

Fig. 5. Illustration of the proposed hexagonal structure (D_{6h}^2) of YbD_2 at ambient temperature and pressures above 14.3 GPa [Yb (\bullet) and D (\blacktriangle)]. The deuterium atoms are arranged in a d.h.c.p. lattice [$2(a)$ and $2(d)$ positions] with stacking sequence $ABA'C$, and the Yb atoms in an h.c.p. lattice [$2(c)$ positions] in the B and C layers of the deuterium lattice. Note that the drawing has been expanded along c for illustrative purposes; the c/a ratio of YbD_2 equals 1.34 at 17 GPa and ambient temperature. When comparing Figs. 3 and 5, $x = (\frac{1}{2})$ and $(\frac{2}{3})$ correspond to B and C layers, $x = (\frac{1}{3})$ and (0) or (1) correspond to A' and A layers.

Conclusions

This neutron powder diffraction study of YbD_2 and YbH_2 has confirmed the previous assumption that at ambient temperature and pressure the crystal structure is D_{2h}^{16} ($Pnma$) with all atoms in the $4(c)$ positions. The lattice constants of both compounds are in agreement with those previously determined by X-ray experiments (Korst & Warf, 1956; Warf & Hardcastle, 1966; Staun Olsen *et al.*, 1981). The

positional parameters of the Yb atoms were found to agree with those reported for CaD_2 (Bergsma & Loopstra, 1962). The deuterium positions in YbD_2 (and YbH_2) determined by powder profile analysis of our data are more accurate but in reasonable agreement with those estimated for CaD_2 (Bergsma & Loopstra, 1962) giving nearest-in-plane ($y = \frac{1}{4}$ or $\frac{3}{4}$) Yb–D distances of 2.21, 2.31 and 2.37 Å, and nearest-out-of-plane distances of 2.25, 2.52 and 2.57 Å.

By inference from the structure of YbD_2 at ambient temperature and pressure, we suggest that the room-temperature hexagonal structure observed in YbH_2 at pressures above ~ 14.3 GPa (Staun Olsen *et al.*, 1981) is D_{6h}^4 ($P6_3/mmc$) with the metal atoms in $2(c)$ positions and the hydrogen atoms in $2(a)$ and $2(d)$ positions.

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Tetrasodium Divanadate, $\text{Na}_4[\text{V}_2\text{O}_7]$

BY KATSUO KATO AND ELI TAKAYAMA

National Institute for Research in Inorganic Materials, 1–1 Namiki, Sakura-mura, Niihari-gun, Ibaraki-ken 305, Japan

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Abstract. $M_r = 305.84$, monoclinic, $C2/c$, $a = 15.376$ (2), $b = 5.7573$ (5), $c = 32.564$ (2) Å, $\beta = 95.08$ (1)°, $V = 2871.3$ (4) Å³, $Z = 16$, $D_x = 2.830$ Mg m⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70930$ Å, $\mu = 2.68$ mm⁻¹, $F(000) = 2336$, $T = 298$ K. Final $R = 0.050$ for 6949 unique observed reflections. One of the two independent V_2O_7 groups has a nearly eclipsed conformation with a V–O–V angle of 149.4 (1)°.

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while the other is nearly staggered with V—O—V 133.4 (1)°. Two Na⁺ ions in special positions are surrounded octahedrally by six O atoms; other Na⁺ ions are coordinated rather irregularly by five to seven O atoms.

Introduction. Glazyrin & Fotiev (1964) studied the optical properties of Na₄V₂O₇ and concluded that this compound crystallizes in the monoclinic system. Na₄V₂O₇ was found later by Barker & Hooper (1973) to undergo a phase transition at 702 K. The powder X-ray diffraction patterns of both low- and high-temperature forms were given by them. Our sample of Na₄V₂O₇, obtained by cooling a melt slowly to 873 K and then rapidly to room temperature, gave a powder pattern similar to, but not identical with that of their low-temperature form. The sample was highly hygroscopic as described in *Gmelin's Handbuch der anorganischen Chemie* (1967). The present study was undertaken as the structure of Na₄V₂O₇ itself was still unknown while that of its hydrate, Na₄V₂O₇·18H₂O, has recently been determined by Bjoernberg (1979).

