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X-ray Structure Determination of Divanadium Hydride, β_1-V_2H, and Divanadium Deuteride, β-V_2D

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Abstract. β_1-V_2H: $M_r = 102\cdot89$, tetragonal, $I4_1/amd$, $a = 6\cdot0349\,(4)$, $c = 6\cdot8716\,(3)$ Å, $V = 250\cdot3$ Å^3, $D_x = 5\cdot46$ Mg m^{-3}, $Z = 8$, $\lambda(\text{Mo }K\alpha) = 0\cdot7107$ Å, $\mu = 13\cdot65$ mm^{-1}, $F(000) = 376\cdot0$, room temperature, final $R = 0\cdot031$ for 154 independent reflections; β-V_2D: $M_r = 103\cdot9$, monoclinic, Cm, $a = 4\cdot4554\,(7)$, $b = 3\cdot0090\,(3)$, $c = 4\cdot4719\,(7)$ Å, $\beta = 95\cdot30\,(1)°$, $V = 59\cdot70\,(1)$ Å^3, $D_x = 5\cdot78$ Mg m^{-3}, $Z = 2$, $\lambda(\text{Mo }K\alpha) = 0\cdot7107$ Å, $\mu = 14\cdot31$ mm^{-1}, $F(000) = 94\cdot0$, room temperature, final $R = 0\cdot024$ got 598 independent reflections. The crystal structures of β_1-V_2H and β-V_2D have been studied using a four-circle diffractometer with Mo $K\alpha$ radiation, and refined by the full-matrix least-squares method. The specimens examined were grown under tensile stresses. The positional and thermal parameters of V atoms in β_1-V_2H and β-V_2D are found to be hydrogen-isotope dependent and reflect directly the respective ordered arrangements of the H and D atoms which are located in the different types of octahedral interstices of the metal lattices.

Introduction. The vanadium–hydrogen(deuterium) system has been the subject of extensive studies because of its significant isotope effects on equilibrium phase diagrams (Asano & Hirabayashi, 1973, 1977; Schober & Wenzel, 1978; Moss, 1983), diffusion constant (Völkl & Alefeld, 1978; Bowman, Attalla & Craft, 1983) and crystal structures (Somenkov & Shil'shtein, 1980; Asano & Hirabayashi, 1979, 1981).

The atomic arrangements of hydrogen in β_1-V_2H and of deuterium in β-V_2D have been studied by several workers by X-ray, neutron and electron diffraction. The structural models proposed so far for these two compounds are summarized in Table 1. In all the models, the H(D) atoms occupy orderly specific octahedral interstices in the fundamental body-centered lattice of the V atoms. The metal lattice proposed is either monoclinic or tetragonal with the axial ratio $c_0/a_0 \simeq 1\cdot1$. For the monoclinic model, the space groups $C2$, Cm and $C2/m$ are assumed for the hydride, and Cm is chosen for the deuteride. The tetragonal model of space group $I4_1/amd$ is presented alternatively for the deuteride. The monoclinic and tetragonal models are illustrated in Fig. 1: in the monoclinic model (*a*), the rows of the H(D) atoms in the base-centered positions of the metal lattice are parallel to those in the edge-centered positions, while they are normal to each other in the tetragonal model (*b*). On the other hand, some fraction of H(D) atoms in β_1-V_2H (Wanagel, Sass & Batterman, 1972) and in β-V_2D (Westlake, Mueller & Knott, 1973) were suggested to occupy tetrahedral sites surrounding the H(D) atom at an octahedral site.

A recent study by single-crystal neutron diffraction (Kajitani & Hirabayashi, 1985) indicates that the crystal structure of β_1-V_2H differs from that of β-V_2D in the arrangement of H(D) atoms, and corresponds to the model of $I4_1/amd$. In the neutron diffraction study, however, vanadium atoms cannot be seen since its

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coherent scattering cross section for thermal neutrons is small as compared with H and D atoms.

