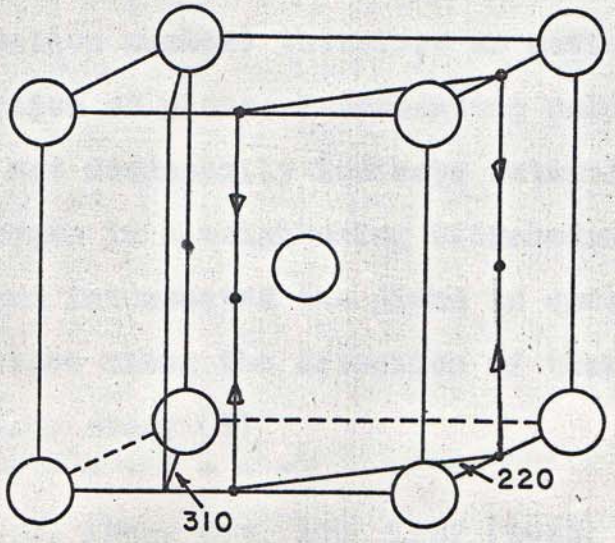
Diffraction planes in Vanadium b.c.c. lattice showing octahedral and tetrahedral intersections.






200
211


110
321
222


310
220

With just the percentage broadening information one cannot unequivocally distinguish between octahedral and tetrahedral occupation or between face-face or edge-edge site restrictions in octahedral occupation. The fact that so many appreciably broadened diffraction lines are from planes intersecting only octahedral points at first seems to indicate octahedral occupancy in the lattice. We must, however, realize that the octahedral and tetrahedral sites for hydrogen in the lattice are not mere mathematical points. Both the interstitial atomic and the hydridic model (3) for vanadium hydrides treat the hydrogen in the lattice as a small share of electron density. For the interstitial model the radius of the hydrogen sphere is .55 A° for 4 coordination and .60 A° for 6 coordination. In the hydridic model the H^- has a radius of 1.32 A°(which increases with coordination number) therefore no matter which model is used, distortion of planes intersecting only octahedral points does not necessarily indicate octahedral occupation since a hydrogen in a neighboring tetrahedral site whose electron cloud intersected the plane in question could distort the lattice along the direction of that plane.
Roberts' N.M.R. study (7)

- - - - - - - - - - - - - - -

(7) Roberts, B. Phys. Rev. 100 1257 (1955)

- - - - - - - - - - - - - - -

of the V $D_{.7}$ system indicates that the deuteriums are $a_o \frac{\sqrt{2}}{2}$ apart. This fact would support octahedral occupation if the hydrogen sites were mere geometric points, since no combination of octahedral and tetrahedral sites in a b.c.c. lattice is separated by that geometry. However with the hydrogen possessing a finite atomic radius, this simple argument breaks down. Such considerations make any meaningful correlation between the rough average broadening of the diffraction lines and octahedral or tetrahedral occupancy seem dubious. For example, the broadened 211 line could result from distortion of the plane by hydrogen occupying the octahedral site in that plane or by hydrogen from a neighboring tetrahedral site distorting the plane by overlap, since the hydrogen has a finite size.

Naively, we might expect the greatest percentage lattice deformation and greatest line broadening in the planes with the densest packing and smallest area in the unit cell. In the planes of greater area one could predict that the stress deformation of the V lattice along the plane would be less than for those of smaller area since the stress from the hydrogen would tend to fall off at greater distances from the hydrogen. Such a conclusion would be valid, however, only if the same number of hydrogens were acting to distort each plane, and only if interaction with electron clouds from neighboring sites were the same. Clearly this cannot

be assumed since some of the larger planes can accommodate two hydrogens on opposite faces or edges even when considering bulky H^- ions. That this effect is not applicable is also seen with the densely packed and small area 211, 310 and 321 planes all of which intersect only 1 octahedral point and no tetrahedral points. The 211 plane is evidently distorted more than the other two. It seems futile to speculate at present as to the cause for this since we know neither the configuration of hydrogen in the lattice nor the degree to which electron density from hydrogens adjacent to the planes may affect the distortion.