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# Crystal Structures of $V_nO_{2n-1}(2 \leqslant n \leqslant 7)$

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The crystal structures of $V_3O_5$, $V_6O_{11}$, and $V_7O_{13}$ have been refined by the single crystal intensity data collected by a counter method, and the structural relationships of homologous series, $V_nO_{2n-1}(2 \leqslant n \leqslant 7)$, have been discussed in detail.

The structures of the series consist of octahedra of $VO_6$. The bond distances and angles of the octahedra $VO_6$ systematically change according to the distance from the crystallographic shear plane (*CSP*) in each structure. The V–V distances across the shared octahedral faces in the *CSP* are almost identical with 2.768 ~ 2.780 Å from $V_4O_7$ to $V_7O_{13}$. The V–V distances across the shared octahedral edges are largest (3.161 ~ 3.250 Å) in the *CSP* and gradually become smaller with the increase of the distance from the *CSP* and the smallest distances are 2.798 Å of $V_7O_{13}$.

When the composition approaches to $V_2O_3$ in the series, the octahedra of $VO_6$ show greater distortions and expansions, especially in the *CSP*, though the displacement of vanadium atoms from the center of octahedra is smaller compared with the phases with larger $n$ values in the series.

## Introduction

Since the introduction of the concept of homologous series by Magneli (*1*) on the molybdenum oxides, various kinds of such series have been found in metal oxides. They have been extensively investigated because of much interest on their crystallographic and physical properties.

The existence of discrete phases with general formula $V_nO_{2n-1}$ $(4 \leqslant n \leqslant 8)$ was first revealed by Andersson (*2*) by the X-ray powder method. On the basis of the structure of $Ti_5O_9$ (Andersson (*3*)), Andersson and Jahnberg (*4*) determined the relationship of lattices between $M_nO_{2n-1}$ ($M$ represents V and Ti) and rutile, and proposed structure models of $M_nO_{2n-1}$ using their X-ray powder patterns. The structures of homologous series $M_nO_{2n-1}$ $(4 \leqslant n \leqslant 8)$ take the triclinic symmetry.

Crystallographic study on the homologous series of $V_nO_{2n-1}$ $(3 \leqslant n \leqslant 8)$ was made at room temperature by Horiuchi et al. (*5*) with single crystals synthesized by a chemical transport method by Nagasawa (*6*). According to them, the homologous series of $V_nO_{2n-1}$ $(4 \leqslant n \leqslant 8)$ ($\mathbf{a}_n$, $\mathbf{b}_n$, and $\mathbf{c}_n$) can be systematically expressed by the following relations based on the parent rutile-type lattice ($\mathbf{a}_r$, $\mathbf{b}_r$, and $\mathbf{c}_r$)[1],

$$\begin{aligned} \mathbf{a}_n &= -\mathbf{a}_r + \mathbf{c}_r, \\ \mathbf{b}_n &= \mathbf{a}_r + \mathbf{b}_r + \mathbf{c}_r, \\ \mathbf{c}_n &= \tfrac{1}{2}(2n-1)(\mathbf{b}_r + \mathbf{c}_r). \end{aligned} \tag{1}$$

In these expressions, the $\mathbf{a}_n$ and $\mathbf{b}_n$ axes coincide with those by Andersson and Jahnberg (*4*), and the length of the $\mathbf{c}_n$ axis changes as a function of the $n$-value. The cell dimensions of $V_nO_{2n-1}$ are listed in Table I. Although $V_3O_5$ belongs to monoclinic symmetry ($P2_1/n$, Horiuchi et al. (*5*)), it can be expressed by a triclinic lattice with $2\mathbf{a}_3$, $\mathbf{b}_3$, and $\mathbf{c}_3$ in Eq. (1). This will be discussed later in detail. Recently

[1] The transformation matrix between $a_r$, $b_r$, and $c_r$ in Eq. (1) and $a_1$, $a_2$, and $c$ of the conventional tetragonal cell of rutile (*7*) is $(010/\bar{1}00/001)$.

TABLE I

THE CELL DIMENSIONS AND SPACE GROUPS OF $V_nO_{2n-1}$

| $V_nO_{2n-1}$ | Space group | $a(A)$ | $b(A)$ | $c(A)$ | $\alpha°$ | $\beta°$ | $\gamma°$ |
|---|---|---|---|---|---|---|---|
| $V_2O_3$ | $R\bar{3}c$ | 4.990 | | 13.980 | | | |
| $V_3O_5$ | $P2_1/n$ | 10.004 | 5.040 | 9.854 | | 137.9 | |
| | $P2_1/n \rightarrow P\bar{1}$ | 5.601 × 2 | 6.990 | 13.850 | 42.1 | 71.9 | 109.0 |
| $V_4O_7$ | $P\bar{1}$ | 5.504 | 7.007 | 19.243 | 41.3 | 72.5 | 109.4 |
| $V_5O_9$ | $P\bar{1}$ | 5.470 | 7.005 | 24.669 | 41.4 | 72.5 | 109.0 |
| $V_6O_{11}$ | $P\bar{1}$ | 5.448 | 6.998 | 30.063 | 41.0 | 72.5 | 108.9 |
| $V_7O_{13}$ | $P\bar{1}$ | 5.439 | 7.005 | 35.516 | 40.9 | 72.6 | 109.0 |

Asbrink (*8*) reported the space group $P2/n$ or $Pn$ for $V_3O_5$ in which the structure has no 2-fold screw axis, however, the detail of the structure has not been reported yet. The reflections $0k0$ with $k = 2n - 1$ have not been observed in the precession photographic works by Horiuchi et al. (*5*).

The crystal structures of $V_4O_7$ and $V_5O_9$ were precisely determined first by Horiuchi et al. (*9*, *10*) and precise measurements of the changes of cell parameters and the refinements of the structures of $M_4O_7$ and $M_5O_9$ ($M$ represents V and Ti) were carried out at room and lower temperatures by Marezio et al. (*11–14*). The refined structures indicate considerable displacements of atoms from the ideal structures proposed by Andersson and Jahnberg (*4*).

In this investigation, the crystal structures of $V_3O_5$, $V_6O_{11}$, and $V_7O_{13}$ have been precisely determined at room temperature using single crystals, and structural relationships of homologous series, $V_nO_{2n-1}$ ($2 \leqslant n \leqslant 7$), have been discussed in detail.

## Experimental

Small fragments of single crystals of $V_3O_5$, $V_6O_{11}$, and $V_7O_{13}$ synthesized by a chemical transport method by Nagasawa (*6*) were used for determinations of the cell dimensions and crystal structures. The crystal sizes, maximum values of $\mu r$ used for intensity collection and number of reflections used for structure analyses are $0.15 \times 0.15 \times 0.09$ *mm*, 0.66, $567(0 < \sin\theta/\lambda \lesssim 0.60)$ for $V_3O_5$, $0.15 \times 0.09 \times 0.04$ *mm*, 0.65, $1560(0 < \sin\theta/\lambda \lesssim 0.65)$ for $V_6O_{11}$ and $0.04 \times 0.12 \times 0.06$ *mm*, 0.51, $1434(0 < \sin\theta/\lambda \lesssim 0.60)$ for $V_7O_{13}$, respectively.

The cell dimensions of $V_nO_{2n-1}$ ($3 \leqslant n \leqslant 7$) were obtained by Horiuchi et al. (*5*). Those of $V_2O_3$ were determined based on the three reflections, 660, 060, and 0018 which were obtained by the Rigaku four-circle goniometer. The standard deviations of the cell dimensions of $V_2O_3$ are ±0.001 Å and ±0.002 Å for $a$ and $c$, respectively.

All intensities were collected by the Rigaku four-circle automatic diffractometer by the $2\theta$–$\omega$ scan technique. Zr-filtered MoK$\alpha$ radiation was used.

## Derivation of the Ideal Structures

For the structures of $V_nO_{2n-1}$ the expressions of lattices by Horiuchi *et al.* (*5*) have been used in this work. The starting atomic parameters $x_i$, $y_i$, and $z_i$ in the triclinic lattices are derived by the following relations similar to Eq. (1),

$$\begin{aligned} x_i &= y_r + z_r \\ y_i &= x_r - y_r + z_r \\ z_i &= \frac{2}{2n-1}(-x_r + 2y_r - z_r) + \frac{1}{2(2n-1)}, \end{aligned} \tag{2}$$

where $x_r$, $y_r$, and $z_r$ are the atomic coordinates of the rutile structures. The final term, $1/2(2n-1)$, is introduced to coincide the origins of the structures of all the homologous series.

