

## The crystal structure of vanadium pentoxide

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With 1 figure

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### Auszug

Die Neubestimmung der Kristallstruktur von Vanadinpentoxyd,  $V_2O_5$ , wurde mit dreidimensionalen Daten — erhalten aus photographischen und Zählrohr-Aufnahmen — durchgeführt. Die Verfeinerung erfolgte durch Differentialsynthesen. Die Ergebnisse stimmen besser mit den Resultaten von BYSTRÖM, WILHELMI und BROTZEN überein als mit denen von KETELAAR. Die wahrscheinliche Raumgruppe ist  $Pmmn$  und die Gitterkonstanten betragen:  $a = 11,510 \text{ \AA}$ ,  $b = 4,369 \text{ \AA}$  und  $c = 3,563 \text{ \AA}$ . Die Struktur ist aufgebaut aus verzerrten, trigonal-bipyramidalen Koordinationspolyedern des Sauerstoffs um Vanadium, die sich mit gemeinsamen Kanten zu Doppelketten in Zickzackanordnung in Richtung  $[001]$  verknüpfen. Über gemeinsame Ecken in Richtung  $[100]$  verbinden sich die Doppelketten zu Schichten in der  $az$ -Ebene.

### Abstract

The crystal structure of vanadium pentoxide,  $V_2O_5$ , has been redetermined with three-dimensional data obtained by photographic and by counter methods, and has been refined by differential syntheses. The results are in closer agreement with those of BYSTRÖM, WILHELMI and BROTZEN than with those of KETELAAR. The probable space group is  $Pmmn$  and the unit-cell dimensions are  $a = 11.510 \text{ \AA}$ ,  $b = 4.369 \text{ \AA}$ ,  $c = 3.563 \text{ \AA}$ . The structure is built up from distorted trigonal bipyramidal coordination polyhedra of O around V, which share edges to form zigzag double chains along  $[001]$  and are cross-linked along  $[100]$  through shared corners, thus forming sheets in the  $az$  plane.

### Introduction

Crystal structures for vanadium pentoxide,  $V_2O_5$ , have been proposed by KETELAAR<sup>1</sup> and by BYSTRÖM, WILHELMI and BROTZEN<sup>2</sup> which differ in space group, and, to some extent, in atomic parameters.

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KETELAAR collected his data from rotation and powder photographs, estimated intensities visually on the former and photometrically on the latter, processed these data with the appropriate expression for each method, and took some account of absorption and temperature-factor effects. On the basis of the known crystal class and the systematically absent reflections he reduced the possible space groups to  $Pmn2_1$  and  $Pmnm$ . Optimum values for the variable parameters in each space group were deduced from the effect of changes in these parameters on the calculated intensities, and KETELAAR came to the conclusion that the space group must be  $Pmn2_1$ . As confirmatory evidence he cites hemimorphic symmetry of some of his crystals, a difference in the rates of solubility in dilute sodium hydroxide solution at opposite ends of the  $y$  axis, and some of the etch figures produced by this reagent on the (010) face.

BYSTRÖM, WILHELM and BROTZEN repeated the structure determination because they were dissatisfied with the very short (2.14 Å) distance between certain pairs of oxygen atoms in the structure proposed by KETELAAR. They redetermined the cell dimensions with focusing cameras, collected their intensity data from zero- and first-level [001] and [010] Weissenberg photographs, corrected for the Lorentz and polarization factors, and placed all values of  $|F_o|$  on the same scale. The signs of most of the  $F_o$ 's were established by the use of KETELAAR's coordinates for the first structure factor calculation. Refinement was carried out partly by trial and error, and partly on the basis of electron-density projections down [001], including a partial difference map for the calculation of which the contributions of the vanadium atoms were subtracted from the values of  $F_o$ . The final  $R$  factors were 0.10 for  $\{hk0\}$ , 0.14 for  $\{hkl\}$  and 0.14 for  $\{h0l\}$ . In the last case,  $F_o$  was replaced by  $F_{\text{corr}} = (1/K)F_o$ , for which  $K$  was obtained from a plot of  $F_o/F_c$  against  $h$ , but this correction

<sup>1</sup> J. A. A. KETELAAR, Die Kristallstruktur des Vanadinpentoxyds. Z. Kristallogr. **95** (1936) 9–27; Kristalstructuur en kolloïdehemische eigenschappen van vanadiumpentoxyde. Chem. Weekblad **33** (1936) 51–57; Crystal structure and shape of colloidal particles of vanadium pentoxide. Nature **137** (1936) 316.

<sup>2</sup> A. BYSTRÖM, K. A. WILHELM and O. BROTZEN, Vanadium pentoxide — a compound with five-coordinated vanadium atoms. Acta Chem. Scand. **4** (1950) 1119–1130. *Corrigenda*: p. 1119, KETELAAR's setting in  $C_{2v}^7$  should read  $Pmn2_1$ , KETELAAR's  $y$  for two O in 2(a) should read 0.08; p. 1125, setting in  $D_{2h}^{13}$  should read  $Pmnm$  (also p. 1129),  $y_1$  in third set of coordinates for 4V in 4(f) should read  $\bar{y}_1$ .

Table 1.

*Crystal data*

	K	B
<i>a</i>	$11.48 \pm 0.01 \text{ \AA}^*$	$11.519 \pm 0.006 \text{ \AA}$
<i>b</i>	$4.36 \pm 0.005 \text{ \AA}^*$	$4.373 \pm 0.002 \text{ \AA}$
<i>c</i>	$3.55 \pm 0.005 \text{ \AA}^*$	$3.564 \pm 0.002 \text{ \AA}$
Space group	$Pmn2_1 (C'_{2v})$	$Pnmm (D'_{2h})$
<i>Z</i>	2	2
<i>D<sub>c</sub></i>	3.37 g/ml	—
<i>D<sub>o</sub></i>	3.32 g/ml	—

*Fractional atomic coordinates*

	K			B		
	<i>x</i>	<i>y</i>	<i>z</i>	<i>x</i>	<i>y</i>	<i>z</i>
V	0.148	0.097	0	0.1486	0.105	0
O <sub>1</sub>	0.148	0.45	−0.08	0.149	0.458	0
O <sub>2</sub>	0.20	0.03	0.46	0.180	0	$\frac{1}{2}$
O <sub>3</sub>	0	0.08	−0.11	0	0	0

\* probably kX units;  $a = 11.50_3 \text{ \AA}$ ,  $b = 4.36_9 \text{ \AA}$ ,  $c = 3.55_7 \text{ \AA}$

K, KETELAAR<sup>1</sup>; B, BYSTRÖM, WILHELM and BROTZEN<sup>2</sup>

was applied only after final refinement of the atomic parameters, and is believed to take care of absorption, temperature factor, undefinable crystal effects, and perhaps spot shape<sup>3</sup>. BYSTRÖM *et al.* found no discrepancies between  $F_o$  and  $F_c$  to suggest that the space group should be  $Pmn2_1$  rather than  $Pnmm$ . They do not consider that arguments for hemihedral symmetry based on crystal habit are valid for  $V_2O_5$  grown from the melt because of the manner in which the crystals are attached to the walls of small cavities, and they report that the etch pits on (010) which they obtained with two concentrations of sodium hydroxide solution, and one of sulphuric acid, clearly demonstrate the presence of a centre of symmetry.

Unit-cell and space-group data, and the fractional coordinates of the atoms, for both structures are summarized in Table 1; V, O<sub>1</sub>, and

<sup>3</sup> K. A. WILHELM, Private communication (1952).

O<sub>2</sub> are in three sets of four-fold positions, and O<sub>3</sub> is in a set of two-fold positions. In  $Pmn2_1$ , these sets are

$$\begin{aligned} (b) \quad & x, y, z; \quad \bar{x}, y, z; \quad \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z; \quad \frac{1}{2} + x, \bar{y}, \frac{1}{2} + z, \\ (a) \quad & 0, y, z; \quad \frac{1}{2}, \bar{y}, \frac{1}{2} + z, \end{aligned}$$

while in  $Pmnm$ , they are

$$\begin{aligned} (f) \quad & \text{same as } Pmn2_1 (b), \text{ but with } z = 0 \text{ or } \frac{1}{2}, \\ (a) \quad & \text{same as } Pmn2_1 (a), \text{ but with } z = 0 \text{ or } \frac{1}{2}. \end{aligned}$$

KETELAAR interprets his structure in terms of chains of oxygen tetrahedra around V, sharing corners and extending parallel to [001], and cross-linked by additional corner sharing along [100] to form two-dimensional nets. This constitutes four-fold coordination of O around V (V—O, 1.57 Å to 1.83 Å), although KETELAAR does point out that the inclusion of an oxygen atom in an adjacent cell, and at the slightly greater distance of 2.02 Å from V, would increase the coordination to five-fold. MACHATSCHKI<sup>4</sup>, on the basis of fibre diagrams, reports cell dimensions of  $a = 11.4$  Å,  $b = 4.4$  Å,  $c = 3.55$  Å (probably kX units), but on morphological grounds contends that KETELAAR's structure should be considered solely in terms of single chains of tetrahedra parallel to [001] linked laterally along [100] by O bridges.

BYSTRÖM, WILHELM and BROTZEN, on the other hand, describe their structure in terms of distorted trigonal bipyramids sharing corners along [100] and [001]. In these coordination polyhedra they include the O at 2.02 Å from V, which had been rejected by KETELAAR but is only 1.88 Å from V in their structure, and they retain another O at 1.83 Å from V in KETELAAR's structure but which is at 2.02 Å from V in their own. Thus they consider the oxygen atoms to be five-fold coordinated in V<sub>2</sub>O<sub>5</sub>. BYSTRÖM *et al.* also draw attention to the fact that very distorted octahedral coordination could be achieved by the inclusion of a sixth O at the much greater V—O distance of 2.81 Å, but this would imply stronger bonds between successive V—O layers along [010] than would be expected from the perfect {010} cleavage. Finally, it may be noted that the adjacent pairs of corners of the trigonal bipyramids of BYSTRÖM *et al.* which are shared along [001]

<sup>4</sup> F. MACHATSCHKI, Über einen künstlichen anorganischen Faserstoff. *Naturwissenschaften* 24 (1936) 742–743.

define edges of the bipyramids so that it is more convenient to describe the structure as composed of double, or zigzag, chains of trigonal bipyramids sharing edges along [001] and cross-linked along [100] through shared corners.

MAGNÉLI and BLOMBERG<sup>5</sup> report the cell dimensions as  $a = 11.505 \text{ \AA}$ ,  $b = 4.373 \text{ \AA}$ ,  $c = 3.564 \text{ \AA}$  and the measured density as  $3.37^6$ . MAGNÉLI and OUGHTON<sup>7</sup> claim good agreement with the V and O parameters of BYSTRÖM *et al.* on the basis of an electron-density projection calculated from data collected with a zero-level [001] Weissenberg photograph, assuming  $z = 0$  or  $\frac{1}{2}$ .