The present study is aimed to refine the host V structure of β_1-V_2H and β-V_2D by X-ray diffraction. Because of the small atomic scattering factor of hydrogen (deuterium), it cannot be easily detected by X-ray or electron diffraction (Wanagel, Sass & Batterman, 1972). However, the diffraction intensities are affected by the V-atom displacements induced by the ordering of H(D) atoms (Metzger, Jo, Moss & Westlake, 1978; Metzger, Jo & Moss, 1979; Jo, Moss & Westlake, 1980; Moss, 1983). Since the static displacement reflects directly the interaction between V and H(D) atoms, its evaluation is important for elucidating the stability of metal hydrides (deuterides).

Experimental. (1) *Specimen preparation and X-ray intensity measurement.* Single crystals of β_1-V_2H and β-V_2D were prepared by the reaction of vanadium single crystals with hydrogen or deuterium gas using a Sieverts-type apparatus. The vanadium single crystals, 8 mm in diameter and 40 mm in length, were initially grown by electron-beam zone melting and then machined to have a narrow neck, 1 mm in diameter, at one end of the specimen. Under deformation at the neck by application of tensile stress, the hydrogen (deuterium) gas was charged up to $0{\cdot}5 \times 10^5$ Pa in the temperature range below 820 K. The α-phase single crystals thus obtained were cooled under stress to room temperature for two weeks. Because of the large pseudo-tetragonality of β_1-V_2H and β-V_2D, single crystals grew at the neck part of the sample. Except that the deformation was elastic in the case of β_1-V_2H but plastic in case of β-V_2D, growth conditions were the same for both crystals. The single crystals of β_1-V_2H and β-V_2D were cut with a wheel and ground into spheres 0·173 (8) and 0·186 (8) mm in diameter under a stereomicroscope with a piece of #1000 emery paper.

Table 1. *Crystal structures proposed for β_1-V_2H and β-V_2D*

Crystal system	Space group	References
β_1-V_2H		
Monoclinic*	*Cm*	Asano, Abe & Hirabayashi (1976); Moss (1983)
	*C*2, *Cm*, *C*2/*m*	Wanagel, Sass & Batterman (1972)
Tetragonal†	*I*4$_1$/*amd*	Kajitani & Hirabayashi (1985)
β-V_2D		
Monoclinic*	*Cm*	Somenkov, Éntin, Chervyakov, Shil'shtein & Chertkov (1972); Westlake, Mueller & Knott (1973); Asano, Abe & Hirabayashi (1976); Moss (1983)
Tetragonal†	*I*4$_1$/*amd*	Asano & Hirabayashi (1973)

* The unit-cell dimensions of the monoclinic system are $a \simeq c \simeq (a_0^2+c_0^2)^{1/2}$, $b \simeq a_0$ and $\beta \simeq 95°$, where a_0 and c_0 are the dimensions of the fundamental body-centered cell.

† The unit-cell dimensions of the tetragonal system are $a \simeq 2a_0$ and $c \simeq 2c_0$.

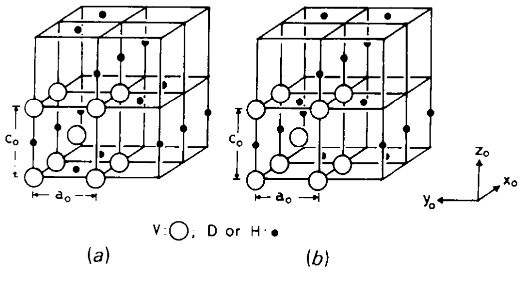


Fig. 1. Structures of β_1-V_2H or β-V_2D. Vanadium atoms are drawn only for one fundamental body-centered cell of the metal lattice. (*a*) Monoclinic model. (*b*) Tetragonal model.