The rutile structure belongs to space group $P4_2/mnm$. The relationships of Eq. (2) were applied for vanadium and oxygen atoms at positions (2*a*) and (4*g*), respectively. The positions (2*a*) has equivalent sites of 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and (4*g*), $x_r, \bar{x}_r, 0, \bar{x}_r, x_r, 0, \frac{1}{2}+x_r, \frac{1}{2}+x_r, \frac{1}{2}$ and $\frac{1}{2}-x_r, \frac{1}{2}-x_r, \frac{1}{2}$. The value of 0.305 was used for $x_r$, which was determined for the high temperature form of $VO_2$ by Westman (*15*). Among the values calculated by the Eq. (2) using the above coordinates and their translated ones, the atomic coordinates of $0 \leqslant x_i < 1$, $0 \leqslant y_i < 1$ and $0 \leqslant z_i < 1$ are

TABLE II(a)

FINAL ATOMIC PARAMETERS OF $V_3O_5$

| Atoms | *x* | *y* | *z* | *B* |
|---|---|---|---|---|
| V1A | .15937(33) | .74408(47) | .27888(34) | .33(4) |
| V1B | .65960(33) | .24614(47) | .27887(33) | .32(4) |
| V20 | .24832(33) | .25201(47) | .50088(34) | .35(4) |
| O1A | .2138(15) | .5929(21) | .1611(15) | 1.13(15) |
| O1B | .7210(13) | .0962(17) | .1608(12) | .30(15) |
| O2A | .1140(13) | .9071(19) | .4398(13) | .56(17) |
| O2B | .6100(13) | .4053(19) | .4417(14) | .66(17) |
| O30 | .0024(14) | .4440(20) | .2509(14) | .77(11) |

TABLE II(b)

COMPARISON OF THE FINAL COORDINATES $(x,y,z)$ AND THE IDEAL ONES $(x_i,y_i,z_i)$

| Atoms | | Ideal $x_i$ and $y_i$ coordinates | Refined parameters $(x,y,z)$ and ideal $z_i$ coordinates $V_3O_5$ | | $V_6O_{11}$ | $V_7O_{13}$ |
|---|---|---|---|---|---|---|
| V1 | *x* | .0 | .01184 | .00772 | −.00506(68) | −.00252(83) |
| | *y* | .5 | .47198 | .46739 | .44815(78) | .45066(94) |
| | *z* | | .12457 | .12687 | .06207(18) | .05220(18) |
| | *B* | | .32 | .32 | .23(2) | .33(3) |
| | $z_i$ | | .1 | .1 | .045 | .038 |
| V2 | *x* | .0 | −.01184 | −.00772 | −.02670(68) | −.02908(83) |
| | *y* | .0 | −.05170 | −.04805 | −.07425(77) | −.07677(95) |
| | *z* | | .13641 | .13459 | .06734(18) | .05763(19) |
| | *B* | | .33 | .32 | .19(2) | .35(3) |
| | $z_i$ | | .1 | .1 | .045 | .038 |
| V3 | *x* | .0 | .00402 | −.00402 | −.03621(70) | −.03877(83) |
| | *y* | .5 | .49979 | .50021 | .45742(80) | .45346(94) |
| | *z* | | .50054 | .49946 | .24248(18) | .20618(18) |
| | *B* | | .35 | .35 | .31(2) | .32(3) |
| | $z_i$ | | .5 | .5 | .227 | .192 |
| V4 | *x* | .0 | −.00402 | .00402 | −.04519(70) | −.04913(84) |
| | *y* | .0 | −.00825 | .00825 | −.05395(79) | −.06302(95) |
| | *z* | | .50456 | .49544 | .24331(81) | .20821(19) |
| | *B* | | .353 | .353 | .29(2) | .36(3) |
| | $z_i$ | | .5 | .5 | .227 | .192 |
| V5 | *x* | .0 | | | −.02496(72) | −.03579(85) |
| | *y* | .5 | | | .46771(82) | .45384(96) |
| | *z* | | | | .41727(19) | .35639(19) |
| | *B* | | | | .40(2) | .41(3) |
| | $z_i$ | | | | .409 | .346 |
| V6 | *x* | .0 | | | −.01866(71) | −.02066(84) |
| | *y* | .0 | | | −.02304(81) | −.02454(96) |
| | *z* | | | | .41532(19) | .35202(19) |
| | *B* | | | | .35(3) | .38(3) |
| | $z_i$ | | | | .409 | .346 |

TABLE II(b) (*continued*)

| Atoms | | Ideal $x_i$ and $y_i$ coordinates | Refined parameters $(x,y,z)$ and ideal $z_i$ coordinates $V_3O_5$ | | $V_6O_{11}$ | $V_7O_{13}$ |
|---|---|---|---|---|---|---|
| V7 | $x$ | .0 | | | | .0 |
| | $y$ | .5 | | | | .5 |
| | $z$ | | | | | .5 |
| | $B$ | | | | | .43(3) |
| | $z_i$ | | | | | .5 |
| V8 | $x$ | .0 | | | | .0 |
| | $y$ | .0 | | | | .0 |
| | $z$ | | | | | .5 |
| | $B$ | | | | | .36(3) |
| | $z_i$ | | | | | .5 |
| O1 | $x$ | .695 | .6893 | .6858 | .6939(28) | .6889(34) |
| | $y$ | .390 | .4111 | .3977 | .4177(32) | .4124(38) |
| | $z$ | | .0736 | .0813 | .03280(74) | .02784(75) |
| | $B$ | | .66 | .56 | .29(10) | .46(10) |
| | $z_i$ | | .066 | .066 | .030 | .025 |
| O2 | $x$ | .305 | .3142 | .3076 | .3196(31) | .3196(34) |
| | $y$ | .610 | .5476 | .5265 | .5560(35) | .5594(39) |
| | $z$ | | .1457 | .1564 | .06693(82) | .05591(75) |
| | $B$ | | 1.13 | .30 | .73(12) | .47(10) |
| | $z_i$ | | .134 | .134 | .061 | .052 |
| O3 | $x$ | .695 | .6858 | .6893 | .6845(30) | .6831(33) |
| | $y$ | .5 | .4740 | .4675 | .4672(34) | .4646(38) |
| | $z$ | | .2329 | .2371 | .10880(78) | .09284(74) |
| | $B$ | | .56 | .66 | .51(11) | .43(10) |
| | $z_i$ | | .222 | .222 | .101 | .085 |
| O4 | $x$ | .305 | .3880 | .3880 | .3743(29) | .3666(34) |
| | $y$ | .5 | .6418 | .6342 | .6208(33) | .6095(39) |
| | $z$ | | .3045 | .3074 | .14527(76) | .12549(76) |
| | $B$ | | .77 | .77 | .38(11) | .52(11) |
| | $z_i$ | | .378 | .378 | .172 | .145 |
| O5 | $x$ | .695 | .6924 | .6858 | .6983(29) | .3666(34) |
| | $y$ | .390 | .4112 | .4193 | .4130(33) | .4085(40) |
| | $z$ | | .4640 | .4598 | .21149(76) | .18020(78) |
| | $B$ | | .30 | .30 | .42(11) | .63(11) |
| | $z_i$ | | .466 | .466 | .212 | .179 |
| O6 | $x$ | .305 | | | .3137(30) | .3121(34) |
| | $y$ | .610 | | | .5890(34) | .5912(38) |
| | $z$ | | | | .24710(78) | .20865(75) |
| | $B$ | | | | .52(11) | .45(10) |
| | $z_i$ | | | | .242 | .205 |
| O7 | $x$ | .695 | | | .6677(29) | .6659(34) |
| | $y$ | .5 | | | .4465(32) | .4464(39) |
| | $z$ | | | | .29735(75) | .25189(75) |
| | $B$ | | | | .35(10) | .48(10) |
| | $z_i$ | | | | .282 | .239 |

TABLE II(b) (*continued*)

| Atoms | | Ideal $x_i$ and $y_i$ coordinates | Refined parameters $(x,y,z)$ and ideal $z_i$ coordinates $V_3O_5$ | $V_6O_{11}$ | $V_7O_{13}$ |
|---|---|---|---|---|---|
| O8 | $x$ | .305 | | .3131(30) | .3208(34) |
| | $y$ | .5 | | .5928(34) | .5357(39) |
| | $z$ | | | .34820(78) | .29412(76) |
| | $B$ | | | .53(10) | .49(10) |
| | $z_i$ | | | .353 | .299 |
| O9 | $x$ | .695 | | .7079(30) | .7016(35) |
| | $y$ | .390 | | .4271(34) | .4175(39) |
| | $z$ | | | .38849(78) | .33115(77) |
| | $B$ | | | .48(11) | .62(11) |
| | $z_i$ | | | .394 | .333 |
| O10 | $x$ | .305 | | .3164(29) | .3066(35) |
| | $y$ | .610 | | .5962(32) | .5915(40) |
| | $z$ | | | .42607(75) | .36205(78) |
| | $B$ | | | .35(10) | .66(11) |
| | $z_i$ | | | .425 | .359 |
| O11 | $x$ | .695 | | .6903(30) | .6813(35) |
| | $y$ | .5 | | .4721(34) | .4656(40) |
| | $z$ | | | .47108(78) | .40000(78) |
| | $B$ | | | .62(11) | .64(11) |
| | $z_i$ | | | .465 | .393 |
| O12 | $x$ | .305 | | | .3143(34) |
| | $y$ | .5 | | | .5279(39) |
| | $z$ | | | | .44830(76) |
| | $B$ | | | | .54(11) |
| | $z_i$ | | | | .453 |
| O13 | $x$ | .695 | | | .6950(34) |
| | $y$ | .390 | | | .4092(39) |
| | $z$ | | | | .48466(76) |
| | $B$ | | | | .52(11) |
| | $z_i$ | | | | .487 |

Atomic coordinates of $V_3O_5$ are converted into those by the triclinic cell.

adopted as starting atomic coordinates of $V_nO_{2n-1}$. The structures derived by Eq. (2) are called "ideal structures" in this work. The coordinates of the ideal structures are listed in Table II(*b*) by $x_i$, $y_i$, and $z_i$. The structural relation between $V_3O_5$ and other phases are explained later in detail.