In recent years the structures of a number of vanadium oxides and salts, including both mineral and synthetic specimens, have been studied in several laboratories. Many of these contain pentavalent vanadium so that the coordination polyhedra in vanadium pentoxide have become of increasing interest. The present investigation, therefore, was undertaken in an attempt to resolve the differences between KETELAAR and BYSTRÖM *et al.* on the basis of three-dimensional data of increased accuracy, although it was recognized from the start that the details of the structure proposed by BYSTRÖM *et al.* probably were essentially correct.

### Data collection and structure determination

Suitable crystals were obtained by inserting a thin brass rod into molten  $\text{V}_2\text{O}_5$ , contained in a crucible, and withdrawing the rod as soon as a cluster of needle-like crystals started to form at the tip. Unit cell and intensity data were collected both by photographic and by counter methods.

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<sup>5</sup> A. MAGNÉLI and B. BLOMBERG, Studies on the vanadium pentoxide-molybdenum trioxide system. II. Phase analysis. *Acta Chem. Scand.* **5** (1951) 585–589.

<sup>6</sup> The Handbook of Chemistry and Physics (Chemical Rubber Publishing Co. Cleveland, 1959) p. 681, gives the density as  $3.357 \text{ g/ml}$  at  $18^\circ\text{C}$ . The National Bureau of Standards Circular 539, Standard X-ray Diffraction Powder Patterns (U.S. Government Printing Office, Washington, 1959, vol. 8) gives  $a = 11.51 \text{ \AA}$ ,  $b = 3.559 \text{ \AA}$ ,  $c = 4.371 \text{ \AA}$  in  $Pmmn$ , calculated density =  $3.372 \text{ g/cm}^3$  at  $25^\circ\text{C}$ .

<sup>7</sup> A. MAGNÉLI, and B. M. OUGHTON, Studies on the vanadium pentoxide-molybdenum trioxide system. I. The relation between the crystal structures of the two oxides. *Acta Chem. Scand.* **5** (1951) 581–584.

*Photographic methods.* The unit cell dimensions were determined by the method of FARQUHAR and LIPSON<sup>8</sup> with  $\text{CuK}\alpha_1$  radiation ( $\lambda = 1.5443 \text{ \AA}$ ) as  $a = 11.496 \text{ \AA}$ ,  $b = 4.365 \text{ \AA}$ ,  $c = 3.560 \text{ \AA}$ , from which the calculated density ( $Z = 2$ ) is  $3.381 \text{ g/ml}$ . The space group was confirmed as  $Pmn2_1$  or  $Pmnm$  from Buerger precession photographs.

Intensity data were collected with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ). The crystals employed had cross-sections of approximately  $0.03 \text{ mm} \times 0.40 \text{ mm}$  and absorption corrections were not applied ( $\mu = 52 \text{ cm}^{-1}$ ). Two complete sets of three-dimensional data were obtained with the multiple-film equi-inclination Weissenberg method, from twenty-five levels along  $[100]$ , eight levels along  $[001]$ , and the  $h0l$  level. Those levels having reflections of suitable intensity for photometric measurements were recorded on both non-integrated and integrated films, and, even for the former, horizontal integration was adopted for all upper levels in order to reduce differences in spot size on the two halves of the patterns<sup>9</sup>. Visual estimations of intensities were made by comparison with a scale prepared with a rotating sector; photometric measurements were carried out with a split-beam photometer. With many reflections common to both non-integrated and integrated films, and by correlation of the reflections common among the various levels along  $[100]$  and  $[001]$ , after correction for the Lorentz and polarization factors, the intensities of all the observed reflections were placed on the same relative scale, and then on an approximately absolute scale<sup>10</sup>.

*Preliminary structure study.* While the collection of data for a three-dimensional analysis was proceeding, electron-density projections on  $(001)$  and on  $(010)$  were calculated on the basis of  $Pmn2_1$ , KETELAAR's coordinates, atomic scattering factors of THOMAS and FERMI<sup>11</sup> for V and of MCWEENY<sup>12</sup> for O, and a temperature factor

<sup>8</sup> M. C. M. FARQUHAR and H. LIPSON, The accurate determination of cell dimensions from single-crystal x-ray photographs. *Proc. Physic. Soc. [London]* **58** (1946) 200–206.

<sup>9</sup> E. STANLEY, A one-dimensional integrating method for estimating the intensities on upper-level equi-inclination Weissenberg photographs. *Acta Crystallogr.* **8** (1955) 58–59.

<sup>10</sup> A. J. C. WILSON, Determination of absolute from relative x-ray intensity data. *Nature* **150** (1942) 152.

<sup>11</sup> Internationale Tabellen zur Bestimmung von Kristallstrukturen (Borntraeger, Berlin 1935) 2. Band, 572.

<sup>12</sup> R. MCWEENY, X-ray scattering by aggregates of bonded atoms. I. Analytical approximations in single-atom scattering. *Acta Crystallogr.* **4** (1951) 513–519.

( $B = 0.4$ ) deduced from a Wilson plot. Refinement of the coordinates by the use of difference syntheses led to an  $R$  factor of approximately 0.15 for each zone, coordinates closer to those of BYSTRÖM *et al.*, and probable space group  $Pmnm$  ( $z = 0$  or  $\frac{1}{2}$  for all atoms), but indications that a small shift of  $O_1$  off the mirror plane might be necessary.

As soon as all the intensity data had been collected, therefore, a three-dimensional Patterson function was evaluated in order to obtain a new and unbiased set of atomic coordinates. All peaks in this synthesis occurred at  $z = 0$  or  $\frac{1}{2}$  except for one spurious peak at 0, 0.3, 0.4 of comparable weight to that for an O—O vector. It was clear, therefore, that any departure from  $Pmnm$  could only be due to very small shifts of one or more oxygen atoms away from the special positions for which  $z = 0$  or  $\frac{1}{2}$ . The  $R$  factor for all the observed three-dimensional data was 0.15<sub>6</sub> at this stage, based on  $Pmnm$ , the coordinates deduced from the Patterson synthesis (see Table 4), and the same atomic scattering curves and temperature factor as had been adopted for the projections. Observed and calculated differential syntheses, however, showed that the observed electron density for  $O_1$  was much less, and was more widely distributed in the  $xz$  plane, than the corresponding calculated density, or than either the observed or calculated electron densities for  $O_2$  or  $O_3$ .

Refinement, therefore, was carried out in  $Pmn2_1$ , with temperature-factor constants of  $B = 0.4$  for V and 0.6 for O, and scattering factor curves based on the values for  $V^{2+}$  and  $O^{1-}$  given by FREEMAN<sup>13</sup> (whose paper had just become available at this time) modified for low values of  $\sin \theta$  according to the degree of ionization assumed. One cycle of structure-factor calculations, followed by observed and calculated differential syntheses, and revision of the coordinates, reduced  $R$  to 0.14. Four additional cycles, including corrections for finite-summation errors, adjustment of isotropic temperature factors separately for each atom at every stage, and tests of the small-angle reflections ( $\sin \theta < 0.2$ ) with scattering factors for  $V^{5+}$  and  $O^{2-}$ ,  $V^{2.5+}$  and  $O^{1-}$ , and  $V^0$  and  $O^0$ , brought  $R$  down to 0.12<sub>5</sub>. The best agreement between  $F_o$  and  $F_c$  was obtained with the atomic scattering factors for  $V^{5+}$  and  $O^{2-}$ , and  $B = 0.5, 1.0, 0.7_5$ , and 0.9 for V,  $O_1$ ,  $O_2$ , and  $O_3$ , respectively. The r.m.s. of the estimated standard deviations of the atomic coordinates were 0.002 Å for V, and 0.009 Å for O, based on

<sup>13</sup> A. J. FREEMAN, Atomic scattering factors for spherical and aspherical charge distributions. *Acta Crystallogr.* **12** (1959) 261–271, Table 1.

CRUICKSHANK's method of estimation<sup>14</sup>, and including a factor of 2 because of the absence of a centre of symmetry<sup>15</sup>. The e.s.d.'s of the interatomic distances were 0.003 Å for V—V, 0.009 Å for V—O, and 0.013 Å for O—O.

Although these results were reasonably satisfactory, their reliability and accuracy were not as high as had been desired. Furthermore, it was found, as expected, that equally good agreement between the  $F_c$ 's and  $F_o$ 's could be obtained by refinement in  $Pmn\bar{m}$  and the use of anisotropic temperature factors to account for the small apparent departures of the fractional  $z$  coordinates of O<sub>1</sub> (0.029), O<sub>2</sub> (0.002), and O<sub>3</sub> (0.001) from 0 or  $\frac{1}{2}$ . With the exception of the  $z$  coordinate of O<sub>1</sub>, the maximum difference between any of the fractional coordinates resulting from refinement in  $Pmn2_1$  and in  $Pmn\bar{m}$  was only 0.003.

*Counter methods.* With the acquisition of a single-crystal orienter<sup>16</sup> for the x-ray spectrogoniometer it was decided to remeasure the unit-cell constants, and collect a new set of three-dimensional intensity data, with Mo radiation (Zr filter) and a krypton-filled proportional-counter tube.

The crystal selected had a cross-section of 0.06 mm  $\times$  0.10 mm and a length of 0.17 mm; it was mounted with its long axis (corresponding to  $c$ ) along the  $\varphi$ -axis of the goniostat. The cell dimensions were measured at a take-off angle of 1° and with a narrow slit (0.02°), and the values obtained were  $a = 11.510$  Å,  $b = 4.369$  Å,  $c = 3.563$  Å, with e.s.d.'s of 0.008 Å, 0.005 Å, 0.003 Å, respectively. The calculated density ( $Z = 2$ ) is 3.371 g/ml.

The integrated intensities of all 697 observable reflections within the range of  $\sin\theta$  from 0 to about 0.87 were measured at a take-off angle of 2° by the moving-counter moving-crystal method and fast scan<sup>16</sup>. An estimate of the background intensity, including that of the white radiation streak, for each reflection was obtained by setting the counter at the highest value of  $2\theta$  reached in the scan, leaving the goniostat settings ( $\varphi$ ,  $\chi$ ,  $\omega$ ) unchanged, and recording the count for the same time as that taken for the scan but with the crystal and counter stationary. The intensity of the 200 reflection was remeasured

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<sup>14</sup> D. W. J. CRUICKSHANK, The accuracy of electron-density maps in x-ray analysis with special reference to dibenzyl. *Acta Crystallogr.* **2** (1949) 65–82.

<sup>15</sup> D. W. J. CRUICKSHANK, Corrigenda: The accuracy of electron-density maps in x-ray analysis with special reference to dibenzyl. *Acta Crystallogr.* **3** (1950) 72–73.