Table 2. *Experimental conditions for X-ray measurement*

	β_1-V_2H	β-V_2D
Temperature (K)	295	297
μr(Mo $K\alpha$)	1·27	1·24
Monochromator	Graphite ($2\theta_M = 12{\cdot}285°$)	
Collimator	0·5 mm diameter	
Slit	No slit	5·5 mm diameter
Scan mode	ω scan ($2\theta \le 100°$)	
	θ–2θ scan($60° \le 2\theta \le 150°$)	θ–2θ scan($50° \le 2\theta \le 150°$)
Scan width	7°(ω scan)	2·5°
	$(3 + \tan\theta)°$(θ–2θ scan)	$(2{\cdot}2 + 0{\cdot}5 \tan\theta)°$
Scan rate	2° min^{-1} in θ	
$2\theta_{\max}$[$(\sin\theta/\lambda)_{\max}$]	150°[1·359 Å^{-1}]	

Integrated intensities were measured at room temperature using an automated four-circle diffractometer (Rigaku AFC-3) and Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The peak half-width for the 202 reflection of β_1-V_2H was 0·40° in θ, indicating that the quality of the sample used was fairly good. Any variants which might be introduced during the transformation from the α (b.c.c.) to the β_1-V_2H or β-V_2D phase in the cooling process of crystal growth were not observed in the 2θ range up to 150°. The peaks trailed on both sides of the ω-scan axis owing to a strain which was possibly caused either in the phase transformation from α to $\beta_1(\beta)$ or in the preparation process of the spherical samples. The integrated intensity obtained by the ω-scan mode was greater than that obtained by the θ–2θ-scan mode for low-angle reflections owing to the trails. Hence, the ω-scan technique was used for the low-angle reflections. For the high-angle reflections, the θ–2θ-scan mode was adopted, since the peak splitting by the $K\alpha_1$ and $K\alpha_2$ components could not be covered by the ω-scan technique. In the intermediate region ($40° \le 2\theta \le 100°$) the reflections were measured by both scan techniques and the data of higher integrated intensity were adopted for the analysis. The experimental conditions are listed in Table 2.

In all, 1106 non-zero intensities (154 independent) were obtained for β_1-V_2H and 1647 (598) for β-V_2D. In the latter, the reflections with $2\theta < 80°$ in one hemisphere of reciprocal space were measured in addition to those with $2\theta < 150°$ in the other. The intensities of these reflections were modulated by the static displacements of the V atom caused by the ordering of the H(D) atoms.

The unit-cell dimensions listed in the *Abstract* were determined by least-squares calculation using 26 reflections in the 2θ range from 70 to 75° with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}70926$ Å).

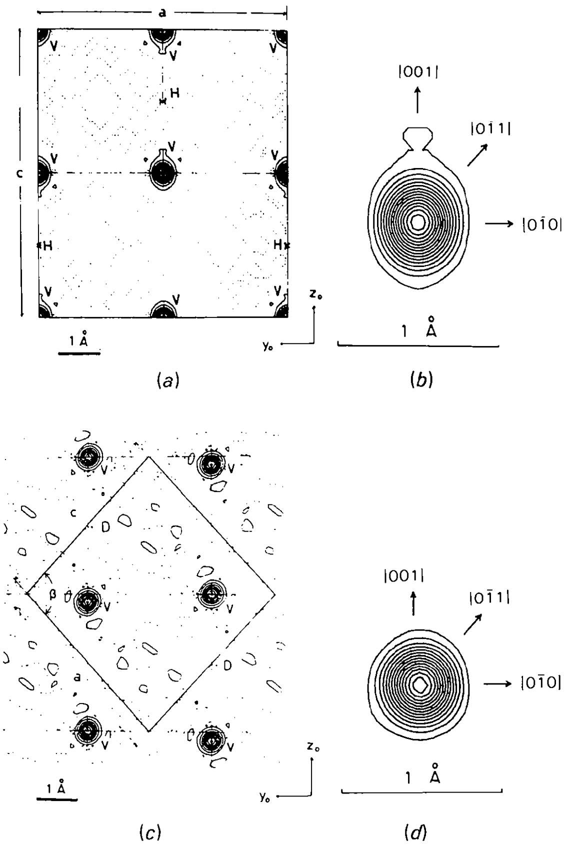
(2) *Structure determination.* Corrections for the diffraction intensity were made for Lorentz, polarization and absorption effects. The absorption correction was performed by the Lagrange interpolation method for spherical crystals with the transmission factors taken from *International Tables for X-ray Crystallography* (1959). The absorption-correction factors for $|F_o|$'s were in the range 0·41 to 0·52.