Vanadium atoms of the ideal structures have the atomic coordinates of $x=0$, and $y=0$ and $\frac{1}{2}$. The symbols of V1, V3, V5, ..., are given to the vanadium atoms with $y=\frac{1}{2}$, and V2, V4, V6, ..., to those with $y=0$ by the increasing order of the distance from the origin, respectively. Oxygen atoms are similarly called O1, O2, O3, ..., by the distance from the origin. The structure of $V_6O_{11}$ is a combination of the structure of $V_5O_9$ and additional vanadium and oxygen atoms. The additional part has the rutile-type structure. The structure of $V_7O_{13}$ can be obtained similarly from $V_6O_{11}$. The ideal structures in this study are essentially identical to "ideal"

ones proposed by Andersson and Jahnberg (*4*) except for O1. O1 atoms have the ideal atomic coordinates of $x = 0.695$ and $y = 0.390$, and $z = 0.047$, 0.037, 0.030, and 0.025 for $V_4O_7$, $V_5O_9$, $V_6O_{11}$, and $V_7O_{13}$, respectively, in this study. However, Andersson and Jahnberg gave $x = 0.695$ and $y = 0.500$, and $z = 0.016$, 0.013, 0.010, and 0.009 to the corresponding ones from $V_4O_7$ to $V_7O_{13}$.

The atomic coordinates of $V_3O_5$ in the monoclinic cell are converted into those in the triclinic cell by the following relations,

$$\begin{aligned} x' &= \quad -y_m \quad + 1, \\ y &= -2x_m - 2y_m + z_m + 2, \\ z &= \quad x_m + y_m - z_m - \tfrac{1}{2}, \end{aligned} \tag{3}$$

where, $x_m$, $y_m$, and $z_m$ are the atomic coordinates in the monoclinic cell and $x'$, $y$ and $z$ in the triclinic cell. The constant terms are introduced to coincide the origin of the triclinic cell with that of other phases of $V_nO_{2n-1}$ ($4 \leqslant n \leqslant 7$). The triclinic cell of $V_3O_5$, thus obtained, however, has the $a_3$ axis twice longer than that in Eq. (1) and the center of symmetry is located at the $\frac{1}{4}a_3$ from the origin along the $a_3$ axis. The triclinic cell must, therefore, be divided into two cells along the $a_3$ axis and $x'$ coordinates derived from Eq. (3) must be transformed by the following relations to compare with the other phases of the series;

$x = (x' - \frac{1}{4}) \times 2$: for the lower-half part,

$x = (x' - \frac{3}{4}) \times 2$: for the upper-half part.

The right and left columns of the atomic coordinates for $V_3O_5$ in Table II(*b*) correspond to the lower-half and upper-half parts of the unit cell, respectively.

## Structure determinations and refinements

The starting values of $x$ and $y$ coordinates of $V_6O_{11}$ were derived from the results of $V_5O_9$ by Horiuchi et al. (*10*). In order to obtain $z$ coordinates of $V_6O_{11}$ from those of $V_5O_9$, the ratio of the $c$ length between $V_5O_9$ and $V_6O_{11}$ was used. As for the additional vanadium and oxygen atoms in $V_6O_{11}$, the ideal atomic positions derived from Eq. (2) were used. In the same way, the refined structure of $V_6O_{11}$ was used for $V_7O_{13}$. This method resulted in a rapid convergence of the $R$ values, especially for $V_nO_{2n-1}$ with large values of $n$.

The refinement of the structure of $V_3O_5$ was initiated from the positional parameters given by Asbrink et al. (*16*).

Isotropic temperature factors of 0.30 $A^2$ were used as the starting values for both vanadium and oxygen atoms. Atomic scattering factors of $V^{3+}$, $V^{4+}$ by Fukamachi (*17*) and $O^{2-}$ by Tokonami (*18*) were used. The scattering factors of $V^{3+}$ were applied to V1 and V2, and those of $V^{4+}$, to other vanadium atoms. However, this assignment does not necessarily mean the ordering of $V^{3+}$ and $V^{4+}$ in the structure.

The function minimized in the refinements was $\Sigma 1/\sigma^2_{hkl}(s|Fo| - |Fc|)^2$, where $\sigma_{hkl}$ is the value given by the counting statistics when $|Fo| \neq 0$, and 10.0 when $|Fo| = 0$, and $s$ is the scale factor. Only the final refinements were carried out using unit weight for all reflections. The procedure of refinement was identical for all phases. The first several cycles of the least-squares refinement were carried out by varying only the positional coordinates and scale factor, and a few cycles were followed with the change of the positional parameters and the isotropic temperature factors. Finally, the atomic coordinates and the isotropic temperature factors were refined using unit weight for all reflections. In this final stage, the parameter for the secondary extinction effects was refined by the trial and error method using the equation by Zachariasen (*19*). A modified version of ORFLS (*20*) was used for refinements.

The $R$ values for all reflections are 0.099, 0.093 and 0.098 for $V_3O_5$, $V_6O_{11}$, and $V_7O_{13}$, respectively, and those for nonzero reflections, 0.089, 0.086, and 0.088, respectively. The estimated secondary extinction parameter $C$'s are $9.5 \times 10^{-6}$, $7.0 \times 10^{-6}$, and $3.0 \times 10^{-6}$, respectively. *Fo* and *Fc* tables are deposited.[2] The final atomic coordinates and temperature

[2] See NAPS documents No 02745 for 24 pages of supplementary material. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. Remit in advance for each NAPS accession number $3.00 for microfiche or $6.00 for photocopies. Make checks payable to Microfiche Publications.

TABLE III

THE POSITIONAL SHIFTS OF ATOMS FROM IDEAL POSITIONS

| Atoms | $V_3O_5$ | | $V_4O_7$* | $V_5O_9$* | $V_6O_{11}$ | $V_7O_{13}$ |
|---|---|---|---|---|---|---|
| V1 | +−+ .287 | +−+ .288 | −−+ .300 | −−+ .298 | −−+ .316 | −−+ .322 |
| V2 | −−+ .287 | −−+ .288 | −−+ .294 | −−+ .289 | −−+ .327 | −−+ .335 |
| V3 | +−+ .026 | −+− .026 | −−+ .107 | −−+ .154 | −−+ .205 | −−+ .217 |
| V4 | −−+ .027 | ++− .027 | −−+ .109 | −−+ .161 | −−+ .177 | −−+ .207 |
| V5 | | | | — | −−+ .080 | −−+ .115 |
| V6 | | | | — | −−+ .063 | −−+ .071 |
| V7 | | | | | | — |
| V8 | | | | | | — |
| O1 | −++ .241 | −++ .250 | −++ .237 | −++ .230 | −++ .237 | −++ .246 |
| O2 | +−+ .366 | +−+ .420 | +−+ .364 | +−+ .328 | +−+ .329 | +−+ .320 |
| O3 | −−+ .083 | −−+ .130 | −−+ .114 | −−+ .120 | −−+ .115 | −−+ .131 |
| O4 | ++− .379 | ++− .350 | ++− .309 | ++− .290 | ++− .297 | ++− .259 |
| O5 | −+− .136 | −+− .189 | −+− .163 | +++ .148 | ++− .144 | +++ .165 |
| O6 | | | −−+ .238 | +−+ .157 | +−+ .149 | +−+ .128 |
| O7 | | | −−+ .197 | −−+ .170 | −−+ .194 | −−+ .181 |
| O8 | | | | ++− .128 | ++− .105 | ++− .105 |
| O9 | | | | −+− .153 | ++− .127 | ++− .128 |
| O10 | | | | | +−+ .121 | +−+ .094 |
| O11 | | | | | −−+ .111 | −−+ .109 |
| O12 | | | | | | ++− .087 |
| O13 | | | | | | ++− .104 |

The directions of shifts are shown by + or − along $a$, $b$, and $c$ axes, respectively. Numbers are the magnitudes (A) of deviations from ideal positions. *-marked atomic coordinates $(x,y,z)$ for $V_4O_7$ and $V_5O_9$ were obtained by the matrixes $(x/y/z) = (1,0,4/0,1,5/0,0,-2)(x_M/y_M/z_M) + (\frac{1}{2}/\frac{1}{2}/\frac{1}{2})$ and $(x/y/z) = (1,0,2/0,1,3/0,0,-1)(x_M/y_M/z_M) + (0/\frac{1}{2}/\frac{1}{2})$, respectively. Where, $x_M$, $y_M$, and $z_M$ are atomic coordinates given by Marezio et al. (*13*, *14*).