<sup>16</sup> T. C. FURNAS, Single crystal orienter instruction manual (General Electric Co., Milwaukee, 1957).



at short intervals of time (20 to 40 minutes), and the values obtained were employed for the reduction of all the intensity data to the same scale on the assumption that any observed changes could be considered as uniform over these short time intervals. For each of the 00 $l$  reflections ( $\chi = 90^\circ$ ) it was found that the measured intensities remained constant from  $\varphi = 0^\circ$  to  $\varphi = 50^\circ$ , but dropped by 2% at  $\varphi = 60^\circ$ , 4% at  $\varphi = 70^\circ$ , 10% at  $\varphi = 80^\circ$ , and 17% at  $\varphi = 90^\circ$ ; this effect was attributed to absorption, and an approximate correction, taken as a function of  $\varphi$ , was applied to all measured intensities.

Calculation of the required instrument settings ( $\varphi$ ,  $\chi$ ,  $2\theta$ ), and of  $1/Lp$  (normal beam), for each possible reflection, and reduction of the observed data, including subtraction of background, application of scale and  $1/Lp$  factors, approximate absorption corrections, and computation of  $|F_o|$ , were carried out on an IBM 650 computer by means of specially prepared programmes.

*Final structure analysis.* The structure was first refined in  $Pmnm$  with the new data, because the only possibly significant departure from the centrosymmetrical space group obtained on the basis of the photographically recorded intensities was in the  $z$  coordinate of a single oxygen atom ( $O_1$ ). Three cycles of observed and calculated differential syntheses were carried out, including corrections for finite-summation errors. For the first cycle, the structure factors were calculated with the final atomic coordinates from the previous refinement in  $Pmnm$ , with atomic scattering factors for  $V^{2.5+}$  and  $O^{1-}$ , and with the same temperature-factor constant,  $B = 0.5$ , for all atoms. On this basis,  $R$  was 0.085 for all observed reflections, which was a marked improvement over the best values obtained previously. For the second cycle, the coordinates were altered according to the shifts indicated by the first set of differential syntheses, and separate isotropic temperature factors, with  $B = 0.5, 1.2, 0.7$ , and  $0.9$ , for  $V$ ,  $O_1$ ,  $O_2$ , and  $O_3$ , respectively, were introduced. As a result, the value of  $R$ , for the observed reflections, dropped to 0.07 $_4$ .

Anisotropic temperature-factor constants, with the values shown in Table 2, were derived from the relative values of the observed and calculated electron densities and curvatures for each atom obtained from the second set of differential syntheses. The relatively higher values of  $B_y$ , if not representative of a real temperature anisotropy, may arise from some inaccuracy in the estimation of the absorption corrections, which would be most serious along the direction of the  $y$  axis of the crystal employed for the data collection. At this stage,

also, the effects of atomic scattering curves for  $V^{5+}$  and  $O^{2-}$ ,  $V^{2.5+}$  and  $O^{1-}$ ,  $V^0$  and  $O^0$  were separately investigated as before by calculating the structure factors with each pair for the 22 reflections for which  $\sin \theta < 0.2$ , and it was found that both the overall and individual

Table 2. *Estimated anisotropic temperature factors ( $\text{\AA}^2$ )*

Space group	Atom	$B_x$	$B_y$	$B_z$	Mean
$Pmn2_1$	V	0.4	0.7	0.4	0.5
	O <sub>1</sub>	0.9 <sub>5</sub>	1.0	0.7 <sub>5</sub>	0.9
	O <sub>2</sub>	0.5 <sub>5</sub>	1.0	0.5 <sub>5</sub>	0.7
	O <sub>3</sub>	0.6 <sub>5</sub>	1.2	0.8 <sub>5</sub>	0.9
$Pmnm$	V	0.4	0.7	0.4	0.5
	O <sub>1</sub>	1.2	1.3	1.4	1.3
	O <sub>2</sub>	0.5	1.0	0.5	0.7
	O <sub>3</sub>	0.6	1.2	0.9	0.9

agreement between  $|F_c|$  and  $|F_o|$  for these reflections now was best for  $V^0$ ,  $O^0$ . The third, and final, set of structure factors, therefore, was calculated with coordinates modified according to the shifts indicated by the second set of differential syntheses, with the anisotropic temperature-factor constants listed in Table 2, and with atomic scattering curves for  $V^0$  and  $O^0$ . The final value of  $R$  for all observed reflections was 0.04<sub>4</sub>.

Table 3. *Observed and calculated electron densities ( $e.\text{\AA}^{-3}$ ) and curvatures ( $e.\text{\AA}^{-5}$ )*

Space group	Atom	$\rho$		$\rho_{xx}$		$\rho_{yy}$		$\rho_{zz}$	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
$Pmn2_1$	V	218	221	5876	5835	5783	5982	7174	7190
	O <sub>1</sub>	43	43	950	992	1263	1258	1069	1035
	O <sub>2</sub>	46	46	1243	1217	939	1000	1598	1545
	O <sub>3</sub>	44	44	1174	1091	1051	1104	1317	1351
$Pmnm$	V	219	221	5861	5809	5774	5947	7185	7162
	O <sub>1</sub>	41	39	928	908	1290	1220	840	841
	O <sub>2</sub>	47	47	1268	1261	988	1063	1616	1585
	O <sub>3</sub>	44	44	1170	1090	1065	1096	1318	1345

The third cycle of refinement gave the electron densities and curvatures shown in Table 3, where the comparatively high values

reflect the influence of the relatively low temperature factors. For example, the electron densities were recalculated with the same equations and numerical data except for the replacement of the temperature factors by a fictitious one for which  $B$  was assumed to

Table 4. *Fractional atomic coordinates*

Atom	PATTER- SON (3-D)	Final	
		$Pmn2_1$	$Pmnm$
V $x$	0.1487	0.1487	0.1487
	0.1075	0.1087	0.1086
	0	0.0000	0
O <sub>1</sub> $x$	0.1460	0.1460	0.1460
	0.4625	0.4709	0.4713
	0	0.0278	0
O <sub>2</sub> $x$	0.1807	0.1808	0.1809
	0.0050	0.0028	0.0026
	$\frac{1}{2}$	0.5036	$\frac{1}{2}$
O <sub>3</sub> $x$	0	0	0
	-0.0040	-0.0035	-0.0031
	0	0.0020	0

be 4.0 for all atoms; as a result, the values for the electron densities dropped to  $55 e \cdot \text{\AA}^{-3}$  for V and  $14 e \cdot \text{\AA}^{-3}$  for O.

Final values of the atomic coordinates obtained after application of the shifts indicated by the last refinement cycle in  $Pmnm$  are listed in Table 4, and various interatomic distances and angles are given in Table 5.

Refinement of the structure with the new data was then repeated in  $Pmn2_1$ , starting with the final atomic coordinates from the previous refinement in this space group, and following the same se-

quence as that adopted with the new data in  $Pmnm$ . The same atomic scattering factors, and the same isotropic temperature factor, were employed for the initial structure factor calculations, and the  $R$  factor was 0.08<sub>0</sub>. Separate isotropic temperature factors, with  $B = 0.5, 0.8_5, 0.7$ , and  $0.8_5$ , for V, O<sub>1</sub>, O<sub>2</sub>, and O<sub>3</sub>, respectively, were applied in the second structure-factor calculation, and the coordinates were adjusted by 1.7 times the corrected shifts indicated by the first set of differential syntheses. As a result,  $R$  dropped to 0.07<sub>5</sub>. At this stage the effects of scattering curves for V and O, with different degrees of ionization, on the small-angle reflections were examined, and again the best results were obtained with V<sup>0</sup>, O<sup>0</sup>. The anisotropic temperature-factor constants shown in Table 2 were derived from the results of the second set of differential syntheses. The last set of structure factors was calculated with coordinates modified by 1.7 times the corrected shifts indicated by the second set of differential syntheses, with the anisotropic temperature-factor constants listed in Table 2, and with atomic scattering curves for V<sup>0</sup> and O<sup>0</sup>. The final value of  $R$  for all observed reflections in this case was 0.04<sub>4</sub>.

Table 5. *Interatomic distances (Å) and angles (°) and estimated standard deviations of final values*(K, KETELAAR; B, BYSTRÖM, WILHELMI and BROTZEN; P, *present paper*)

	<i>Pmn2<sub>1</sub></i>		<i>Pnnm</i>		
	K	P	B	P	$\sigma$
V—O <sub>1</sub> (1)	1.565	1.586	1.544	1.585	0.004
V—O <sub>1</sub> (2)	2.835	2.788	2.829	2.785	0.005
V—O <sub>2</sub> (1)	1.836	2.022	2.027	2.021	0.003
V—O <sub>2</sub> (2)	1.763	1.889	1.875	1.878	0.002
V—O <sub>2</sub> (3)	2.029	1.865	1.875	1.878	0.002
V—O <sub>3</sub>	1.745	1.780	1.772	1.780	0.002
O <sub>1</sub> (1)—O <sub>2</sub> (1)	2.729	2.875	2.809	2.873	0.005
O <sub>1</sub> (1)—O <sub>2</sub> (2)	2.717	2.686	2.705	2.744	0.004
O <sub>1</sub> (1)—O <sub>2</sub> (3)	2.525	2.798	2.705	2.744	0.004
O <sub>1</sub> (1)—O <sub>3</sub>	2.345	2.670	2.638	2.668	0.005
O <sub>2</sub> (1)—O <sub>2</sub> (2)	2.130	2.390	2.403	2.388	0.003
O <sub>2</sub> (1)—O <sub>2</sub> (3)	2.130	2.390	2.403	2.388	0.003
O <sub>2</sub> (1)—O <sub>3</sub>	3.486	3.674	3.686	3.673	0.004
O <sub>2</sub> (2)—O <sub>2</sub> (3)	3.550	3.563	3.564	3.563	0.003
O <sub>2</sub> (2)—O <sub>3</sub>	3.068	2.743	2.734	2.740	0.003
O <sub>2</sub> (3)—O <sub>3</sub>	2.766	2.736	2.734	2.740	0.003
O <sub>1</sub> (2)—O <sub>2</sub> (1)	2.864	3.044	3.082	3.042	0.005
O <sub>1</sub> (2)—O <sub>2</sub> (2)	3.229	2.904	2.987	2.954	0.004
O <sub>1</sub> (2)—O <sub>2</sub> (3)	3.069	3.008	2.987	2.954	0.004
O <sub>1</sub> (2)—O <sub>3</sub>	3.232	2.847	2.926	2.846	0.005
O <sub>1</sub> (1)—V—O <sub>2</sub> (1)	106.4	105.0	102.9	105.0	0.2
O <sub>1</sub> (1)—V—O <sub>2</sub> (2)	109.3	100.9	104.1	104.5	0.3
O <sub>1</sub> (1)—V—O <sub>2</sub> (3)	88.3	108.1	104.1	104.5	0.3
O <sub>1</sub> (1)—V—O <sub>3</sub>	90.1	104.8	105.2	104.8	0.3
O <sub>2</sub> (1)—V—O <sub>2</sub> (2)	72.5	75.2	75.9	75.5	0.2
O <sub>2</sub> (1)—V—O <sub>2</sub> (3)	66.7	75.8	75.9	75.5	0.2
O <sub>2</sub> (1)—V—O <sub>3</sub>	153.5	150.1	151.9	150.1	0.2
O <sub>2</sub> (2)—V—O <sub>2</sub> (3)	138.7	143.3	143.7	143.1	0.2
O <sub>2</sub> (2)—V—O <sub>3</sub>	122.0	96.7	97.1	97.0	0.2
O <sub>2</sub> (3)—V—O <sub>3</sub>	94.0	97.2	97.1	97.0	0.2

The electron densities and curvatures given by the third set of differential syntheses are shown in Table 3, final values of the atomic coordinates (after application of 1.7 times the corrected shifts indicated by the last refinement cycle in *Pmn2<sub>1</sub>*) are listed in Table 4, and various interatomic distances and angles are given in Table 5.