Experimental. Synthetic material, crystal of irregular shape, 0.25 × 0.30 × 0.30 mm, enclosed in thin-wall (0.01 mm) glass capillary. Four-circle Rigaku diffractometer. Lattice constants based on 22 reflections with 67 < 2θ < 78°. No absorption correction. Intensity measurement to (sinθ)/λ = 0.91 Å⁻¹ within range -27 ≤ h ≤ 27, 0 ≤ k ≤ 10, -58 ≤ l ≤ 58 carried out in several separate runs; intensities reduced to common scale using standard reflections 2,0,26, 80 $\bar{8}$, 82 $\bar{8}$ and 531; 18786 reflections measured, 4984 unobserved [*I* < σ(*I*) or too weak to be scanned], 6949 considered observed. Structure solved by Patterson method. Atomic coordinates, anisotropic thermal parameters and a scale factor refined by least-squares method based on *F*. *R* = 0.050, *wR* = 0.034, *S* = 3.18; *w* = 1/σ² [σ = σ(*I*)/F(2*I*)]. Parameter shift in final cycle ≤ 0.001σ. Δρ = -2.1-1.1 e Å⁻³. Atomic scattering factors of Cromer & Mann (1968) with dispersion corrections of Cromer & Liberman (1970). Computer programs used: *URLAP* in software system of diffractometer for determination of lattice constants, local version of *ORFFE* (Busing, Martin & Levy, 1964) for calculation of bond lengths and angles, and other unpublished programs written by one of the authors.

Discussion. The positional and equivalent isotropic thermal parameters are listed in Table 1.* Fig. 1 shows a [010] projection of the structure. The asymmetric unit consists of two V₂O₇ groups and nine Na⁺ ions. The

V₂O₇ groups are illustrated in Fig. 2 which also shows interatomic distances and angles. The group including V(1) and V(2) has a nearly eclipsed conformation, while the other is nearly staggered.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters of Na₄V₂O₇ with e.s.d.'s in parentheses

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Na(1)	¼	¼	0	1.17 (2)
Na(2)	0	0.1887 (3)	¼	2.26 (3)
Na(3)	0.14053 (8)	0.8183 (2)	0.02207 (4)	1.83 (2)
Na(4)	0.43097 (8)	0.2694 (2)	0.06042 (4)	1.72 (2)
Na(5)	0.10437 (7)	0.7773 (2)	0.12776 (4)	1.53 (2)
Na(6)	0.23785 (8)	0.3249 (2)	0.10446 (4)	1.69 (2)
Na(7)	0.49271 (8)	0.6947 (3)	0.14948 (4)	2.02 (2)
Na(8)	0.30778 (7)	0.7248 (2)	0.18892 (4)	1.42 (2)
Na(9)	0.12030 (9)	0.7099 (2)	0.23082 (4)	2.24 (2)
V(1)	0.05025 (3)	0.29511 (8)	0.05369 (1)	0.796 (6)
V(2)	0.32892 (3)	0.77231 (8)	0.07032 (1)	0.793 (6)
V(3)	0.19589 (3)	0.24633 (7)	0.19533 (1)	0.753 (6)
V(4)	0.40702 (3)	0.20095 (8)	0.17688 (1)	0.724 (6)
O(1)	0.0940 (1)	0.2091 (4)	0.01055 (6)	1.35 (3)
O(2)	0.0709 (1)	0.5771 (3)	0.06449 (7)	1.61 (3)
O(3)	0.0918 (1)	0.1310 (4)	0.09309 (6)	1.95 (4)
O(4)	0.4333 (1)	0.7485 (4)	0.07032 (7)	2.51 (4)
O(5)	0.2656 (1)	0.5807 (4)	0.04285 (7)	1.71 (3)
O(6)	0.2897 (1)	0.0416 (3)	0.06207 (6)	1.63 (3)
O(7)	0.3358 (2)	0.6928 (4)	0.11981 (6)	2.18 (4)
O(8)	0.1665 (1)	0.4964 (3)	0.17028 (7)	1.58 (3)
O(9)	0.1155 (1)	0.0468 (3)	0.18989 (6)	1.36 (3)
O(10)	0.2199 (1)	0.3124 (4)	0.24458 (6)	1.75 (3)
O(11)	0.2900 (1)	0.1390 (3)	0.17005 (6)	1.13 (3)
O(12)	0.4511 (1)	0.2500 (4)	0.13244 (6)	1.81 (4)
O(13)	0.4547 (1)	-0.0277 (4)	0.20176 (7)	1.80 (4)
O(14)	0.4198 (1)	0.4351 (3)	0.20780 (6)	1.44 (3)