TABLE IV

COMPARISON OF THE V–O DISTANCES

| Octahedra | Bonded oxygen | $V_3O_5$ | | | | $V_6O_{11}$ | $V_7O_{13}$ |
|---|---|---|---|---|---|---|---|
| V1 | O1*a* | O2*A* | 2.11 | O2*B* | 2.16 | 2.11 | 2.13 |
| | O1*f* | $O2B_{06}$ | 2.11 | $O2A_{06}$ | 2.02 | 1.95 | 1.95 |
| | O2 | O1*A* | 1.78 | O1*B* | 1.83 | 1.78 | 1.75 |
| | O3*a* | $O2B_{16}$ | 1.99 | $O2A_{11}$ | 2.01 | 1.96 | 1.97 |
| | O4*g* | O30 | 2.05 | $O30_{11}$ | 2.08 | 2.10 | 2.11 |
| | O6*c* | $O1A_{16}$ | 1.98 | $O1B_{12}$ | 1.96 | 1.87 | 1.86 |
| | Mean | | 1.99 | | 2.01 | 1.96 | 1.96 |
| V2 | O1*f* | $O2B_{06}$ | 1.99 | $O2A_{06}$ | 2.01 | 2.00 | 2.00 |
| | O2*f* | $O1A_{06}$ | 1.98 | $O1B_{07}$ | 1.96 | 1.95 | 1.95 |
| | O3*c* | $O2B_{17}$ | 2.11 | $O2A_{13}$ | 2.02 | 1.96 | 1.95 |
| | O3*f* | $O2A_{24}$ | 2.11 | $O2B_{20}$ | 2.16 | 2.13 | 2.14 |
| | O4*c* | $O30_{24}$ | 2.05 | $O30_{06}$ | 2.08 | 2.01 | 2.00 |
| | O5*c* | $O1A_{24}$ | 1.78 | $O1B_{20}$ | 1.83 | 1.74 | 1.75 |
| | Mean | | 1.99 | | 2.01 | 1.97 | 1.97 |
| V3 | O1*b* | $O2B_{03}$ | 2.03 | $O2A_{04}$ | 2.00 | 2.08 | 2.06 |
| | O4 | $O30_{09}$ | 2.02 | $O30_{21}$ | 2.05 | 2.05 | 2.05 |
| | O5*a* | $O1A_{25}$ | 2.06 | $O1B_{22}$ | 1.95 | 2.00 | 1.99 |
| | O6 | $O1B_{18}$ | 1.95 | $O1A_{14}$ | 2.06 | 1.93 | 1.90 |
| | O7*a* | $O30_{19}$ | 2.05 | $O30_{01}$ | 2.02 | 1.86 | 1.86 |
| | O10*c* | $O2A_{10}$ | 2.00 | $O2B_{08}$ | 2.03 | 1.88 | 1.86 |
| | Mean | | 2.02 | | 2.02 | 1.97 | 1.96 |
| V4 | O2 | O1*A* | 2.06 | O1*B* | 1.95 | 2.08 | 2.11 |
| | O3 | $O2A_{11}$ | 2.00 | $O2B_{15}$ | 2.03 | 2.03 | 2.02 |
| | O4 | $O30_{09}$ | 2.05 | $O30_{21}$ | 2.02 | 2.04 | 2.03 |
| | O7*c* | $O30_{16}$ | 2.02 | $O30_{05}$ | 2.05 | 1.91 | 1.91 |
| | O8*c* | $O2B_{25}$ | 2.03 | $O2A_{23}$ | 2.00 | 1.89 | 1.86 |
| | O9*c* | $O1B_{08}$ | 1.95 | $O1A_{06}$ | 2.06 | 1.85 | 1.84 |
| | Mean | | 2.02 | | 2.02 | 1.97 | 1.96 |
| V5 | O5*b* | | | | | 2.06 | 2.05 |
| | O8 | | | | | 1.93 | 1.94 |
| | O9*a* | | | | | 1.95 | 1.93 |
| | O10 | | | | | 1.98 | 1.95 |
| | O11*a* | | | | | 1.90 | 1.91 |
| | O13*i* | | | | | O9*i* 1.95 | 1.86 |
| | Mean | | | | | 1.96 | 1.94 |
| V6 | O6 | | | | | 1.99 | 1.99 |
| | O7 | | | | | 1.96 | 1.95 |
| | O8 | | | | | 1.95 | 1.96 |
| | O11*c* | | | | | 1.91 | 1.92 |
| | O12*c* | | | | | O11*i* 1.94 | 1.90 |
| | O13*c* | | | | | O10*i* 1.93 | 1.93 |
| | Mean | | | | | 1.95 | 1.94 |

TABLE IV (*continued*)

| Octahedra | Bonded oxygen | $V_3O_5$ | $V_6O_{11}$ | $V_7O_{13}$ |
|---|---|---|---|---|
| V7 | O9*b* | | | 1.98 |
| | O12 | | | 1.92 |
| | O13*a* | | | 1.95 |
| | O9*i* | | | 1.98 |
| | O12*e* | | | 1.92 |
| | O13*d* | | | 1.95 |
| | Mean | | | 1.95 |
| V8 | O10 | | | 1.97 |
| | O11 | | | 1.93 |
| | O12 | | | 1.93 |
| | O10*i* | | | 1.97 |
| | O11*i* | | | 1.93 |
| | O12*i* | | | 1.93 |
| | Mean | | | 1.94 |

The relations of symbols for oxygen atoms between $V_7O_{13}$ and other phases are also shown. The suffix of italic and numerical letters are symmetry operation codes. Standard errors are around 0.01 Å for each phase.

SYMMETRY OPERATIONS

| Monoclinic phase $V_3O_5$ | | | | Triclinic phase $V_nO_{2n-1}(4 \leqslant n \leqslant 7)$ | | | |
|---|---|---|---|---|---|---|---|
| Symbols | Symmetry operations | | | Symbols | Symmetry operations | | |
| None | $x$ | $y$ | $z$ | None | $x$ | $y$ | $z$ |
| 01 | $x$ | $y$ | $-1+z$ | *a* | $-1+x$ | $y$ | $z$ |
| 02 | $1+x$ | $-1+y$ | $z$ | *b* | $x$ | $1+y$ | $z$ |
| 03 | $-1+x$ | $y$ | $-1+z$ | *c* | $-1+x$ | $-1+y$ | $z$ |
| 04 | $x$ | $-1+y$ | $-1+z$ | *d* | $1-x$ | $1-y$ | $1-z$ |
| 05 | $1+x$ | $y$ | $z$ | *e* | $-x$ | $1-y$ | $1-z$ |
| 06 | $1-x$ | $1-y$ | $1-z$ | *f* | $1-x$ | $1-y$ | $-z$ |
| 07 | $2-x$ | $-y$ | $-z$ | *g* | $1-x$ | $2-y$ | $-z$ |
| 08 | $1-x$ | $1-y$ | $-z$ | *h* | $-x$ | $1-y$ | $-z$ |
| 09 | $-x$ | $1-y$ | $-z$ | *i* | $-x$ | $-y$ | $1-z$ |
| 10 | $-x$ | $2-y$ | $-z$ | *j* | $-x$ | $-y$ | $-z$ |
| 11 | $\frac{1}{2}-x$ | $-\frac{1}{2}+y$ | $\frac{1}{2}-z$ | | | | |
| 12 | $\frac{3}{2}-x$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ | | | | |
| 13 | $\frac{3}{2}-x$ | $-\frac{1}{2}+y$ | $\frac{3}{2}-z$ | | | | |
| 14 | $\frac{1}{2}-x$ | $-\frac{1}{2}+y$ | $-\frac{1}{2}-z$ | | | | |
| 15 | $\frac{3}{2}-x$ | $-\frac{1}{2}+y$ | $\frac{1}{2}-z$ | | | | |
| 16 | $\frac{1}{2}-x$ | $\frac{1}{2}+y$ | $\frac{1}{2}-z$ | | | | |
| 17 | $\frac{3}{2}-x$ | $\frac{1}{2}+y$ | $\frac{3}{2}-z$ | | | | |
| 18 | $\frac{1}{2}-x$ | $\frac{1}{2}+y$ | $-\frac{1}{2}-z$ | | | | |
| 19 | $-\frac{1}{2}-x$ | $\frac{1}{2}+y$ | $-\frac{1}{2}-z$ | | | | |
| 20 | $\frac{1}{2}+x$ | $\frac{1}{2}-y$ | $\frac{1}{2}+z$ | | | | |
| 21 | $\frac{1}{2}+x$ | $\frac{1}{2}-y$ | $-\frac{1}{2}+z$ | | | | |
| 22 | $-\frac{1}{2}+x$ | $\frac{1}{2}-y$ | $-\frac{1}{2}+z$ | | | | |
| 23 | $\frac{1}{2}+x$ | $\frac{3}{2}-y$ | $-\frac{1}{2}+z$ | | | | |
| 24 | $\frac{1}{2}+x$ | $\frac{3}{2}-y$ | $\frac{1}{2}+z$ | | | | |
| 25 | $-\frac{1}{2}+x$ | $\frac{3}{2}-y$ | $-\frac{1}{2}+z$ | | | | |
| 26 | $\frac{3}{2}+x$ | $-\frac{1}{2}-y$ | $-\frac{1}{2}+z$ | | | | |
| 27 | $1-x$ | $2-y$ | $1-z$ | | | | |
| 28 | $x$ | $-1+y$ | $z$ | | | | |