For comparison purposes, the interatomic distances and angles in the structures according to KETELAAR and to BYSTRÖM *et al.* have

Table 6. *Designations of reference atoms*  
(P, *present paper*; K, KETELAAR; B, BYSTRÖM, WILHELMI and BROTZEN)

P	Equipoints			K	B
V	$x_1$	$y_1$	$z_1$	V	V
O <sub>1</sub> (1)	$x_2$	$y_2$	$z_2$	O <sub>1</sub>	O <sub>1</sub>
O <sub>1</sub> (2)	$x_2$	$y_2-1$	$z_2$		O <sub>1</sub>
O <sub>2</sub> (1)	$\frac{1}{2}-x_3$	$\bar{y}_3$	$z_3-\frac{1}{2}$	O <sub>2</sub>	O <sub>2</sub>
O <sub>2</sub> (2)	$x_3$	$y_3$	$z_3$	O <sub>3</sub>	O <sub>2</sub>
O <sub>2</sub> (3)	$x_3$	$y_3$	$z_3-1$	O <sub>3</sub>	O <sub>2</sub>
O <sub>3</sub>	0	$y_4$	$z_4$	O <sub>4</sub>	O <sub>3</sub>

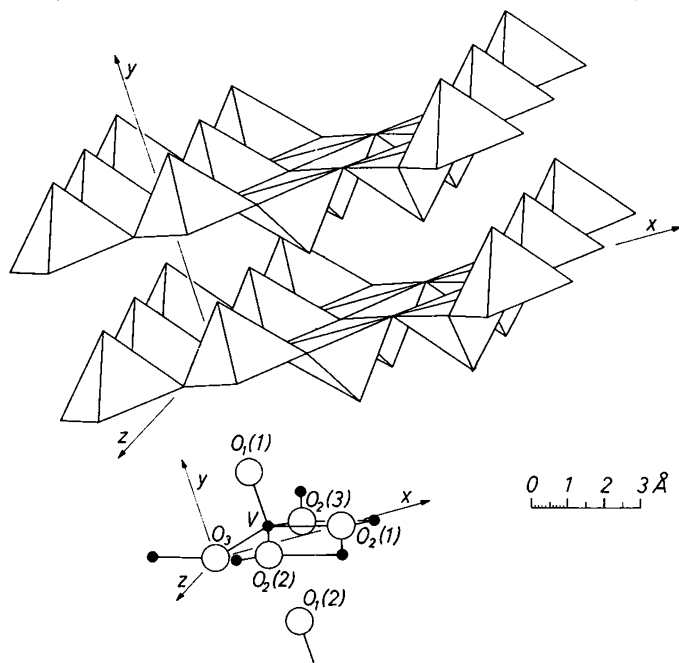


Fig. 1.

been included in Table 5; all values have been recalculated from the unit-cell dimensions and fractional atomic coordinates of Table 1, and the appropriate equipoints of Table 6, regardless of whether or not they are given in the original papers.

It is obvious from the data in Table 4 that the only apparently significant difference between the fractional coordinates of any of the atoms obtained after refinement of the structure separately in the two space groups is 0.0278 for the  $z$  coordinate of O<sub>1</sub>. But this is a relatively

doubtful discrepancy because it is shown by a single coordinate of a relatively light atom which is comparatively close to a much heavier one,  $V-O_1(1) = 1.585 \text{ \AA}$ , in a non-centrosymmetrical space group. Thus, an arbitrary displacement of  $O_1$  to  $z = 0.0140$ , followed by a cycle of structure-factor calculations, and observed and calculated differential syntheses, indicated a compensatory correction shift only to  $z = 0.0162$ , while the corresponding result for a larger displacement in the opposite direction to  $z = 0.0560$ , after a similar cycle of refinement, was an indicated correction shift to  $z = 0.0388$ . With  $z$  of  $O_1$  so close to zero, its final value after refinement in  $Pmn2_1$  depends largely on where it is placed at the start.

No significance, therefore, can be attached to the departures from 0 or  $\frac{1}{2}$  of the  $z$  coordinates after refinement in  $Pmn2_1$  (Table 4). The space group may be accepted as  $Pmnm$ , and the fractional atomic coordinates as those in the last column of Table 4. If the space group really is  $Pmn2_1$ , only the sites of the oxygen atoms can be involved, and probably that of  $O_1$  alone, and displacement from the mirror plane must be too small for unequivocal detection.

The final structure, with space group  $Pmnm$ , as determined in the present investigation is represented in terms of trigonal bipyramidal coordination polyhedra in Fig. 1.

### Accuracy

The observed structure amplitudes,  $|F_o|$ , and the final calculated structure factors,  $F_c$ , for  $Pmnm$  are given in Table 7.

The structure amplitudes of the 697 observed reflections vary from 3 to 96. The error,  $|\Delta F| = ||F_o| - |F_c||$ , is small in all cases; it is  $< 3$  except in the case of six reflections, for each of which  $|\Delta F| < 6$  and  $|\Delta F| / |F_o| < 13\%$ . Values of the structure amplitudes calculated for the 240 unobserved reflections, which are within the same  $\sin \theta$  range as those observed, also are very small with a maximum of 4.7. According to the method of CRUICKSHANK<sup>14</sup> the r.m.s. of the e.s.d.'s of the final atomic coordinates are  $0.0005 \text{ \AA}$  for V, and  $0.002 \text{ \AA}$  for O. The e.s.d.'s of the V—O and O—O distances are approximately  $0.002 \text{ \AA}$  and  $0.003 \text{ \AA}$ , respectively, and the e.s.d. of the O—V—O angles is about  $0.2^\circ$ . These values, however, may be too low because of the effect of the heavier V on the accuracy with which the positions of the lighter O's can be established, and the e.s.d.'s of the coordinates of  $O_1$ ,  $O_2$ , and  $O_3$  may be expected to be influenced to different degrees by their relative proximity to V.