The space group $I4_1/amd$ instead of Cm was adopted for β_1-V_2H, and Cm, $C2$ and $C2/m$ were assumed for β-V_2D in further structure refinements. Parameters were refined by the full-matrix least-squares program *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979) using all the observed reflections. The function minimized was $\sum w\Delta F^2$, where $w = [\sigma(\text{counting statistics})^2 + (0{\cdot}015\,|F_o|)^2]^{-1}$. In addition to the scaling factor, the parameters refined were the positional and anisotropic thermal parameters of the V atom, and the type I anisotropic secondary-extinction parameters (Coppens & Hamilton, 1970). The parameters of the H(D) atom were fixed at the values obtained from the neutron diffraction study using the same crystal (Kajitani & Hirabayashi, 1985), since the R value was not improved by changing these parameters. The smallest extinction factor $y(=F_o^2/F_c^2)$ was 0·82 for β_1-V_2H and 0·65 for β-V_2D. The scattering factors of neutral V and H(D) atoms were taken from *International Tables for X-ray Crystallography* (1974), taking into account the anomalous-scattering factors. $(\Delta/\sigma)_{\max} = 0{\cdot}13$ and 0·05 for β_1-V_2H and β-V_2D, respectively.

Discussion. Fig. 2 shows Fourier maps of the β_1-V_2H and β-V_2D structures in the plane $x_0 = 0$ of the fundamental body-centered lattice. The static displacement of the V atom in β_1-V_2H is too small to be detected in Fig. 2(*a*), while a charge asphericity elongated in the [001] direction of Fig. 2(*b*) indicated the anisotropy of its thermal motion. The V atoms in β-V_2D shown in Fig. 2(*c*) are displaced alternately up and down along the [001] and $[00\bar{1}]$ directions of the fundamental cell. Their static displacement is due to the alternate distribution of the D atoms between the V atoms. The charge distribution of the V atom in this case is almost spherical, as shown in Fig. 2(*a*). A difference-Fourier synthesis was unsuccessful for detecting the H(D) atoms and the anisotropy of the electronic charge distribution around the V-atom nucleus, because of the limited reliability of the available experimental data.

The refinement of the β_1-V_2H structure with space group $I4_1/amd$ converged to $R = 0{\cdot}024$ for all reflections. On the basis of the centrosymmetric second setting (*International Tables for X-ray Crystallography*, 1969) for the proposed atomic arrangement (Asano & Hirabayashi, 1973), the refinement functions and the final atomic parameters are listed in Table 3. The listed positional parameters of the V atom in 16(*h*) (0,*x*,*z*) deviate from those for the ideal body-centered lattice ($x = \frac{1}{2}$, $z = \frac{1}{4}$). The displacement is estimated to be 0·0225 (18) Å, in almost the $[0\bar{1}\bar{1}]$ direction. This supports the ordered arrangement of H atoms in β_1-V_2H proposed by neutron diffraction results (Kajitani & Hirabayashi, 1985); the V atom tends to shift away from its neighboring H atoms. Note the anisotropic thermal parameters of the V atom; the value of U_{33} in the [001] direction is more than double that of U_{11} in the [100] direction.