TABLE V

COMPARISON OF THE O–O DISTANCES AND O–V–O ANGLES

| | Bonded oxygens | $V_3O_5$ O–O | $V_3O_5$ O–V–O | $V_3O_5$ O–O | $V_3O_5$ O–V–O | $V_6O_{11}$ O–O | $V_6O_{11}$ O–V–O | $V_7O_{13}$ O–O | $V_7O_{13}$ O–V–O | |
|---|---|---|---|---|---|---|---|---|---|---|
| V1 octahedra | O1*a*–O1*f* | 2.59 Å | 77.6° | 2.59 Å | 76.4° | 2.51 Å | 76.3° | 2.54 Å | 76.8° | *e* |
| | O1*a*–O3*a* | 2.58 | 77.9 | 2.58 | 76.4 | 2.57 | 78.9 | 2.59 | 78.1 | *f* |
| | O1*a*–O4*g* | 2.66 | 79.5 | 2.67 | 78.0 | 2.63 | 77.2 | 2.64 | 76.8 | *f* |
| | O1*a*–O6*c* | 2.72 | 83.0 | 2.71 | 82.2 | 2.69 | 84.5 | 2.67 | 83.7 | *e* |
| | O1*f*–O2 | 2.86 | 97.9 | 2.93 | 98.7 | 2.86 | 100.1 | 2.85 | 100.1 | |
| | O1*f*–O4*g* | 2.71 | 83.9 | 2.72 | 82.9 | 2.67 | 82.3 | 2.68 | 82.4 | *e* |
| | O1*f*–O6*c* | 2.95 | 95.4 | 2.98 | 96.7 | 2.88 | 97.7 | 2.87 | 97.4 | |
| | O2–O3*a* | 3.02 | 106.5 | 3.12 | 108.5 | 2.96 | 104.4 | 2.93 | 103.9 | |
| | O2–O4*g* | 2.93 | 99.9 | 3.04 | 101.6 | 2.92 | 97.5 | 2.93 | 98.2 | |
| | O2–O6*c* | 2.84 | 97.9 | 2.87 | 98.5 | 2.82 | 100.9 | 2.80 | 101.4 | |
| | O3*a*–O4*g* | 2.67 | 84.6 | 2.66 | 81.1 | 2.65 | 81.3 | 2.66 | 81.5 | *f* |
| | O3*a*–O6*c* | 2.83 | 90.7 | 2.81 | 90.0 | 2.73 | 90.8 | 2.72 | 90.5 | |
| | O1*a*–O2 | | 175.5 | | 175.0 | | 173.9 | | 174.4 | |
| | O1*f*–O3*a* | | 153.8 | | 150.8 | | 152.0 | | 152.7 | |
| | O4*g*–O6*c* | | 162.2 | | 159.7 | | 161.3 | | 160.0 | |
| | Mean | 2.78 | | 2.81 | | 2.74 | | 2.74 | | |
| V2 octahedra | O1*f*–O2*f* | 2.83 | 90.7 | 2.81 | 90.0 | 2.79 | 90.0 | 2.80 | 90.1 | |
| | O1*f*–O3*f* | 2.58 | 77.9 | 2.58 | 76.4 | 2.57 | 76.8 | 2.59 | 77.3 | *f* |
| | O1*f*–O4*c* | 2.67 | 84.6 | 2.66 | 81.1 | 2.63 | 82.0 | 2.63 | 82.5 | *f* |
| | O1*f*–O5*c* | 3.02 | 106.5 | 3.12 | 108.5 | 3.01 | 106.8 | 3.00 | 106.4 | |
| | O2*f*–O3*c* | 2.95 | 95.4 | 2.98 | 96.7 | 2.89 | 95.3 | 2.87 | 94.4 | |
| | O2*f*–O3*f* | 2.72 | 83.0 | 2.71 | 82.2 | 2.66 | 81.2 | 2.68 | 81.6 | *e* |
| | O2*f*–O5*c* | 2.84 | 97.9 | 2.87 | 98.5 | 2.76 | 96.8 | 2.76 | 96.1 | |
| | O3*c*–O3*f* | 2.59 | 77.6 | 2.59 | 76.4 | 2.54 | 76.7 | 2.53 | 76.3 | *e* |
| | O3*c*–O4*c* | 2.71 | 83.9 | 2.73 | 82.9 | 2.66 | 84.0 | 2.66 | 84.6 | *e* |
| | O3*c*–O5*c* | 2.86 | 97.9 | 2.93 | 98.7 | 2.84 | 100.0 | 2.85 | 100.3 | |
| | O3*f*–O4*c* | 2.66 | 79.5 | 2.67 | 78.0 | 2.65 | 79.6 | 2.66 | 80.0 | *f* |
| | O4*c*–O5*c* | 2.93 | 99.9 | 3.04 | 101.6 | 2.93 | 102.6 | 2.93 | 102.5 | |
| | O1*f*–O3*c* | | 153.8 | | 150.8 | | 151.8 | | 152.3 | |
| | O2*f*–O4*c* | | 162.2 | | 159.7 | | 160.5 | | 161.2 | |
| | O3*f*–O5*c* | | 175.5 | | 175.0 | | 175.9 | | 175.7 | |
| | Mean | 2.78 | | 2.81 | | 2.74 | | 2.75 | | |
| V3 octahedra | O1*b*–O4 | 2.71 | 84.2 | 2.72 | 84.3 | 2.67 | 80.4 | 2.68 | 81.2 | *e* |
| | O1*b*–O5*a* | 2.97 | 93.2 | 2.95 | 96.8 | 2.90 | 90.3 | 2.86 | 89.6 | |
| | O1*b*–O6 | 2.71 | 85.9 | 2.72 | 84.1 | 2.69 | 83.9 | 2.67 | 84.6 | *e* |
| | O1*b*–O7*a* | 3.01 | 95.1 | 2.99 | 96.4 | 2.80 | 90.1 | 2.76 | 89.4 | |
| | O4–O5*a* | 2.88 | 90.0 | 2.84 | 90.6 | 2.72 | 84.1 | 2.71 | 84.3 | |
| | O4–O6 | 2.83 | 91.3 | 2.86 | 88.1 | 2.80 | 89.4 | 2.78 | 89.3 | |
| | O4–O10*c* | 2.99 | 96.4 | 3.01 | 95.1 | 2.91 | 95.5 | 2.89 | 95.4 | |
| | O5*a*–O7*a* | 2.86 | 88.1 | 2.83 | 91.3 | 2.72 | 89.6 | 2.72 | 89.5 | |
| | O5*a*–O10*c* | 2.72 | 84.1 | 2.71 | 85.9 | 2.68 | 87.2 | 2.65 | 86.6 | *e* |
| | O6–O7*a* | 2.84 | 90.6 | 2.88 | 90.0 | 2.81 | 95.9 | 2.80 | 96.0 | |
| | O6–O10*c* | 2.95 | 96.8 | 2.97 | 93.2 | 2.88 | 98.1 | 2.86 | 98.9 | |
| | O7*a*–O10*c* | 2.72 | 84.3 | 2.71 | 84.2 | 2.73 | 93.8 | 2.71 | 93.6 | |
| | O1*b*–O10*c* | | 177.2 | | 177.2 | | 175.4 | | 175.1 | |
| | O4–O7*a* | | 177.9 | | 177.9 | | 168.6 | | 168.7 | |
| | O5*a*–O6 | | 178.3 | | 178.3 | | 172.0 | | 172.0 | |
| | Mean | 2.85 | | 2.85 | | 2.78 | | 2.75 | | |

TABLE V (*continued*)