Table 7. *Observed and calculated structure factors\**

h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>	h k l	F <sub>o</sub>	F <sub>c</sub>
2 0 0	42.5	-37.0	21 2 0	12.1	12.3	13 5 0	<4.3	-3.6	21 0 1	16.3	16.1
4 0 0	76.4	-73.7	22 2 0	<4.7	4.6	14 5 0	18.9	-19.8	23 0 1	16.8	-15.6
6 0 0	87.2	86.3	23 2 0	14.6	-13.3	15 5 0	<4.5	-0.2	25 0 1	<4.6	0.2
8 0 0	20.9	19.4	24 2 0	4.8	-4.4	16 5 0	17.1	17.0	27 0 1	12.8	13.0
10 0 0	45.0	-42.8	25 2 0	<4.5	-2.9	0 6 0	6.3	-5.9	0 1 1	49.9	49.7
12 0 0	17.3	15.0	26 2 0	<4.3	2.5	1 6 0	13.5	-13.3	1 1 1	19.9	21.7
14 0 0	29.5	28.1	27 2 0	12.5	11.9	2 6 0	<4.0	2.6	2 1 1	14.0	-14.0
16 0 0	14.5	-14.4	0 3 0	14.9	-14.8	3 6 0	20.0	20.1	3 1 1	3.3	-0.8
18 0 0	10.9	-10.5	1 3 0	29.7	30.6	4 6 0	9.7	10.6	4 1 1	36.2	-36.6
20 0 0	23.0	21.2	2 3 0	7.7	7.3	5 6 0	<4.1	1.2	5 1 1	6.1	-5.8
22 0 0	<4.7	3.1	3 3 0	42.6	-46.5	6 6 0	<4.1	-3.8	6 1 1	28.4	29.0
24 0 0	16.9	-16.3	4 3 0	28.5	28.8	7 6 0	18.9	-19.7	7 1 1	34.3	34.3
26 0 0	10.6	10.0	5 3 0	<2.7	-2.2	8 6 0	5.2	-5.6	8 1 1	12.1	12.0
28 0 0	10.8	10.1	6 3 0	7.4	-7.6	9 6 0	9.0	9.2	9 1 1	<2.9	-2.3
30 0 0	11.6	-11.5	7 3 0	36.7	37.7	10 6 0	10.9	12.7	10 1 1	26.9	-26.4
0 1 0	80.2	77.6	8 3 0	12.8	-12.8	11 6 0	11.6	12.0	11 1 1	18.8	-17.9
1 1 0	36.4	33.2	9 3 0	16.6	-17.9	12 6 0	<4.5	0.7	12 1 1	4.6	4.4
2 1 0	15.3	-14.8	10 3 0	25.7	25.0	13 6 0	14.7	-14.8	13 1 1	26.4	24.8
3 1 0	50.4	-48.6	11 3 0	20.0	-19.9	14 6 0	8.8	-9.2	14 1 1	16.8	16.8
4 1 0	16.7	-19.5	12 3 0	<4.3	2.4	15 6 0	<4.7	-2.5	15 1 1	5.4	5.2
5 1 0	<2.6	-2.1	13 3 0	23.4	23.2	16 6 0	8.3	9.1	16 1 1	12.8	-12.0
6 1 0	44.9	47.5	14 3 0	13.9	-15.7	0 7 0	5.5	5.0	17 1 1	17.5	-17.2
7 1 0	35.3	36.0	15 3 0	<4.1	3.2	1 7 0	7.9	-9.6	18 1 1	6.5	-6.8
8 1 0	2.6	3.4	16 3 0	15.1	14.2	2 7 0	<4.6	-0.9	19 1 1	13.5	12.4
9 1 0	17.0	-15.9	17 3 0	20.3	-20.1	3 7 0	13.9	14.6	20 1 1	13.8	12.7
10 1 0	16.0	-16.5	18 3 0	7.6	7.2	4 7 0	<4.6	0.3	21 1 1	10.2	9.3
11 1 0	16.7	-16.8	19 3 0	7.4	7.5	5 7 0	<4.6	0.6	0 2 1	49.9	53.3
12 1 0	13.8	12.3	20 3 0	10.2	-10.6	6 7 0	<4.6	4.2	1 2 1	18.3	17.8
13 1 0	20.0	19.2	21 3 0	13.1	11.7	7 7 0	13.4	-14.7	2 2 1	13.7	-15.6
14 1 0	13.4	13.0	22 3 0	5.8	5.0	8 7 0	<4.6	-1.3	3 2 1	<2.6	-1.3
15 1 0	<3.7	2.5	23 3 0	13.4	-12.1	9 7 0	6.2	7.4	4 2 1	37.4	-40.6
16 1 0	6.1	-6.2	0 4 0	15.8	-17.8	10 7 0	<4.7	1.5	5 2 1	6.6	-6.2
17 1 0	15.7	-15.7	1 4 0	6.3	5.9	11 7 0	7.7	9.0	6 2 1	31.4	33.2
18 1 0	<4.5	-4.3	2 4 0	6.6	7.4	12 7 0	<4.8	2.4	7 2 1	24.7	24.0
19 1 0	5.5	6.0	3 4 0	9.6	-10.2	13 7 0	10.2	-12.1	8 2 1	13.5	14.1
20 1 0	13.0	12.3	4 4 0	23.1	25.5	0 8 0	14.3	13.6	9 2 1	4.5	2.9
21 1 0	10.0	9.0	5 4 0	<3.1	0	1 8 0	7.7	-7.6	10 2 1	33.3	-33.3
22 1 0	<4.7	2.9	6 4 0	10.6	-11.9	2 8 0	<5.0	-3.6	11 2 1	13.4	-12.0
23 1 0	9.6	-9.3	7 4 0	8.1	8.4	3 8 0	12.2	11.4	12 2 1	7.7	6.1
24 1 0	11.3	-10.1	8 4 0	10.6	-11.6	4 8 0	7.4	-7.8	13 2 1	15.4	15.0
25 1 0	<4.6	-2.2	9 4 0	4.6	-5.2	5 8 0	<4.8	0.8	14 2 1	22.4	22.0
26 1 0	7.4	7.1	10 4 0	25.2	26.5	6 8 0	9.9	10.4	15 2 1	6.1	5.2
27 1 0	8.2	8.4	11 4 0	4.6	-4.7	7 8 0	11.8	-11.6	16 2 1	16.4	-16.6
28 1 0	6.7	7.3	12 4 0	<3.9	-0.2	8 8 0	<4.8	2.3	17 2 1	9.0	-9.0
0 2 0	63.8	61.8	13 4 0	5.4	6.5	9 8 0	6.1	5.3	18 2 1	9.3	-9.0
1 2 0	32.0	34.0	14 4 0	17.8	-18.1	10 8 0	6.7	-7.3	19 2 1	7.4	7.6
2 2 0	11.3	-11.3	15 4 0	<4.3	0.3	0 9 0	13.9	14.1	0 3 1	46.0	47.2
3 2 0	49.9	-52.4	16 4 0	17.7	17.1	1 9 0	<5.1	-0.2	1 3 1	17.3	-17.8
4 2 0	17.3	-17.0	17 4 0	6.2	-6.0	2 9 0	<5.0	-3.9	2 3 1	12.1	-13.5
5 2 0	<2.6	-1.7	18 4 0	7.5	8.1	3 9 0	<5.0	-0.1	3 3 1	41.3	43.1
6 2 0	33.7	34.3	19 4 0	<4.7	2.5	4 9 0	9.4	-9.2	4 3 1	34.1	-36.8
7 2 0	39.0	40.9	20 4 0	13.8	-14.6	5 9 0	<4.8	0	5 3 1	<2.8	-1.6
8 2 0	3.5	2.7	0 5 0	24.4	-23.5	6 9 0	9.8	10.7	6 3 1	28.4	30.0
9 2 0	21.2	-20.0	1 5 0	<3.6	-2.4	7 9 0	<4.7	-0.4	7 3 1	17.7	-18.2
10 2 0	7.5	-7.1	2 5 0	8.5	8.0				8 3 1	12.6	13.6
11 2 0	20.1	-20.9	3 5 0	4.3	3.1	1 0 1	63.3	63.6	9 3 1	19.1	18.1
12 2 0	7.7	7.7	4 5 0	25.5	26.5	3 0 1	53.1	-55.0	10 3 1	30.5	-31.0
13 2 0	26.0	25.0	5 5 0	<3.6	0	5 0 1	11.9	-10.9	11 3 1	9.2	9.1
14 2 0	7.4	5.9	6 5 0	14.6	-15.3	7 0 1	73.4	73.5	12 3 1	5.5	5.0
15 2 0	<3.9	2.8	7 5 0	<3.8	-3.8	9 0 1	14.8	-14.8	13 3 1	8.3	-8.3
16 2 0	<4.1	0.6	8 5 0	11.7	-12.4	11 0 1	34.9	-34.1	14 3 1	22.0	21.2
17 2 0	21.6	-21.2	9 5 0	<3.9	1.8	13 0 1	41.4	40.1	15 3 1	<4.1	0.8
18 2 0	<4.3	-1.9	10 5 0	26.7	27.7	15 0 1	9.3	8.8	16 3 1	15.1	-15.3
19 2 0	8.9	8.6	11 5 0	<4.1	2.2	17 0 1	29.5	-29.0	17 3 1	10.6	10.1
20 2 0	4.8	4.7	12 5 0	<4.4	-0.8	19 0 1	16.1	15.7	18 3 1	9.4	-8.9

Table 7 (continued)

h k l	$ F_o $	$F_c$	h k l	$ F_o $	$F_c$	h k l	$ F_o $	$F_c$	h k l	$ F_o $	$F_c$
19 3 1	< 4.6	0.7	10 7 1	11.8	13.5	5 2 2	< 3.0	- 1.4	8 5 2	11.1	- 11.3
20 3 1	17.1	16.5	0 8 1	13.8	- 12.9	6 2 2	25.0	24.2	9 5 2	< 4.1	1.8
0 4 1	9.6	9.2	1 8 1	6.7	6.0	7 2 2	34.0	34.3	10 5 2	24.9	25.4
1 4 1	15.3	- 16.7	2 8 1	< 5.0	3.6	8 2 2	< 3.1	2.1	11 5 2	< 4.3	2.2
2 4 1	< 3.1	- 3.0	3 8 1	6.7	- 6.3	9 2 2	17.5	- 17.1	12 5 2	< 4.3	- 0.7
3 4 1	34.4	36.7	4 8 1	9.6	10.1	10 2 2	6.1	- 5.9	13 5 2	< 4.5	- 3.4
4 4 1	7.3	- 8.0	5 8 1	< 4.8	- 1.4	11 2 2	18.0	- 18.4	14 5 2	17.0	- 18.5
5 4 1	< 3.2	- 1.5	6 8 1	9.8	- 9.5	12 2 2	6.8	6.7	15 5 2	< 4.6	- 0.3
6 4 1	6.5	6.7	7 8 1	10.0	10.2	13 2 2	23.3	22.7	16 5 2	15.0	15.9
7 4 1	18.1	- 20.4	8 8 1	5.1	- 4.2	14 2 2	5.8	5.1	0 6 2	6.5	- 5.7
8 4 1	< 3.5	3.0	9 8 1	< 4.8	- 2.4	15 2 2	< 4.1	2.6	1 6 2	12.8	- 12.1
9 4 1	18.8	18.4	10 8 1	9.7	10.4	16 2 2	< 4.2	0.6	2 6 2	< 4.3	2.5
10 4 1	8.4	- 8.3	0 9 1	< 5.1	- 0.6	17 2 2	20.1	- 19.9	3 6 2	18.3	18.3
11 4 1	10.3	10.8	1 9 1	8.1	6.8	18 2 2	< 4.5	- 1.7	4 6 2	9.5	9.9
12 4 1	< 4.0	1.6	2 9 1	< 5.0	0.2	19 2 2	8.2	8.1	5 6 2	< 4.3	1.1
13 4 1	12.6	- 13.6	3 9 1	9.0	- 8.6	20 2 2	5.4	4.2	6 6 2	< 4.3	- 3.7
14 4 1	6.7	5.9	4 9 1	< 4.9	0.2	21 2 2	11.6	11.6	7 6 2	17.2	- 18.1
15 4 1	< 4.3	0.7	5 9 1	< 4.8	- 1.3	22 2 2	5.7	4.3	8 6 2	5.1	- 5.4
16 4 1	5.2	- 5.1	6 9 1	< 4.8	- 0.6	23 2 2	13.2	- 12.7	9 6 2	8.2	8.5
17 4 1	13.9	14.0	7 9 1	10.3	11.3	0 3 2	11.8	- 12.4	10 6 2	9.8	11.9
0 5 1	4.1	- 4.6				1 3 2	24.4	24.0	11 6 2	10.8	11.1
1 5 1	18.2	- 18.0	0 0 2	95.6	101.3	2 3 2	6.5	5.6	12 6 2	< 4.7	0.7
2 5 1	< 3.6	1.3	2 0 2	23.2	- 23.8	3 3 2	35.6	- 37.0	13 6 2	12.1	- 13.8
3 5 1	34.4	35.4	4 0 2	50.3	- 52.0	4 3 2	22.3	22.1	14 6 2	7.7	- 8.9
4 5 1	< 3.6	2.9	6 0 2	59.9	60.6	5 3 2	< 3.1	- 1.7	0 7 2	< 4.9	4.7
5 5 1	< 3.7	- 0.4	8 0 2	15.6	15.1	6 3 2	6.7	- 6.9	1 7 2	8.3	- 9.0
6 5 1	3.9	- 3.6	10 0 2	36.2	- 35.8	7 3 2	31.9	31.8	2 7 2	< 4.8	- 0.9
7 5 1	22.2	- 23.2	12 0 2	12.9	12.7	8 3 2	10.6	- 10.6	3 7 2	12.6	13.7
8 5 1	< 3.9	- 0.9	14 0 2	25.2	24.9	9 3 2	15.7	- 15.5	4 7 2	< 4.7	0.2
9 5 1	16.7	17.7	16 0 2	13.6	- 13.4	10 3 2	22.5	21.5	5 7 2	< 4.7	0.6
10 5 1	< 4.1	3.3	18 0 2	9.6	- 9.8	11 3 2	17.4	- 17.6	6 7 2	< 4.7	3.9
11 5 1	12.8	13.2	20 0 2	20.6	19.8	12 3 2	< 3.9	2.1	7 7 2	12.6	- 13.9
12 5 1	< 4.3	- 1.4	22 0 2	< 4.7	3.0	13 3 2	20.6	21.2	0 8 2	11.9	12.8
13 5 1	15.4	- 15.1	24 0 2	15.0	- 15.4	14 3 2	13.8	- 14.2	1 8 2	7.5	- 7.1
14 5 1	< 4.5	- 2.6	0 1 2	52.4	53.8	15 3 2	< 4.2	2.9	2 8 2	< 5.0	- 3.4
15 5 1	< 4.5	- 0.5	1 1 2	23.6	23.2	16 3 2	13.8	13.1	3 8 2	9.9	10.7
16 5 1	< 4.6	2.2	2 1 2	10.9	- 11.5	17 3 2	18.9	- 18.7	4 8 2	7.1	- 7.4
17 5 1	15.9	15.6	3 1 2	34.9	- 35.0	18 3 2	5.7	6.6	5 8 2	< 5.0	0.7
0 6 1	22.5	- 22.3	4 1 2	17.9	- 18.7	19 3 2	7.9	7.1	6 8 2	8.6	9.7
1 6 1	6.8	- 6.8	5 1 2	< 2.6	- 1.5	20 3 2	10.5	- 9.9	7 8 2	10.4	- 10.7
2 6 1	6.6	6.3	6 1 2	35.3	35.6	0 4 2	15.7	- 16.5	0 9 2	12.1	13.3
3 6 1	15.7	16.4	7 1 2	28.0	27.9	1 4 2	5.5	5.4			
4 6 1	17.2	17.4	8 1 2	3.5	4.2	2 4 2	6.1	6.5	1 0 3	30.8	31.9
5 6 1	< 4.1	- 1.0	9 1 2	13.7	- 13.1	3 4 2	8.4	- 9.2	3 0 3	32.1	- 33.8
6 6 1	14.8	- 16.0	10 1 2	15.3	- 15.5	4 4 2	19.9	22.3	5 0 3	6.2	- 5.6
7 6 1	7.6	- 8.4	11 1 2	15.0	- 14.5	5 4 2	< 3.5	- 0.1	7 0 3	44.9	45.3
8 6 1	6.7	- 7.2	12 1 2	11.4	10.5	6 4 2	9.8	- 11.0	9 0 3	11.3	- 11.5
9 6 1	7.2	9.3	13 1 2	17.5	17.0	7 4 2	7.3	7.7	11 0 3	26.4	- 25.5
10 6 1	16.2	17.4	14 1 2	12.9	12.1	8 4 2	9.9	- 10.4	13 0 3	33.5	31.9
11 6 1	5.0	4.5	15 1 2	< 4.4	2.3	9 4 2	4.4	- 4.7	15 0 3	7.5	7.1
12 6 1	< 4.6	- 3.4	16 1 2	6.8	- 6.0	10 4 2	23.1	24.1	17 0 3	26.4	- 24.9
13 6 1	5.1	- 5.2	17 1 2	15.0	- 14.5	11 4 2	4.4	- 4.5	19 0 3	14.3	13.7
14 6 1	12.2	- 13.2	18 1 2	< 4.8	- 4.2	12 4 2	< 4.1	- 0.3	21 0 3	15.3	13.9
15 6 1	< 4.7	0.8	19 1 2	6.1	5.6	13 4 2	5.4	6.1	0 1 3	28.9	28.2
16 6 1	8.5	9.3	20 1 2	12.9	11.6	14 4 2	15.2	- 17.1	1 1 3	15.1	15.1
0 7 1	15.2	- 16.4	21 1 2	8.9	8.5	15 4 2	< 4.5	0.3	2 1 3	7.9	- 8.1
1 7 1	< 4.7	0.3	22 1 2	< 4.7	2.8	16 4 2	16.8	16.0	3 1 3	9.4	- 10.1
2 7 1	< 4.6	4.7	23 1 2	8.4	- 8.9	0 5 2	21.3	- 20.8	4 1 3	21.7	- 22.0
3 7 1	< 4.6	3.6	24 1 2	10.2	- 9.7	1 5 2	< 3.9	- 2.3	5 1 3	3.2	- 3.6
4 7 1	10.7	12.7	25 1 2	< 4.5	- 2.1	2 5 2	7.3	7.0	6 1 3	19.9	18.7
5 7 1	< 4.6	- 1.2	0 2 2	40.5	39.1	3 5 2	< 3.9	3.1	7 1 3	25.0	24.9
6 7 1	11.3	- 12.2	1 2 2	25.9	26.1	4 5 2	23.0	23.6	8 1 3	8.4	8.4
7 7 1	< 4.6	2.0	2 2 2	7.4	- 7.6	5 5 2	< 3.9	0	9 1 3	< 3.5	- 3.6
8 7 1	4.7	- 5.1	3 2 2	39.8	- 40.4	6 5 2	14.0	- 14.0	10 1 3	20.5	- 19.7
9 7 1	< 4.7	2.6	4 2 2	13.0	- 12.0	7 5 2	4.4	- 3.7	11 1 3	14.7	- 14.6