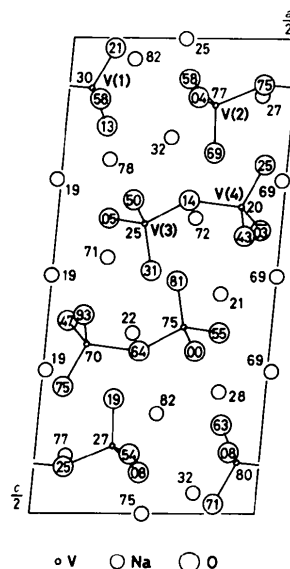


Fig. 1. Structure of Na₄V₂O₇ projected onto (010). The numbers indicate the *y* coordinates of atoms in units of $\frac{b}{100}$.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38731 (68 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Calvo & Faggiani (1975) surveyed the V—O bond lengths and V—O—V bond angles in various divalent metal ion divanadates and concluded that the average bridging V—O bond length increases with decreasing V—O—V angle while the average terminal V—O bond length shows no systematic variations. The average bridging V—O bond lengths and V—O—V angles in the $M_2V_2O_7$ compounds given in Table 5 of their paper as well as those in $Mg_2V_2O_7$ (Gopal & Calvo, 1974), $Ca_2V_2O_7 \cdot 2H_2O$ (Konnert & Evans, 1975) and $Na_4V_2O_7$ (this work) are plotted in Fig. 3. For $Mg_2V_2O_7$, the data are taken only from the one side of the anion where the interaction with a fifth O atom is probably not significant. In Fig. 3 also the average length of all V—O bonds in each V_2O_7 group is plotted against the V—O—V angle. It is the total average V—O bond length rather than the average of the bridging bonds only that increases steadily as the V—O—V angle decreases. The former may be expected to reflect the

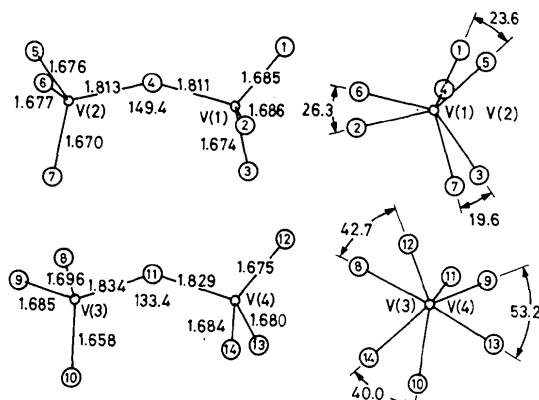


Fig. 2. Interatomic distances (Å), bond angles and torsion angles (°) in V_2O_7 groups. E.s.d.'s are 0.002 Å and 0.1°. The numbers in the circles are the atom numbers of the O atoms. Symmetry code for V(1), O(1), O(2), O(3): $\frac{1}{2} + x, \frac{1}{2} + y, z$.

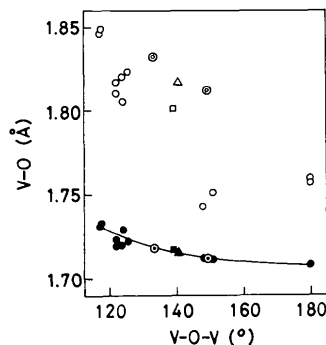


Fig. 3. Relation between average V—O distance and V—O—V angle of V_2O_7 groups in various compounds. Open symbols for the average of bridging bonds and filled ones for the average of all V—O bonds. Curve drawn by eye. Single circles: $M_2V_2O_7$ compounds (see text); triangles: $Mg_2V_2O_7$; squares: $Ca_2V_2O_7 \cdot 2H_2O$; double circles: $Na_4V_2O_7$.

Table 2. Na—O distances (Å) with e.s.d.'s in parentheses

Coordination number	Na—O distances		
	Min.	Mean	Max.
Na(1)	2.360 (2)	2.403	2.464 (2)
Na(2)	2.289 (2)	2.498	2.876 (2)
Na(3)	2.290 (2)	2.605	3.076 (3)
Na(4)	2.312 (2)	2.648	3.122 (2)
Na(5)	2.283 (2)	2.382	2.543 (2)
Na(6)	2.323 (2)	2.524	2.681 (2)
Na(7)	2.362 (2)	2.543	2.734 (3)
Na(8)	2.300 (2)	2.464	2.672 (2)
Na(9)	2.351 (2)	2.653	2.970 (3)

inherent behaviour of the V_2O_7 group more distinctly, because rather large fluctuations in separate bonds affected by environmental conditions are compensated by each other (Shannon & Calvo, 1973).

The Na—O distances are listed in Table 2, where the largest Na—O distance not exceeding any Na—Na or Na—V distances is taken as the maximum distance for each Na^+ ion. Except for Na(1) and Na(2), which lie in special positions and are surrounded octahedrally by six O atoms, the coordination polyhedra of the Na^+ ions are considerably distorted.

The hydrate, $Na_4V_2O_7 \cdot 1.8H_2O$, contains $Na_2(H_2O)_9$ and V_2O_7 groups giving a structural formula $[Na_2(H_2O)_9]_2V_2O_7$. The structure, which is disordered with respect to the orientation of the anion and the position of one of the cation groups (Bjoernberg, 1979), has, as a whole, no similarities to the present structure.

If the pentavalent V in $Na_4V_2O_7$ is substituted by a quadrivalent cation, say Si, and one of the Na^+ ions simultaneously by a trivalent cation (R), a compound of related composition, $Na_3RSi_2O_7$, will be obtained. The compounds $Na_3ScSi_2O_7$ and $Na_3YSi_2O_7$ do exist; their structures contain, however, a three-dimensional network of edge-sharing Si_2O_7 and RO_6 ($R = Sc$ or Y) groups (Voronkov, Sizova, Ilykhin & Belov, 1973).

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