In the case of β-V_2D, the refinement functions for each space group Cm, $C2$ and $C2/m$ converged satisfactorily to nearly identical values, as listed in Table 4. The final atomic parameters are given in Table 5, where a V atom in $C2$ or $C2/m$ is classified as V(1)



(*a*) (*b*)

(*c*) (*d*)

Fig. 2. (*a*) Fourier map and (*b*) charge distribution of V atom in β_1-V_2H in the plane $x_0 = 0$ of the fundamental body-centered lattice; (*c*) and (*d*) correspondingly in β-V_2D. Contours in (*a*) and (*c*) are drawn at 10 and 40 e Å^{-3} followed by every 40 e Å^{-3}, and in (*b*) and (*d*) at 10 e Å^{-3} followed by every 20 e Å^{-3}; dotted lines indicate zero level.

and V(2). The origin of the *x* and *z* coordinates in *Cm* is chosen arbitrarily to put V(2) at $(\frac{3}{4}, 0, \frac{3}{4})$, and the origin of the *y* coordinate in *C*2 is chosen to be the V-atom position. Among the three space groups, the final *wR* value for *Cm* is the smallest (0·0491) but is very close to the other two values (0·0494, 0·0500). Hence Hamilton's significance tests (*International Tables for X-ray Crystallography,* 1974) were performed to decide whether the extra parameters introduced in the refinement for *Cm* yield any significant reduction of *wR*. The refinement for *C*2/*m* corresponds to an unrestricted case of *Cm* with dimension (*b*) of 4 (= 17–13) and freedom (*n–p*) of 1630 (= 1647–17). The *wR*-factor ratio of *Cm* to *C*2/*m* is $\mathscr{R}_{4,1630} = 1{\cdot}0183$ (= 0·0500/ 0·0491), which is larger than 1·0046 of $\mathscr{R}_{b,n\text{-}p,\alpha} = \mathscr{R}_{4,1630,0.005}$. A comparison of *Cm* with *C*2 results in $\mathscr{R}_{2,1630} = 1{\cdot}0061$, which is larger than $\mathscr{R}_{2,1630,0.005} = 1{\cdot}0032$. The space groups *C*2/*m* and *C*2 are, therefore, rejected at the significance level $\alpha = 0{\cdot}005$. As seen in Table 5, the displacement of the V(1) atom in *Cm* seems to be twice as large as that in the cases of *C*2 and *C*2/*m*, but this is because the V(2) atom is fixed at $(\frac{3}{4}, 0, \frac{3}{4})$ of an ideal body-centered lattice site. The average displacement is estimated to be 0·1037 (1) Å in the $[10\bar{1}]$ direction, that is the $[00\bar{1}]$ direction of the fundamental body-centered cell. The result reflects the ordered arrangement of D atoms in every second layer of $(\bar{1}01)$ planes of the fundamental cell (Okada, Asano & Hirabayashi, 1980; Asano & Hirabayashi, 1981).

The thermal parameters of the V atoms in β-V_2D are almost isotropic.* The difference between the thermal parameters of the split V atom, V(1) and V(2), is attributed to the difference in the distribution of D atoms at neighboring tetrahedral sites (Kajitani & Hirabayashi, 1985).

The present study proposes two different crystal structures for β_1-V_2H and β-V_2D. For comparison between their host V lattice, Fig. 3 shows the reduced fundamental cells and Table 6 gives their crystal data. The atomic parameters listed for β-V_2D are averaged for the two V atoms. There are slight but clear differences between the two structures. The c_0/a_0 ratio of β_1-V_2H is larger than 1·1 but that of β-V_2D is smaller than 1·1, and a slight inclination (*ca* 12′) of the c_0 axis appears in β-V_2D. The V-atom displacement is remarkable in β-V_2D in the $[00\bar{1}]$ direction of the fundamental body-centered lattice, which is in contrast to that in β_1-V_2H which is small and in the $[0\bar{1}\bar{1}]$ direction. This is consistent with the fact that the shortest V—V interatomic distance in β_1-V_2H is larger than that in β-V_2D, while the V–D distance in β-V_2D is larger than the V–H distance in β_1-V_2H.