Table 7 (continued)

h k l	$ F_o $	$F_e$	h k l	$ F_o $	$F_e$	h k l	$ F_o $	$F_e$	h k l	$ F_o $	$F_e$
12 1 3	3.9	3.5	0 5 3	<4.4	- 4.2	12 1 4	8.8	7.7	9 5 4	<4.5	1.6
13 1 3	21.6	20.6	1 5 3	15.3	- 14.6	13 1 4	14.2	13.2	10 5 4	20.0	20.4
14 1 3	13.8	14.0	2 5 3	<4.2	1.2	14 1 4	9.7	10.0	0 6 4	5.4	- 5.0
15 1 3	4.5	4.4	3 5 3	27.9	28.6	15 1 4	<4.5	1.8	1 6 4	9.8	- 9.6
16 1 3	10.6	- 10.2	4 5 3	<4.2	2.8	16 1 4	5.2	- 5.2	2 6 4	<4.8	1.9
17 1 3	15.6	- 15.4	5 5 3	<4.2	- 0.4	17 1 4	11.9	- 11.9	3 6 4	14.5	14.5
18 1 3	5.8	- 5.9	6 5 3	<4.3	- 3.3	0 2 4	21.3	18.8	4 6 4	7.7	8.1
19 1 3	11.5	10.9	7 5 3	18.9	- 19.6	1 2 4	16.8	16.5	5 6 4	<4.7	0.9
20 1 3	11.3	11.2	8 5 3	<4.3	- 1.0	2 2 4	4.5	- 4.0	6 6 4	<4.7	- 3.2
21 1 3	9.7	8.4	9 5 3	14.6	14.9	3 2 4	25.6	- 26.0	7 6 4	14.3	- 14.5
0 2 3	35.1	34.9	10 5 3	<4.5	3.2	4 2 4	7.7	- 6.6	8 6 4	<4.8	- 4.6
1 2 3	9.3	8.8	11 5 3	11.4	11.2	5 2 4	<3.7	- 1.0	9 6 4	6.5	6.9
2 2 3	10.3	- 10.2	0 6 3	19.9	- 18.8	6 2 4	14.2	13.9	10 6 4	9.0	9.9
3 2 3	<3.1	- 1.6	1 6 3	6.6	- 6.1	7 2 4	23.4	23.9	0 7 4	<5.0	3.9
4 2 3	27.3	- 27.6	2 6 3	6.7	5.3	8 2 4	<3.9	0.9	1 7 4	7.7	- 7.7
5 2 3	5.0	- 3.6	3 6 3	13.4	14.1	9 2 4	13.1	- 12.5	2 7 4	<5.0	- 0.8
6 2 3	24.1	24.0	4 6 3	14.6	14.7	10 2 4	5.0	- 4.0	3 7 4	11.3	11.6
7 2 3	16.0	14.8	5 6 3	<4.5	- 1.0	11 2 4	14.2	- 14.2	4 7 4	<4.9	0
8 2 3	10.4	10.6	6 6 3	13.5	- 13.6	12 2 4	5.2	4.9	5 7 4	<4.8	0.5
9 2 3	<3.6	1.9	7 6 3	7.0	- 7.5	13 2 4	18.5	18.2	6 7 4	<4.8	3.3
10 2 3	25.8	- 26.1	8 6 3	5.8	- 6.2	14 2 4	<4.5	3.5	7 7 4	11.9	- 11.9
11 2 3	10.9	- 9.1	9 6 3	6.9	8.1	15 2 4	<4.6	- 2.2	8 7 4	10.6	10.7
12 2 3	5.4	5.0	10 6 3	14.5	15.1	16 2 4	<4.6	0.6	1 8 4	5.7	- 5.8
13 2 3	12.4	11.7	0 7 3	13.5	- 14.6	17 2 4	16.7	- 16.6	2 8 4	<4.9	- 2.9
14 2 3	18.4	18.9	1 7 3	<4.9	0.3	0 3 4	7.6	- 8.2	3 8 4	8.7	8.8
15 2 3	5.0	4.2	2 7 3	<4.9	4.2	1 3 4	16.1	15.4	4 8 4	5.5	- 6.3
16 2 3	14.8	- 14.4	3 7 3	<4.9	3.0	2 3 4	<3.8	3.3	5 8 4	<4.7	0.6
17 2 3	7.9	- 7.7	4 7 3	10.3	11.3	3 3 4	24.3	- 24.3	6 8 4	7.9	8.2
18 2 3	7.8	- 8.0	5 7 3	<4.8	- 1.1	4 3 4	13.8	13.9	7 8 4	9.0	- 9.0
19 2 3	7.1	6.6	6 7 3	10.0	- 11.0	5 3 4	<4.0	- 1.1	8 8 4	9.8	11.3
0 3 3	33.0	32.1	7 7 3	<4.8	1.8	6 3 4	6.1	- 4.9			
1 3 3	12.2	- 11.7	8 7 3	<4.8	- 4.7	7 3 4	23.1	22.6	1 0 5	16.8	17.5
2 3 3	8.8	- 9.3	9 7 3	<4.8	2.2	8 3 4	8.3	- 7.6	3 0 5	19.9	- 20.3
3 3 3	27.5	27.3	10 7 3	10.3	12.2	9 3 4	12.6	- 11.5	5 0 5	<4.1	- 3.4
4 3 3	25.3	- 25.8	0 8 3	12.1	- 11.2	10 3 4	15.8	15.7	7 0 5	28.9	28.1
5 3 3	<3.5	- 1.2	1 8 3	5.8	5.2	11 3 4	14.2	- 13.6	9 0 5	9.0	- 8.0
6 3 3	22.0	21.9	2 8 3	<4.9	3.2	12 3 4	<4.4	1.4	11 0 5	19.5	- 18.1
7 3 3	13.1	- 13.3	3 8 3	6.3	- 5.6	13 3 4	16.3	16.8	13 0 5	24.5	23.2
8 3 3	10.6	10.3	4 8 3	9.4	8.8	14 3 4	10.4	- 11.3	0 1 5	16.9	16.7
9 3 3	14.3	13.6	0 9 3	<4.9	- 0.7	15 3 4	<4.7	2.3	1 1 5	10.2	9.9
10 3 3	24.3	- 24.6	1 9 3	6.5	6.0	16 3 4	10.6	10.5	2 1 5	4.9	- 4.9
11 3 3	7.1	7.1	2 9 3	<4.8	0.2	0 4 4	13.1	- 13.3	3 1 5	8.4	- 8.9
12 3 3	<4.1	4.2	3 9 3	7.7	- 7.8	1 4 4	<4.3	4.3	4 1 5	13.7	- 13.6
13 3 3	6.7	- 6.9				2 4 4	4.9	4.8	5 1 5	<4.1	- 2.5
14 3 3	18.6	18.0	0 0 4	47.8	48.2	3 4 4	7.4	- 7.3	6 1 5	12.9	12.0
15 3 3	<4.5	0.7	2 0 4	13.0	- 12.3	4 4 4	15.3	16.8	7 1 5	18.2	17.3
16 3 3	13.7	- 13.2	4 0 4	28.7	- 28.6	5 4 4	<4.2	- 0.1	8 1 5	5.1	5.6
0 4 3	7.9	7.8	6 0 4	35.3	34.1	6 4 4	8.7	- 9.1	9 1 5	<4.3	- 3.3
1 4 3	12.4	- 13.2	8 0 4	9.5	9.5	7 4 4	6.5	6.4	10 1 5	14.5	- 14.0
2 4 3	<3.7	- 2.5	10 0 4	24.8	- 25.0	8 4 4	8.6	- 8.4	11 1 5	12.2	- 11.4
3 4 3	27.1	28.2	12 0 4	10.0	9.2	9 4 4	<4.4	- 3.9	12 1 5	<4.6	2.6
4 4 3	5.8	- 6.7	14 0 4	18.8	19.1	10 4 4	19.0	19.5	13 1 5	17.0	15.8
5 4 3	<3.9	- 1.2	16 0 4	11.3	- 10.7	11 4 4	<4.5	- 3.9	14 1 5	10.4	10.6
6 4 3	5.5	5.7	0 1 4	31.2	29.8	12 4 4	<4.6	- 0.4	0 2 5	22.7	22.6
7 4 3	16.1	- 17.1	1 1 4	12.6	12.7	13 4 4	4.8	5.2	1 2 5	4.9	4.6
8 4 3	<4.0	2.7	2 1 4	7.8	- 7.3	14 4 4	13.9	- 14.5	2 2 5	6.2	- 6.6
9 4 3	15.3	15.3	3 1 4	20.3	- 19.7	0 5 4	17.1	- 16.1	3 2 5	<4.2	- 0.9
10 4 3	7.6	- 7.3	4 1 4	13.8	- 14.3	1 5 4	<4.6	- 2.1	4 2 5	18.4	- 18.4
11 4 3	8.8	9.5	5 1 4	<3.6	- 0.9	2 5 4	5.7	5.3	5 2 5	<4.2	- 2.3
12 4 3	<4.4	1.4	6 1 4	23.6	22.2	3 5 4	<4.5	2.9	6 2 5	17.2	16.5
13 4 3	12.0	- 11.5	7 1 4	18.4	18.0	4 5 4	17.4	18.1	7 2 5	9.4	8.9
14 4 3	6.6	5.4	8 1 4	<3.8	3.5	5 5 4	<4.5	0.1	8 2 5	7.7	7.6
15 4 3	<4.6	0.5	9 1 4	9.0	- 9.1	6 5 4	10.2	- 11.1	9 2 5	<4.4	1.3
16 4 3	<4.7	- 4.6	10 1 4	12.8	- 12.7	7 5 4	<4.5	- 3.4	10 2 5	20.6	- 19.3
17 4 3	12.2	12.5	11 1 4	10.7	- 10.6	8 5 4	8.8	- 9.1	11 2 5	7.8	- 6.4