| | Bonded oxygens | $V_3O_5$ O–O | $V_3O_5$ O–V–O | $V_3O_5$ O–O | $V_3O_5$ O–V–O | $V_6O_{11}$ O–O | $V_6O_{11}$ O–V–O | $V_7O_{13}$ O–O | $V_7O_{13}$ O–V–O | |
|---|---|---|---|---|---|---|---|---|---|---|
| V4 octahedra | O2–O3 | 2.72 | 84.1 | 2.71 | 85.9 | 2.66 | 80.7 | 2.68 | 80.9 | *e* |
| | O2–O4 | 2.86 | 88.1 | 2.83 | 91.3 | 2.80 | 85.7 | 2.82 | 85.8 | |
| | O2–O7*c* | 2.88 | 90.0 | 2.84 | 90.6 | 2.65 | 83.2 | 2.64 | 82.0 | |
| | O2–O8*c* | 2.97 | 93.2 | 2.95 | 96.8 | 2.84 | 91.7 | 2.81 | 90.0 | |
| | O3–O4 | 2.72 | 84.3 | 2.71 | 84.2 | 2.66 | 81.4 | 2.66 | 82.2 | *e* |
| | O3–O7*c* | 2.99 | 96.4 | 3.01 | 95.1 | 2.86 | 93.0 | 2.84 | 92.7 | |
| | O3–O9*c* | 2.95 | 96.8 | 2.97 | 93.2 | 2.76 | 90.4 | 2.75 | 90.7 | |
| | O4–O8*c* | 3.01 | 95.1 | 2.99 | 96.4 | 2.97 | 98.3 | 2.91 | 96.8 | |
| | O4–O9*c* | 2.84 | 90.6 | 2.88 | 90.0 | 2.94 | 97.9 | 2.92 | 97.7 | |
| | O7*c*–O8*c* | 2.71 | 84.2 | 2.72 | 84.3 | 2.59 | 85.9 | 2.58 | 86.4 | *e* |
| | O7*c*–O9*c* | 2.83 | 91.3 | 2.86 | 88.1 | 2.72 | 92.4 | 2.74 | 93.9 | |
| | O8*c*–O9*c* | 2.71 | 85.9 | 2.72 | 84.1 | 2.80 | 97.2 | 2.81 | 98.5 | |
| | O2–O9*c* | | 178.3 | | 178.3 | | 169.8 | | 170.4 | |
| | O3–O8*c* | | 177.2 | | 177.2 | | 172.3 | | 170.8 | |
| | O4–O7*c* | | 177.9 | | 177.9 | | 168.3 | | 167.4 | |
| | Mean | 2.85 | | 2.85 | | 2.77 | | 2.76 | | |
| V5 octahedra | O5*b*–O8 | | | | | 2.75 | 87.2 | 2.73 | 86.1 | |
| | O5*b*–O9*a* | | | | | 2.87 | 93.1 | 2.84 | 90.8 | |
| | O5*b*–O10 | | | | | 2.68 | 83.2 | 2.65 | 82.7 | *e* |
| | O5*b*–O11*a* | | | | | 2.77 | 88.5 | 2.75 | 87.9 | |
| | O8–O9*a* | | | | | 2.76 | 90.6 | 2.76 | 90.5 | |
| | O8–O10 | | | | | 2.71 | 88.0 | 2.71 | 88.2 | |
| | O8–O13*i* | | | | | 2.80 | 92.4 | 2.78 | 93.7 | |
| | O9*a*–O11*a* | | | | | 2.71 | 89.2 | 2.68 | 88.5 | |
| | O9*a*–O13*i* | | | | | 2.72 | 88.5 | 2.67 | 89.2 | *e* |
| | O10–O11*a* | | | | | 2.79 | 91.7 | 2.78 | 92.2 | |
| | O10–O13*i* | | | | | 2.94 | 97.0 | 2.86 | 97.4 | |
| | O11*a*–O13*i* | | | | | 2.77 | 92.0 | 2.72 | 92.3 | |
| | O5*b*–O13*i* | | | | | | 179.5 | | 179.8 | |
| | O8–O11*a* | | | | | | 175.7 | | 173.9 | |
| | O9*a*–O10 | | | | | | 174.4 | | 173.4 | |
| | Mean | | | | | 2.77 | | 2.74 | | |
| V6 octahedra | O6–O7 | | | | | 2.78 | 89.4 | 2.89 | 90.0 | |
| | O6–O8 | | | | | 2.74 | 88.0 | 2.77 | 88.7 | |
| | O6–O11*c* | | | | | 2.75 | 89.7 | 2.74 | 89.0 | |
| | O6–O12*c* | | | | | 2.77 | 89.7 | 2.74 | 89.7 | |
| | O7–O8 | | | | | 2.59 | 83.0 | 2.58 | 82.8 | *e* |
| | O7–O11*c* | | | | | 2.85 | 95.0 | 2.85 | 95.3 | |
| | O7–O13*c* | | | | | 2.72 | 88.8 | 2.67 | 86.9 | |
| | O8–O12*c* | | | | | 2.89 | 96.1 | 2.87 | 96.1 | |
| | O8–O13*c* | | | | | 2.77 | 91.3 | 2.77 | 90.7 | |
| | O11*c*–O12*c* | | | | | 2.62 | 85.8 | 2.60 | 85.8 | *e* |
| | O11*c*–O13*c* | | | | | 2.73 | 90.9 | 2.75 | 91.4 | |
| | O12*c*–O13*c* | | | | | 2.79 | 92.1 | 2.79 | 93.4 | |
| | O6–O13*c* | | | | | | 178.1 | | 176.9 | |
| | O7–O12*c* | | | | | | 178.8 | | 178.9 | |
| | O8–O11*c* | | | | | | 177.0 | | 177.0 | |
| | Mean | | | | | 2.75 | | 2.74 | | |

TABLE V (*continued*)

| | Bonded oxygens | $V_3O_5$ O–O | $V_3O_5$ O–V–O | $V_3O_5$ O–O | $V_3O_5$ O–V–O | $V_6O_{11}$ O–O | $V_6O_{11}$ O–V–O | $V_7O_{13}$ O–O | $V_7O_{13}$ O–V–O | |
|---|---|---|---|---|---|---|---|---|---|---|
| V7 octahedra | O9*b*–O12 | | | | | | | 2.75 | 89.7 | |
| | O9*b*–O12*e* | | | | | | | 2.77 | 90.3 | |
| | O9*b*–O13*a* | | | | | | | 2.89 | 94.7 | |
| | O9*b*–O13*d* | | | | | | | 2.67 | 85.3 | *e* |
| | O9*i*–O12 | | | | | | | 2.77 | 90.3 | |
| | O9*i*–O12*e* | | | | | | | 2.75 | 89.7 | |
| | O9*i*–O13*a* | | | | | | | 2.67 | 85.3 | *e* |
| | O9*i*–O13*d* | | | | | | | 2.89 | 94.7 | |
| | O12–O13*a* | | | | | | | 2.76 | 90.9 | |
| | O12–O13*d* | | | | | | | 2.72 | 89.1 | |
| | O12*e*–O13*a* | | | | | | | 2.72 | 89.1 | |
| | O12*e*–O13*d* | | | | | | | 2.76 | 90.9 | |
| | O9*b*–O9*i* | | | | | | | | 180.0 | |
| | O12–O12*e* | | | | | | | | 180.0 | |
| | O13*a*–O13*d* | | | | | | | | 180.0 | |
| | Mean | | | | | | | 2.76 | | |
| V8 octahedra | O10–O11 | | | | | | | 2.78 | 91.0 | |
| | O10–O11*i* | | | | | | | 2.73 | 90.0 | |
| | O10–O12 | | | | | | | 2.76 | 90.0 | |
| | O10–O12*i* | | | | | | | 2.75 | 90.0 | |
| | O10*i*–O11 | | | | | | | 2.73 | 89.0 | |
| | O10*i*–O11*i* | | | | | | | 2.78 | 91.0 | |
| | O10*i*–O12 | | | | | | | 2.75 | 90.0 | |
| | O10*i*–O12*i* | | | | | | | 2.76 | 90.0 | |
| | O11–O12 | | | | | | | 2.60 | 84.7 | *e* |
| | O11–O12*i* | | | | | | | 2.85 | 95.3 | |
| | O11*i*–O12 | | | | | | | 2.85 | 95.3 | |
| | O11*i*–O12*i* | | | | | | | 2.60 | 84.7 | *e* |
| | O10–O10*i* | | | | | | | | 180.0 | |
| | O11–O11*i* | | | | | | | | 180.0 | |
| | O12–O12*i* | | | | | | | | 180.0 | |
| | Mean | | | | | | | 2.74 | | |

The relation of symbols for oxygen atoms between $V_7O_{13}$ and other phases should be referred to Table IV. Standard errors are around 0.02 Å and 0.6° for distances and angles, respectively. *e*, oxygen atoms of shared edges; and *f*, oxygen atoms of shared faces.

factors of $V_3O_5$ are listed in Table II(*a*) and those of $V_3O_5$ (converted into triclinic cell), $V_6O_{11}$, and $V_7O_{13}$ in Table II(*b*). The interatomic distances V–O (Table IV), O–O (Table V) and V–V (Table VI) and angles O–V–O (Table V) are given for $V_3O_5$, $V_6O_{11}$, and $V_7O_{13}$. The distances and angles were calculated by using a version of the program RDA4 of UNICS system (*21*).

All the computations were carried out by NEAC-700 and FACOM 230-60 computers at Computation Center Osaka University and Data Processing Center of Kyoto University, respectively.

## Discription and discussion of the structure

### *a. General Features*

The structures of $V_nO_{2n-1}$ ($2 \leqslant n \leqslant 7$) are constructed by $VO_6$ octahedra. Oxygen atoms are approximately in the hexagonal close packing.

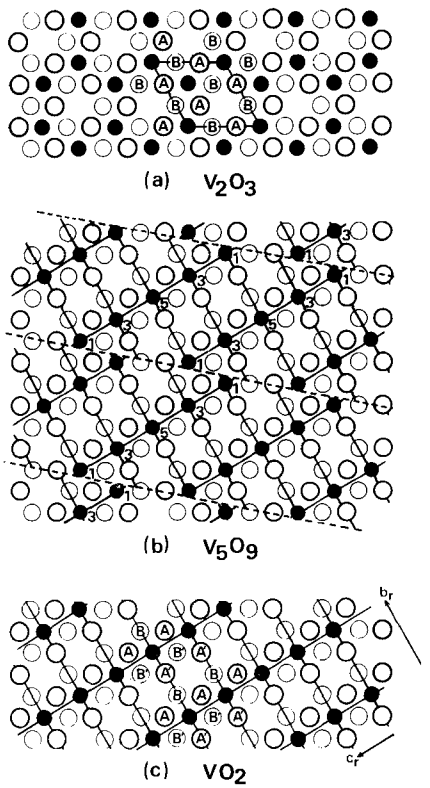


FIG. 1. Parts of the structures of $V_2O_3$, $V_5O_9$, and $VO_2$ based upon the hexagonal close packing of oxygen atoms. Open and black circles represent oxygen and vanadium atoms, respectively. *A* and *B* show the oxygen atoms with different height. Real lines show a hexagonal corundum-type cell in $V_2O_3$ and a rutile-type cell projected along the $a_r$ axis in $V_5O_9$ and $VO_2$.