Table 3. *Refinement functions and final atomic parameters for* β_1-V_2H (*I*4₁/*amd*)

Observed reflections (*n*)	1106
Parameters (*p*)	13
R(*F*)	0·024
wR(*F*)	0·039
$S(=\lvert\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n-p)\rvert^{1/2})$	2·33
Internal consistency between equivalent reflections	0·013
Independent reflections	154
R(*F*)	0·031
wR(*F*)	0·032

Positional parameters

V at 16(*h*): (0, *x*, *z*); *x* = 0·4979 (2), *z* = 0·2473 (2)

H at 8(*c*): (0, 0, 0)

Thermal parameters (Å²)*

V	U_{11}	0·0041 (3)	H	U_{11}	0·059
	U_{22}	0·0072 (4)		U_{22}	0·060
	U_{33}	0·0109 (1)		U_{33}	0·029
	U_{23}	0·0025 (3)		U_{23}	—
	$U_{12} = U_{13} = 0{\cdot}0$			$U_{12} = U_{13} = 0{\cdot}0$	

* Parameters for H are taken from the neutron diffraction study (Kajitani & Hirabayashi, 1985).

Table 4. *Refinement functions for three possible space groups for* β-V_2D

	Cm	*C*2	*C*2/*m*
For observed reflections (*n* = 1647)			
Parameters (*p*)	17	15	13
R(*F*)	0·0232	0·0230	0·0234
wR(*F*)	0·0491	0·0494	0·0500
S	2·87	2·89	2·93
Internal consistency = 0·008			
For 598 independent reflections			
R(*F*)	0·0238	0·0236	0·0239
wR(*F*)	0·0468	0·0471	0·0476

Table 5. *Atomic parameters for the three possible space groups for* β-V_2D

Parameters for D are taken from the neutron diffraction study (Kajitani & Hirabayshi, 1985).

Cm		*C*2		*C*2/*m*	
V(1) at 2(*a*): (*x*,0,*z*)		V at 4(*c*): (*x*,*y*,*z*)		V at 4(*i*): (*x*,0,*z*)	
V(2) at 2(*a*): (*x*,0,*z*)					
D at 2(*a*): (*x*,0,*z*)		D at 2(*b*): (0,*y*,½)		D at 2(*c*): (0,0,½)	
(*a*) Positional parameters					
V(1)	*x* 0·28057 (6)	V	*x* 0·26526 (3)	V	*x* 0·26528 (3)
	z 0·21775 (7)		*y* 0·0		*z* 0·23390 (3)
V(2)	*x* 0·75		*z* 0·23390 (3)		
	z 0·75				
D	*x* 0·0	D	*y* 0·0		
	z 0·5				
(*b*) Thermal parameters (Å²)					
V(1)	U_{11} 0·00516 (11)	V	U_{11} 0·00593 (5)	V	U_{11} 0·00590 (5)
	U_{22} 0·00515 (8)		U_{22} 0·00565 (5)		U_{22} 0·00561 (5)
	U_{33} 0·00556 (19)		U_{33} 0·00586 (6)		U_{33} 0·00586 (6)
	U_{13} 0·00029 (9)		U_{12} 0·00063 (12)		U_{13} 0·00046 (3)
V(2)	U_{11} 0·00682 (16)		U_{13} 0·00048 (3)		$U_{12}=U_{23}=0$
	U_{22} 0·00618 (1)		U_{23} 0·00045 (14)		
	U_{33} 0·00617 (23)				
	U_{13} 0·00071 (11)				
	$U_{12}=U_{23}=0{\cdot}0$				
D	U_{11} 0·022	D	U_{11} 0·030	D	U_{11} 0·030
	U_{22} 0·035		U_{22} 0·015		U_{22} 0·017
	U_{33} 0·015		U_{33} 0·018		U_{33} 0·017
	U_{13} 0·020		U_{13} 0·017		U_{13} 0·016
	$U_{12}=U_{23}=0$		$U_{12}=U_{23}=0$		$U_{12}=U_{23}=0$

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* Lists of structure factors for β_1-V_2H and β-V_2D have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42168 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

On the basis of the self-trapping model, the H(D) atoms in a b.c.c. metal lattice are stabilized at octahedral sites with tetragonal elongation along the *c* axis (Fukai, 1983). The displacement of the nearest-neighbor V atom is caculated as 0·188 Å for β_1-V_2H (Fukai, 1983) and 0·14 Å for β-V_2D (Sugimoto, 1984); these values are larger than those observed in the present study.