Table 7 (continued)

$h\ k\ l$	$ F_o $	$F_c$	$h\ k\ l$	$ F_o $	$F_c$	$h\ k\ l$	$ F_o $	$F_c$	$h\ k\ l$	$ F_o $	$F_o$
12 2 5	< 4.6	3.8	0 0 6	28.8	29.2	11 3 6	9.5	- 9.7	1 2 7	< 5.0	2.5
13 2 5	8.3	8.3	2 0 6	9.4	- 7.8	0 4 6	10.2	- 10.3	2 2 7	6.5	- 4.5
14 2 5	15.3	14.8	4 0 6	18.3	- 18.1	1 4 6	< 4.9	3.4	3 2 7	< 4.8	- 0.1
0 3 5	21.3	21.1	6 0 6	23.1	21.8	2 4 6	< 4.9	3.3	4 2 7	12.4	- 12.7
1 3 5	8.5	- 7.6	8 0 6	6.3	6.0	3 4 6	5.1	- 5.6	5 2 7	< 4.7	- 1.7
2 3 5	6.2	- 6.1	10 0 6	17.8	- 17.2	4 4 6	11.3	12.3	6 2 7	12.4	11.5
3 3 5	17.5	17.3	0 1 6	21.1	19.7	5 4 6	< 4.8	- 0.1	0 3 7	14.6	14.1
4 3 5	17.1	- 17.3	1 1 6	8.3	8.1	6 4 6	7.5	- 7.0	1 3 7	5.8	- 5.1
5 3 5	< 4.3	- 1.1	2 1 6	5.7	- 5.2	7 4 6	4.9	5.1	2 3 7	< 4.8	- 4.1
6 3 5	15.6	15.2	3 1 6	13.0	- 12.7	8 4 6	6.3	- 6.6	3 3 7	10.6	11.2
7 3 5	9.6	- 9.2	4 1 6	11.6	- 10.5	9 4 6	< 4.7	- 3.0	4 3 7	11.7	- 11.7
8 3 5	8.1	7.4	5 1 6	< 4.6	- 0.6	10 4 6	14.9	14.7	5 3 7	< 4.7	- 1.0
9 3 5	10.2	9.5	6 1 6	15.9	15.2	0 5 6	12.6	- 11.5	6 3 7	10.4	10.4
10 3 5	18.1	- 18.1	7 1 6	12.6	12.2	1 5 6	< 5.0	- 1.8	0 4 7	5.2	4.7
11 3 5	4.7	4.8	8 1 6	< 4.6	2.6	2 5 6	< 5.0	3.6	1 4 7	7.5	- 7.5
12 3 5	< 4.7	3.2	9 1 6	6.2	- 6.3	3 5 6	< 4.9	2.6	2 4 7	< 4.8	- 1.4
13 3 5	5.1	- 5.2	10 1 6	10.7	- 9.9	4 5 6	12.2	12.8	3 4 7	14.0	14.8
14 3 5	14.3	13.6	11 1 6	7.6	- 7.5	5 5 6	< 4.8	0.1	0 5 7	< 4.8	- 2.9
0 4 5	6.6	6.2	0 2 6	12.6	11.2	6 5 6	6.6	- 8.1	1 5 7	7.8	- 7.8
1 4 5	10.2	- 10.1	1 2 6	11.5	11.2	0 6 6	< 5.0	- 4.0	2 5 7	< 4.6	0.9
2 4 5	< 4.7	- 1.9	2 2 6	< 4.6	- 2.7	1 6 6	7.3	- 6.9	3 5 7	13.8	14.7
3 4 5	20.1	20.7	3 2 6	17.8	- 17.8	2 6 6	< 4.8	1.4			
4 4 5	4.8	- 5.3	4 2 6	4.7	- 4.1	3 6 6	10.4	10.6	0 0 8	17.9	18.6
5 4 5	< 4.6	- 0.9	5 2 6	< 4.6	- 0.7	0 7 6	< 4.7	3.0	2 0 8	5.7	- 5.3
6 4 5	< 4.6	4.6	6 2 6	9.2	8.7	1 7 6	7.1	- 6.1	4 0 8	12.0	- 11.9
7 4 5	13.4	- 13.5	7 2 6	16.9	17.0	2 7 6	< 4.5	- 0.7	6 0 8	13.8	14.1
8 4 5	< 4.7	2.2	8 2 6	< 4.7	0.1	3 7 6	9.0	9.4	0 1 8	13.6	13.5
9 4 5	11.3	11.5	9 2 6	9.3	- 9.0				1 1 8	5.7	5.4
0 5 5	< 5.0	- 3.7	10 2 6	< 4.7	- 2.4	1 0 7	10.7	10.8	2 1 8	4.9	- 3.9
1 5 5	12.4	- 10.9	11 2 6	10.6	- 10.3	3 0 7	13.5	- 12.9	3 1 8	8.4	- 8.5
2 5 5	< 4.9	1.0	0 3 6	5.8	- 5.3	5 0 7	< 4.7	- 2.4	4 1 8	8.7	- 7.9
3 5 5	21.4	21.1	1 3 6	10.8	10.4	7 0 7	18.2	18.3	5 1 8	< 4.4	- 0.4
4 5 5	< 4.8	2.5	2 3 6	< 4.8	2.0	0 1 7	11.6	10.9	6 1 8	11.0	10.5
5 5 5	< 4.7	- 0.5	3 3 6	16.3	- 16.5	1 1 7	6.6	6.8	0 2 8	6.8	6.8
6 5 5	< 4.7	- 2.8	4 3 6	8.4	8.9	2 1 7	< 4.7	- 3.2	1 2 8	6.6	7.7
7 5 5	14.3	- 15.0	5 3 6	< 4.7	- 0.8	3 1 7	7.3	- 6.8	2 2 8	< 4.4	- 1.9
8 5 5	< 4.7	- 0.9	6 3 6	< 4.7	- 3.3	4 1 7	9.5	- 8.9	3 2 8	12.6	- 12.2
9 5 5	11.6	11.3	7 3 6	16.4	15.8	5 1 7	< 4.7	- 2.0	0 3 8	< 4.6	- 3.4
0 6 5	15.0	- 14.0	8 3 6	5.4	- 5.4	6 1 7	8.3	8.1	1 3 8	6.3	6.9
0 7 5	11.3	- 12.0	9 3 6	8.8	- 8.1	7 1 7	12.6	12.2	2 3 8	< 4.3	1.1
0 8 5	8.8	- 8.9	10 3 6	10.3	10.7	0 2 7	16.1	15.4	3 3 8	10.0	- 11.0

\* The entries in the  $F_c$  columns are the  $A_c$  values when  $h+l=2n$ , and the  $B_c$  values when  $h+l=2n+1$

Furthermore, the very small values of  $|\Delta F|$  suggest that errors in the measurements of the axial lengths should be considered in estimations of the standard deviations of the interatomic distances and angles, and, finally, the apparent temperature anisotropy suggests that  $\sigma(x)$ ,  $\sigma(y)$ , and  $\sigma(z)$  may not be identical for a given atom.

The e.s.d.'s of the atomic positions, therefore, were recalculated with the expression given by LIPSON and COCHRAN<sup>17</sup> which takes into account the atomic numbers of the elements in addition to random errors in the intensity measurements, assuming  $\sigma(F_o) = 0.05 |F_o|$ ,

<sup>17</sup> H. LIPSON and W. COCHRAN, The determination of crystal structures (G. Bell and Sons, London, 1953) Table 288a.

and the values of  $\sigma_1(x)$ ,  $\sigma_1(y)$  given in Table 8 were obtained. Errors in the finite-summation corrections were arbitrarily estimated as 10% of the absolute values, and the values of  $\sigma_2(x)$ ,  $\sigma_2(y)$  shown in Table 8 were obtained. Finally, in Table 8,  $\sigma_3(x)$ ,  $\sigma_3(y)$  are the final e.s.d.'s of the atomic positions calculated from  $\sigma_3 = (\sigma_1^2 + \sigma_2^2)^{1/2}$ . The exceptionally low values of  $\sigma_3$  for V suggest that values of  $\sigma_3$  in Table 8 may still be too low, perhaps by a factor of up to 2. It should be noted that  $\sigma(x)$  for  $O_3$ , and  $\sigma(z)$  for V,  $O_1$ ,  $O_2$ , and  $O_3$ , are taken as zero (and are not listed in Table 8) because the corresponding coordinates are fixed by the space group symmetry.