The structures of $V_2O_3$, $V_5O_9$, and $VO_2$ are schematically shown in Fig. 1 with emphasis on the packing layers of the hexagonal close packing of oxygen atoms. The hexagonal unit cell of the corundum-type structure is projected along the *c* axis (Fig. 1*a*) and the tetragonal one of the rutile-type structure is projected along the $a_r$ axis (Fig. 1*c*). Although *A* (*B*) shows the same packing layer in the $V_2O_3$ structure, *A* and *A'* (*B* and *B'*) are not in the same layer but constitute slightly separate layers in the $VO_2$ structure.

In the structure of $V_5O_9$ (Fig. 1*b*) the part between two parallel dotted lines shows the rutile-type structure. The unit cells of the rutile-type structure are shown with real lines. The directions of $a_r$, $b_r$, and $c_r$ are the same as the figure of $VO_2$. The $VO_6$ octahedra of V1, V3, V5, V3, and V1 in $V_5O_9$ share edges with each other and make a finite straight chain along the $c_r$ axis. Those of V2, V4, V6, V4, and V2 are in the upper plane and at the positions with the magnitude of $\frac{1}{2}b_n$ along $\mathbf{b}_n$ ($=\mathbf{a}_r + \mathbf{b}_r + \mathbf{c}_r$) from V1, V3, V5, V3, and V1, respectively. The rutile-type parts are mutually shifted by a vector of $\mathbf{c}_n/(2n-1)$ ($=\frac{1}{2}(\mathbf{b}_r + \mathbf{c}_r)$) in the boundaries shown by dotted lines which is called "crystallographic shear plane (*CSP*)" by Wadsley (*22*).

The end octahedra $V1O_6$ and $V2O_6$ of the straight chains (Fig. 1*b*) share the faces and edges with the octahedra of $V1O_6$ and $V2O_6$ of the neighboring rutile-type part and make a infinite double chain running along the $b_n$ axis. This chain is shown along *b* axes of $V_4O_7$ and $V_5O_9$ in Fig. 2, in which perspective views are given almost parallel to the oxygen packing plane for $V_4O_7$ and $V_5O_9$.

In conclusion, there are three kinds of octahedral chain in the structures of $V_nO_{2n-1}$ ($3 \leqslant n \leqslant 7$). Two of them are zig-zag chains shared by edges like ···–V5–V3–V1–V1–V3–V5–··· and ···–V6–V4–V2–V2–V4–V6–··· (Fig. 1). Another one is an infinite double chain shared by faces and edges like ···–V1–V1–V2–V2–··· (Fig. 2). The three kinds of chains of $V_7O_{13}$ are shown in Fig. 3. The infinite double chain can be found also in the structure of $V_2O_3$.

### *b. Deviations from the Ideal Structures*

The atomic coordinates of $V_3O_5$ are only slightly different from those by Asbrink et al. (*16*) based on space group $C2/c$. The directions and magnitudes of shifts from the ideal positions which are shown by + and − and numbers in Table III are essentially identical for all coordinates corresponding to V1, V2, ..., O1, O2, ..., of the series except $V_3O_5$. The results for $V_4O_7$ and $V_5O_9$ were obtained from those by Marezio et al. (*13*, *14*). The shifts are different in direction for some atoms, however, their absolute values are very small. In the structure of $V_3O_5$ the *x* coordinates of V1 atoms of lower-half and upper-half parts are inversely shifted, respectively, and the magnitudes of shifts of V3 and V4 are very

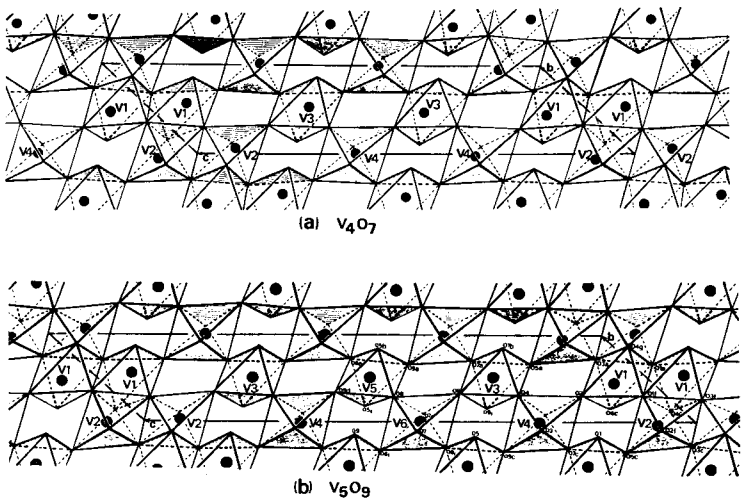


FIG. 2. Perspective views of the structures of $V_4O_7$ and $V_5O_9$ based upon the $VO_6$ octahedra. Black circles show vanadium atoms. Shaded planes are parallel to the packing layers shown in Fig. 1. The *b* and *c* axes are shown in the oblique and horizontal directions, respectively.

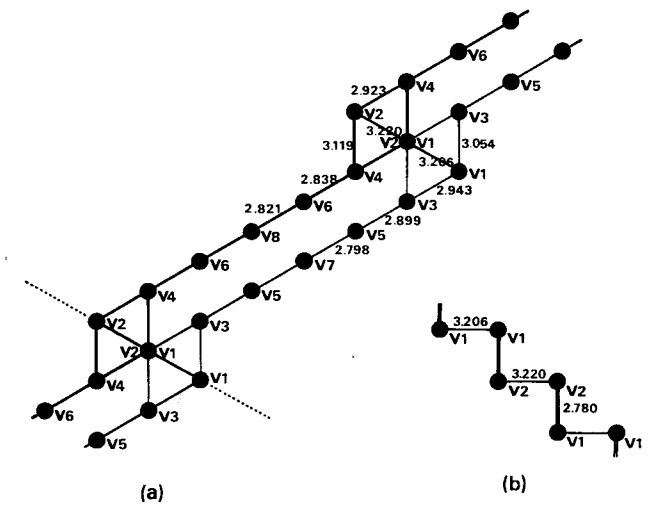


FIG. 3. (a) Arrangements of V atoms in $V_7O_{13}$. Atoms are projected along the $a_r$ axis shown in Fig. 1. The even and odd numbered V atoms show the atoms with different height, respectively. (b) Infinite double chain running along the *b* axis. Double lines show the V–V combinations across the face-shared octahedra.

small and the oxygen atoms have identical tendency of shift with other phases.

The shift from the ideal position is most striking for the V1 and V2 atoms which construct the infinite double chain in the *CSP*, and becomes gradually less remarkable for the vanadium atoms with greater distances from the *CSP*. For example in $V_7O_{13}$, the shifts of V1 and V2 are 0.322 and 0.335 Å, respectively, and those of V3 and V4 are 0.217 and 0.207 Å, respectively, and so on. Oxygen atoms have the similar tendency of shift to that of vanadium atoms.

### *c. Interatomic Distances and Angles*

The interatomic distances of the oxygen atoms on the shared faces and edges of $VO_6$ octahedra are generally smaller than those of

the oxygen atoms at the shared corners. On the other hand, the V–O distances of the oxygen atoms at the shared corners are smaller than those of the oxygen atoms on the shared faces and edges. These features are most remarkable with the oxygen atoms in the infinite double chain in the *CSP* and become less remarkable with those at greater distance from the *CSP*.

The features of the interatomic distances described above are clear for $V_7O_{13}$ (Tables IV and V). The V1 and V2 octahedra on the *CSP* share a face of three oxygen atoms of $O1_a$, $O3_a$ and $O4_g$. The distances of $O1_a$–$O3_a$, $O1_a$–$O4_g$ and $O3_a$–$O4_g$ are 2.59, 2.63, and 2.66 Å, respectively. The V1 octahedra is also connected with $V1O_6$ and two $V3O_6$'s by three edges of $O1_a$–$O1_f$, $O1_a$–$O6_c$ and $O1_f$–$O4_g$ with 2.54, 2.67, and 2.68 Å, respectively. On the other hand, other six distances of the oxygen atoms in the shared corners are greater within the range from 2.72 to 2.93 Å. The V3 and V4 octahedra share three edges with neighboring octahedra, and V5, V6, V7, and V8 octahedra share two edges. The shared edges of each octahedron are shorter than the unshared edges.

The O–V–O angles of oxygen atoms on the shared faces and edges of $VO_6$ octahedra are also generally smaller than those of oxygen atoms at the shared corners.

The V–V distances across the shared faces in the *CSP* are largest in $V_3O_5$ and almost identical in the series from $V_4O_7$ to $V_7O_{13}$ (Table VI). The distances across the shared edges are largest in the combination of V1 and V2 octahedra and they become gradually smaller in the combinations of octahedra with greater distance from the *CSP*. The change of the V–V distances are shown in Fig. 3 for $V_7O_{13}$.

The mean V–O and O–O distances for $VO_6$ octahedra of $V_nO_{2n-1}$ ($2 \leqslant n \leqslant 7$) are listed together with those for $VO_2$ (Table VII). The mean values for the pairs of the octahedra, V1 and V2, V3 and V4, V5 and V6, and V7 and V8, are classified under OCT1, OCT2, OCT3 and OCT4, respectively, because each pair plays structurally the similar role in all phases.