A clear isotopic difference is found in the thermal vibration of the V atom. In β-V_2D, the thermal parameter of the V atom in Table 5 is less than that of a pure V crystal, 0·00758 $Å^2$ (Ohba, Sato & Saito, 1981). In β_1-V_2H, the thermal parameters show a large anisotropy as mentioned before (Table 3); this is mainly attributed to the static displacement in the [001] direction.

Table 6. *Parameters for fundamental body-centered cell*

	β_1-V_2H	β-V_2D
a_0(Å)	3·0174 (2)	3·0080 (4)
c_0(Å)	3·4358 (4)	3·2989 (5)
α_0(°)	90	90·21 (1)
c_0/a_0	1·1387 (2)	1·0970 (8)
Static displacement of V atom (Å)	0·0225 (18) in $[0\bar{1}\bar{1}]$	0·1037 (1)* in $[00\bar{1}]$
Shortest atomic distance (Å)		
V–V	2·730 (1)	2·5700 (3)
V–H(D)	1·699 (2)	1·7530 (3)†
Maximum and minimum thermal vibrational r.m.s. displacements (Å)		
V u_{max}	0·104 (1)	0·0774 (3)
u_{min}	0·064 (2)	0·0753 (3)
H(D) u_{max}	0·24	0·16
u_{min}	0·17	0·12
$B_{eq}(Å^2)$‡		
V	0·65 (3)	0·47 (1)
H(D)	3·9	2·5

* Displacement of V atom in β-V_2D averaged between V(1) and V(2).
† Atomic distances calculated from averaged V-atom position.
‡ Equivalent isotropic thermal parameter $B_{eq} = (8\pi^2/3)\sum_{ij}U_{ij}$.

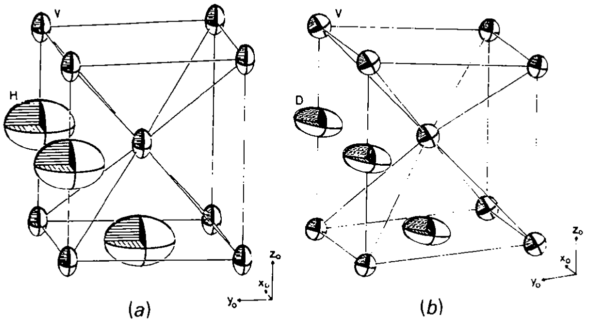

Fig. 3. *ORTEP*II drawings (Johnson, 1976) of the fundamental body-centered cell in (*a*) β_1-V_2H and (*b*) β-V_2D. The H(D) atom is shown only for the octahedral site. All atoms are represented by thermal ellipsoids including 90% probability.

Jo *et al.* (1980) tried the refinement of the β-V_2D structure with space group *Cm*. The static displacement of the V atom in the $[00\bar{1}]$ direction was estimated to be 0·15 Å from the X-ray diffraction intensity measurements of several *h*00 reflections. This value is larger than the result ($0{\cdot}10_4$ Å) of the present study. The thermal Debye–Waller factor $2B$ of 0·825 $Å^2$ reported by these authors is slightly lower than the corresponding value $2B_{eq}$ (0·94 $Å^2$) in this study. The origin of the discrepancies is not clear but they probably arise from microstructural differences in the samples.

Recently, Koike & Suzuki (1984) made two kinds of single crystals of V_2H; one with tetragonal symmetry was obtained under an elastic stress and the other with monoclinic under no stress. This result suggests that the crystal structures of V_2H may depend on the growth conditions of the specimen and the tetragonal structure presented in this study is plausibly formed under the effect of stress-induced ordering of the H atoms.