Table 8. *Estimated standard deviations (Å) of atomic positions* (see text)

Atom	$\sigma_1(x)$	$\sigma_1(y)$	$\sigma_2(x)$	$\sigma_2(y)$	$\sigma_3(x)$	$\sigma_3(y)$
V	0.0006	0.0006	0.0002	0.0001	0.0006	0.0006
$O^1$	0.0024	0.0020	0.0018	0.0032	0.0031	0.0038
$O_2$	0.0021	0.0023	0.0020	0.0020	0.0030	0.0031
$O_3$	—	0.0022	—	0.0018	—	0.0029

In  $Pmnm$  the atomic coordinates are referred to orthogonal axes so that the standard deviation of the distance,  $l$ , between two atoms, 1 and 2, may be obtained directly from the expression of AHMED and CRUICKSHANK<sup>18</sup>,

$$\sigma^2(l_{1,2}) = \sigma^2(x_2 - x_1) \cos^2 \theta_1 + \sigma^2(y_2 - y_1) \cos^2 \theta_2 + \sigma^2(z_2 - z_1) \cos^2 \theta_3.$$

But the terms  $\sigma^2(x_2 - x_1)$ ,  $\sigma^2(y_2 - y_1)$ ,  $\sigma^2(z_2 - z_1)$  should allow for errors in the positions of atoms 1 and 2 arising from random errors in the intensity measurements, errors in the finite-summation corrections, and errors in the axial lengths. Hence,

$$\sigma^2(x_2 - x_1) = \sigma_3^2(x_2) + \sigma_3^2(x_1) + [(x_2 - x_1) \sigma(a)/a]^2$$

and,

$$\cos \theta_1 = (x_2 - x_1)/l_{1,2},$$

and similarly for  $\sigma^2(y_2 - y_1)$ ,  $\sigma^2(z_2 - z_1)$ ,  $\cos \theta_2$ ,  $\cos \theta_3$ , where  $\sigma_3$  is derived as outlined in the preceding paragraph.

<sup>18</sup> F. R. AHMED and D. W. J. CRUICKSHANK, A refinement of the crystal structure analyses of oxalic acid dihydrate. *Acta Crystallogr.* **6** (1953) 385–392, expression (4.3).

Taking  $\sigma_3(x)$  and  $\sigma_3(y)$  from Table 8, and  $\sigma_3(x)$  for  $O_3$  and  $\sigma_3(z)$  for all atoms as zero, the e.s.d.'s of the interatomic distances were calculated and are given in the last column of Table 5.

The standard deviations of the O—V—O angles were estimated according to the method given in the International Tables for X-ray Crystallography<sup>19</sup>. For this purpose the values of  $\sigma_3(y)$  in Table 8 were adopted for the e.s.d.'s of the atomic positions because they are maximum values in all cases, and the calculated e.s.d.'s of the angles were multiplied by 1.5 to allow for errors in the atomic positions owing to errors in the axial lengths. These results also are shown in the last column of Table 5.

### Discussion

The results of the present investigation are in essential agreement with those of BYSTRÖM, WILHELM and BROTZEN.

The atom-numbering system adopted in this paper is illustrated in Fig. 1 and follows that of BYSTRÖM *et al.* but distinguishes among several equivalent atoms of  $O_1$  and  $O_2$  in order to facilitate comparison of interatomic distances and coordination polyhedra. The coordinates of certain specific atoms are given in Table 6 together with their designations according to KETELAAR, BYSTRÖM *et al.*, and the present paper. To avoid confusion it should be noted that KETELAAR's numbering of the oxygen atoms as given in Table 6 refers to the four atoms of his coordination tetrahedron, with his second  $O_3$  designating the fifth atom which he discarded but which converts his tetrahedron into a trigonal bipyramid. KETELAAR distinguishes among the two oxygen atoms in the four-fold positions and the one in the two-fold positions only in terms of the coordinates  $x_1, y_1, z_1$  and  $x_2, y_2, z_2$  for the former and 0,  $u, v$  for the latter, whereas BYSTRÖM *et al.* label them  $O_1, O_2$ , and  $O_3$ , respectively. Hence,  $O_3$  of Table 1 corresponds to KETELAAR's  $O_4$  in Table 6, and KETELAAR's  $O_3$  in Table 6 corresponds to the present  $O_2(2)$ . Throughout the following discussion the designations given in the first column of Table 6 are employed in connection with all three structures.

The coordination tetrahedron of KETELAAR, defined by  $O_1(1)$ ,  $O_2(1)$ ,  $O_2(2)$ , and  $O_3$  (Table 6) becomes the trigonal bipyramid of BYSTRÖM *et al.*, and of the present paper, by the addition of  $O_2(3)$ . In the structure of BYSTRÖM *et al.*,  $O_2(1)$ ,  $O_2(2)$ ,  $O_2(3)$ , and  $O_3$  are all

<sup>19</sup> International Tables for X-ray Crystallography (Kynoch Press, Birmingham, 1959) II 331, expression (17).

in the plane,  $y = 0$ . In the present structure,  $O_2(1)$  is  $0.011 \text{ \AA}$  and  $O_3$  is  $0.014 \text{ \AA}$  off this plane on one side, while  $O_2(2)$  and  $O_2(3)$  are each off the plane by  $0.011 \text{ \AA}$  on the opposite side; these values represent a highly significant departure from co-planarity for these four atoms. In the structure of BYSTRÖM *et al.*, the angles between  $O_1(1)$ —V and V— $O_2(1)$ , V— $O_2(2)$ , V— $O_2(3)$ , and V— $O_3$ , respectively, vary from  $102.9^\circ$  to  $105.2^\circ$ , while in the present structure they are not significantly different from one another ( $104.5^\circ$  to  $105.0^\circ$ , Table 5).

The trigonal bipyramid resembles a distorted tetragonal pyramid with  $O_1(1)$  as apex, and  $O_2(1)$ ,  $O_2(2)$ ,  $O_2(3)$ , and  $O_3$  at the corners of the base. This pyramid could be converted into an octahedron by the addition of  $O_1(2)$  as the second apex. Such a coordination polyhedron is favoured by MAGNÉLI and OUGHTON<sup>7</sup> by analogy with the structure of  $MoO_3$  and because  $V_2O_5$  takes up appreciable amounts of  $MoO_3$  in solid solution. The maximum V—O distance in the trigonal bipyramid (tetragonal pyramid) of  $V_2O_5$ , however, is only  $2.02 \text{ \AA}$  while V— $O_1(2) = 2.78 \text{ \AA}$ . Although qualitatively this may be considered as a vestige of octahedral coordination,  $O_1(2)$  cannot seriously be accepted as bound to V in the same sense as  $O_1(1)$ ,  $O_2(1)$ ,  $O_2(2)$ ,  $O_2(3)$ , and  $O_3$ . The oxygen coordination polyhedron, therefore, must be described as five-fold, and preferably as distorted trigonal bipyramidal, rather than as distorted tetragonal (or square) pyramidal, because  $O_2(1)$ ,  $O_2(2)$ ,  $O_2(3)$ , and  $O_3$  are not co-planar.

The trigonal bipyramid may be chosen in two ways; (a) with  $O_2(2)$ ,  $O_2(3)$  as apices and  $O_1(1)$ ,  $O_2(1)$ ,  $O_3$  as corners of the equatorial triangle, or (b) with  $O_2(1)$ ,  $O_3$  as apices and  $O_1(1)$ ,  $O_2(2)$ ,  $O_2(3)$  as corners of the equatorial triangle. The more suitable choice is (a) because V is in the same plane as  $O_1(1)$ ,  $O_2(1)$ , and  $O_3$ . On this basis, the edges shared with adjacent bipyramids are those ( $O_2(2)$ — $O_2(1)$ ,  $O_2(3)$ — $O_2(1)$ ) from the apices to the same corner of the equatorial triangle, and these are the shortest edges of the bipyramid (see Table 5). The vanadium atom in the plane of the equatorial triangle is displaced away from these shared edges so that there is one lengthened (V— $O_2(1)$ ) and two shortened (V— $O_1(1)$ , V— $O_3$ ) distances between V and O; the two latter in turn are significantly different in length ( $1.58 \text{ \AA}$ ,  $1.78 \text{ \AA}$ ). The shortest V—V distance ( $3.08 \text{ \AA}$ ) is across the shared edges while the next shortest are those along the directions of  $x$  ( $3.42 \text{ \AA}$ ) and  $z$  ( $3.56 \text{ \AA}$ ), respectively. The trigonal bipyramids are joined by the shared edges into zigzag chains with a repeat distance of  $c = 3.563 \text{ \AA}$  along the direction of  $z$ , and these chains are cross-linked through  $O_3$  along the

direction of  $x$  to give two-dimensional layers separated by  $b = 4.369$  Å. The shortest distances between atoms in adjacent layers are  $V-O_1(2) = 2.78$  Å and  $O_1(2)-O_3 = 2.85$  Å (see Fig. 1); the distance between  $O_1(1)$ , at  $x, y, 0$ , and the equivalent  $O_1$  at  $\frac{1}{2} - x, 1 - y, \frac{1}{2}$  is  $2.99_5$  Å. The equatorial triangle of the bipyramid lies in the mirror plane through the origin and perpendicular to  $c$ .  $O_1(1)$  is bonded only to V,  $O_3$  is shared between two V's in adjoining chains, while  $O_2(1)$ ,  $O_2(2)$ , and  $O_2(3)$  are each shared among three V's in adjacent bipyramids of the same chain (see Fig. 1).

As BYSTRÖM, WILHELM and BROTZEN have pointed out, this structure accounts satisfactorily for the perfect  $\{010\}$  cleavage, and for the observation of KETELAAR that  $\{100\}$  cleavage can also be achieved (presumably by the rupture of the  $V-O_2(1)$  bonds which are the longest in the coordination polyhedra) but that  $\{001\}$  cleavage is more difficult to obtain (presumably because it requires rupture of the shorter  $V-O_2(2)$  and  $V-O_2(3)$  bonds).

A summary of the oxygen coordination polyhedra around V, which have been reported in various structures, has been given elsewhere<sup>20</sup>. It is hoped to present a discussion of the relationship of the trigonal bipyramids in  $V_2O_5$  to similar polyhedra in other crystals containing pentavalent V, and some speculations regarding the nature of the V—O bonds, in another paper.

<sup>20</sup> C. H. KELSEY and W. H. BARNES, The crystal structure of metarossite. *Can. Mineral.* 6, Part 4 (1960) 448—466.