The mean V–O and O–O distances are relatively larger in OCT2 than other octahedra, and become gradually smaller in the order of OCT1, OCT3 and OCT4. They are much smaller in $VO_2$ than in other phases. The mean V–O and O–O distances of octa-

TABLE VI

COMPARISON OF THE V–V DISTANCES OF $V_nO_{2n-1}$ ($3 \leqslant n \leqslant 7$)

| Combinations of V atoms | | | $V_3O_5$ | | $V_4O_7$[a] | $V_5O_9$[b] | $V_6O_{11}$ | $V_7O_{13}$ | Mean |
|---|---|---|---|---|---|---|---|---|---|
| Face-sharing octahedra | | V1–V2*h* | 2.795 | 2.795 | 2.768 | 2.768 | 2.774 | 2.780 | 2.780 |
| Edge-sharing octahedra | OCT1 | V1–V1*h* | 3.250 | 3.250 | 3.202 | 3.208 | 3.161 | 3.206 | 3.217 |
| | | V2–V2*j* | 3.250 | 3.250 | 3.189 | 3.190 | 3.229 | 3.220 | |
| | OCT1–OCT2 | V1–V3*c* | 3.040 | 2.998 | 2.930 | 2.947 | 2.944 | 2.943 | |
| | | V1–V3*g* | 2.973 | 2.983 | 3.009 | 3.039 | 3.040 | 3.054 | 3.005 |
| | | V2–V4*c* | 2.973 | 2.983 | 2.964 | 2.958 | 2.966 | 2.923 | |
| | | V2–V4*f* | 3.040 | 2.998 | 3.066 | 3.096 | 3.133 | 3.119 | |
| | OCT2–OCT3 | V3–V5*c* | | | | 2.878 | 2.937 | 2.899 | 2.868 |
| | | V4–V6*c* | | | | 2.823 | 2.828 | 2.838 | |
| | OCT3–OCT4 | V5–V7*c* | | | | | | 2.798 | 2.810 |
| | | V6–V8*c* | | | | | | 2.821 | |

[a, b] The distances of V–V for $V_4O_7$ and $V_5O_9$ were quoted from Marezio et al. (*13*, *14*). Standard errors for $V_3O_5$, $V_6O_{11}$, and $V_7O_{13}$ are around 0.005 Å.

TABLE VII

COMPARISON OF THE MEAN V–O AND O–O DISTANCES (Å), $s_{vO}$, $s_{OO}$, AND $s_{OvO}$

| | | $V_2O_3$[a] | $V_3O_5$ | $V_4O_7$[a] | $V_5O_9$[a] | $V_6O_{11}$ | $V_7O_{13}$ | $VO_2$[a] I | $VO_2$[a] II |
|---|---|---|---|---|---|---|---|---|---|
| Mean of V–O | OCT 1 | 2.010 | 1.999 | 1.977 | 1.969 | 1.964 | 1.964 | | |
| | OCT 2 | | 2.018 | 1.974 | 1.969 | 1.967 | 1.959 | | |
| | OCT 3 | | | | 1.951 | 1.955 | 1.942 | | |
| | OCT 4 | | | | | | 1.947 | | |
| | | | | | | | | 1.937 | 1.925 |
| Mean of O–O | OCT 1 | 2.832 | 2.794 | 2.765 | 2.752 | 2.743 | 2.744 | | |
| | OCT 2 | | 2.849 | 2.786 | 2.776 | 2.774 | 2.757 | | |
| | OCT 3 | | | | 2.755 | 2.762 | 2.743 | | |
| | OCT 4 | | | | | | 2.753 | | |
| | | | | | | | | 2.728 | 2.721 |
| $s_{vO}$ | OCT 1 | 2.2 | 5.6 | 5.8 | 6.2 | 6.9 | 6.9 | | |
| | OCT 2 | | 2.1 | 3.2 | 4.2 | 4.5 | 5.0 | | |
| | OCT 3 | | | | 1.0 | 2.2 | 2.5 | | |
| | OCT 4 | | | | | | 1.2 | | |
| | | | | | | | | 5.9 | 0.3 |
| $s_{OO}$ | OCT 1 | 3.9 | 5.9 | 5.4 | 5.2 | 5.4 | 5.1 | | |
| | OCT 2 | | 4.1 | 3.4 | 3.5 | 3.8 | 3.5 | | |
| | OCT 3 | | | | 2.9 | 2.8 | 2.8 | | |
| | OCT 4 | | | | | | 2.8 | | |
| | | | | | | | | 3.0 | 3.1 |
| $s_{OvO}$ | OCT 1 | 6.6 | 11.7 | 11.5 | 11.4 | 11.7 | 11.7 | | |
| | OCT 2 | | 5.2 | 5.4 | 6.7 | 6.6 | 6.5 | | |
| | OCT 3 | | | | 3.5 | 3.9 | 4.3 | | |
| | OCT 4 | | | | | | 3.5 | | |
| | | | | | | | | 6.8 | 4.0 |

[a] The values were calculated from the interatomic distances and angles by following references: $V_2O_3$, Dernier (*23*); $V_4O_7$, Marezio et al. (*13*) for V–O, O–O, $s_{vO}$ and $s_{OO}$, Horiuchi et al. (*10*) for $s_{OvO}$; $V_5O_9$, Marezio et al. (*14*) for V–O, O–O, $s_{vO}$, and $s_{OO}$, Horiuchi et al. (*10*) for $s_{OvO}$; $VO_2$ I (low temperature form), Longo and Kierkegaard (*24*); $VO_2$ II (high temperature form), McWhan et al. (*25*).

hedra change with the volume of the octahedra. Thus, the value of $v_n/(2n-1)$, where $v_n$ is the unit cell volume of $V_nO_{2n-1}$, is greater in the phase with smaller $n$ values, because the OCT1 or OCT2 occupy a greater part of the whole structure in the phase with smaller $n$ values. This result is in good agreement with that given by Horiuchi et al. (*5*).

### *d. Characteristics of $VO_6$ Octahedra*

It is of interest to note that the arrangements of oxygen atoms for $VO_2$ is denser than $V_2O_3$, though oxygen atoms of $V_2O_3$ arrange close to the ideal hexagonal close-packing and those of $VO_2$ a distorted hexagonal close-packing. This apparent conflict takes place because the size of octahedra is affected by the strong V–V interactions across the shared faces and edges especially in OCT1 and OCT2.

The octahedral configuration of oxygen atoms around vanadium atoms is also affected by the strong V–V interactions in the *CSP*. This effect is expressed quantitatively by $s_{OO}$, $s_{vO}$ and $s_{OvO}$ which are defined by the following equations:

$$s_{00} = \frac{100}{\bar{A}} \cdot \left[ \frac{\sum_{i=1}^{12} (A_i - \bar{A})^2}{11} \right]^{1/2}$$

$$s_{v0} = \frac{100}{\bar{B}} \cdot \left[ \frac{\sum_{i=1}^{6} (B_i - \bar{B})^2}{5} \right]^{1/2}$$

$$s_{0v0} = \frac{100}{90} \cdot \left[ \frac{\sum_{i=1}^{12} (C_i - 90)^2}{11} \right]^{1/2},$$

where $A_i$, $B_i$, and $C_i$ are the O–O, V–O distances and O–V–O angles in each octahedra, respectively, $\bar{A}$ and $\bar{B}$ are their mean values, and summations in the equations are calculated for all combinations of O–O, V–O, and O–V–O in each octahedron. The parts of the square roots in the equations, are the standard deviations of the distances of O–O and V–O and angles of O–V–O for each $VO_6$ octahedron (*26*). The values of $s_{00}$, $s_{v0}$, and $s_{0v0}$ are the standard deviations which are multiplied by 100 and divided by their mean values. The values of $s_{00}$, $s_{v0}$, and $s_{0v0}$ are listed (Table VII). The values of $s_{00}$ are effectively influenced by the distortion from the regular oxygen octahedran, and $s_{v0}$ and $s_{0v0}$, by both distortion and displacement of vanadium atoms from the centers of the oxygen octahedra.

The change of $s_{00}$, $s_{v0}$, and $s_{0v0}$ is most remarkable in the octahedra (OCT1) of the *CSP*. The distortion becomes less remarkable with the distances from the *CSP*. The values of $s_{00}$ become slightly smaller and those of $s_{v0}$ and $s_{0v0}$ become greater for the phase with larger $n$ values. This tendency is more remarkable in the OCT1 and in the octahedra nearer to the *CSP*.

Thus, when the part of the rutile-type structure is wide as in $V_6O_{11}$ or $V_7O_{13}$, the structural characteristics are represented by smaller expansion and distortion of oxygen octahedra and by greater displacement of vanadium atoms from the centers of octahedra. On the other hand, when the part of rutile-type structure is narrow as in $V_3O_5$ or $V_4O_7$, the structural characteristics are represented by greater expansion and distortion of octahedra and smaller displacement of vanadium atoms. The displacement of vanadium atoms from the centers of octahedra and the distortion of octahedra are small in the structure of $V_2O_3$ and the high temperature form $VO_2$ in comparison with the octahedra in the *CSP* (OCT1) of $V_nO_{2n-1}$ ($3 \leqslant n \leqslant 7$). In the low-temperature form $VO_2$, however, great displacement of vanadium atoms is observed though the distortion of octahedra is small. The features of octahedra (OCT1) of $V_nO_{2n-1}$ ($3 \leqslant n \leqslant 7$) at the *CSP* are quite different from those of $V_2O_3$, though both octahedra construct an infinite double chain shared by faces and edges in their structures. The structural characteristics of octahedra with greater distance from the *CSP* are, however, more similar to those of high temperature form $VO_2$.

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