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Structure of a Uranyl Diselenite, $UO_2Se_2O_5$

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Abstract. $M_r = 508$, triclinic, $P\bar{1}$, $a = 9{\cdot}405\,(2)$, $b = 11{\cdot}574\,(2)$, $c = 6{\cdot}698\,(2)$ Å, $\alpha = 93{\cdot}01\,(3)$, $\beta = 93{\cdot}66\,(3)$, $\gamma = 109{\cdot}69\,(1)°$, $V = 683{\cdot}0\,(6)$ Å^3, $Z = 4$, $D_x = 4{\cdot}94$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 33{\cdot}1$ mm^{-1}, $F(000) = 864$, $T = 293$ K, final $R = 0{\cdot}030$ for 2177 observed reflections with $I > 3\sigma(I)$. The material was synthesized by gas–solid reaction around 720 K, using SeO_2 and UO_3. U, as uranyl cations UO_2^{2+}, is sevenfold coordinated. Two pentagonal bipyramids share one edge to form $[U_2O_{12}]$ entities, which are linked by [>Se–O–Se<] groups, giving rise to a lamellar structure with layers parallel to the (010) plane.

Introduction. Studies concerning selenites of transition elements are of particular interest because of: (i) the specific stereochemistry of the Se^{IV} element with the presence of a lone pair (Bertaud, 1974; Kohn, Inoue, Horie & Akimoto, 1976; Meunier, Bertaud & Galy, 1974); (ii) the specific architecture of some of these compounds, which exhibit a low-dimensional character. Both features must sometimes be considered to account for the interesting properties of selenites, *e.g.* magnetism in the case of $CuSe_2O_5$ (Kahn, Verdaguer, Girerd, Galy & Maury, 1980) or $VOSeO_3$ (Gleizes, Trombe, Enjalbert, Galy, Journeaux & Verdaguer, 1983).

Uranyl selenites were first synthesized a century ago, but their characterization was carried out more recently by Claude (1960*a*,*b*) who described various phases such as $UO_2Se_2O_5$, UO_2SeO_3,.... The thermal behaviour of some of these phases was re-examined (Khandelwal & Verma, 1976) and the structure of UO_2SeO_3 was determined by Loopstra & Brandenburg (1978) by using neutron powder data. In the course of our study concerning transition-element selenites, $UO_2Se_2O_5$ was prepared and its structure is reported here.

Experimental. Pale-yellow single crystals grown from reaction, around 720 K, in sealed tube, of a mixture UO_3–$2SeO_2$ (reagent grade, dried before the run) with excess SeO_2: this excess removed by further heating around 470 K. Chemical analyses, U = 46·3, Se = 31·4 wt% in agreement with $UO_2Se_2O_5$. Preliminary study–precession camera (Mo $K\alpha$)–on single crystal, 0·05 × 0·035 × 0·29 mm, bounded by (010), (110) and (001) planes, indicated triclinic system. CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$; cell parameters from least-squares fit of setting angles of 25 reflections with 2θ between 6·9 and 41·5°; 2289 non-zero reflections measured using ω–θ scan for 2θ values 3 to 52° ($h = -11$ to 11, $k = -14$ to 14, $l = 0$ to 8), scan range $1{\cdot}05° + 0{\cdot}347° \tan\theta$; intensities of three reflections ($\bar{3}11$, $\bar{1}41$, $\bar{1}\bar{1}4$), measured every 3600 s during data collection, varied <2%; corrections for Lp and for absorption (transmission factors max. = 0·414, min. = 0·192); structure determination in space group $P\bar{1}$ by heavy-atom method followed by Fourier and least-squares techniques using 2177 reflections with $I > 3\sigma(I)$, full matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all atoms, $R = 0{\cdot}030$ and $wR = 0{\cdot}060$,*

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42408 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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