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A Refinement of the Structure of VO_2

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The structure of VO_2 has previously been determined by Georg Andersson in 1956.[1] Data for the refinement was collected by counter-technique using a completely automatic General Electric single-crystal diffractometer. Description of the data collection and processing is given. Results of least-squares refinement is in good agreement with original parameter determination but much lower standard deviation in the parameters has been achieved.

The structural refinement of VO_2 was undertaken as part of an overall program at this Institute for the accurate determination of interatomic distances of compounds of simple stoichiometry in order to better understand the bonding in these compounds. More specifically, VO_2 was chosen to supplement the information of V—O bonds determined at this Institute for $VOSO_4$ [2] and $VOMoO_4$.[3] Furthermore, the short V—V distance in VO_2 (2.619 Å) is of special interest to a group at this Institute who are studying the magnetic properties of metal-metal interactions.

The single crystal of VO_2 examined was picked from a sample that was prepared by the hydro-thermal technique. Equal weights of water and powdered vanadium oxides were sealed in vacuum using a gold container. The capsule was subjected to a temperature of 500°C and a pressure of 2500 atmospheres in a pressure bomb. The resulting product contained many black single crystals. Enough of the octahedrally shaped crystals of VO_2 were sorted out to give a powder pattern using the Guinier-Hägg type focusing camera with monochromatized Cu$K\alpha_1$ radiation. Potassium chloride (a=6.29228 Å) [4] was used as an internal standard and the $\sin^2\theta$ values were refined using least-squares methods. The resulting unit cell dimensions and standard deviations (σ) at 25°C are:

$$\begin{aligned} a &= 5.7517 \pm 30 \text{ Å} \\ b &= 4.5378 \pm 25 \text{ Å} \\ c &= 5.3825 \pm 25 \text{ Å} \\ \beta &= 122.646° \pm 96 \end{aligned}$$

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These dimensions are in good agreement with those of Andersson.[1]

A well shaped octahedral crystal was chosen for detailed X-ray analysis. It was mounted along the crystallographic c axis by glueing a glass fiber to one of the corners. The eucentric goniometer head containing the glass fiber was then mounted on the (ϕ) phi axis of the G.E. full circle goniostat. The orientation of the crystal was accomplished by the method described by Furnas.[5]

Input tapes for the automatic collection of intensity data were prepared by a program called Auto-Gip [6] which was prepared at this Institute. Input information included all angle position and duration of time of background counts, speed and 2θ interval for integrated intensity measurements. The value of the scan intervals was calculated by Auto-Gip according to the formula:

$$\Delta 2\theta = b(\tan\theta) + a$$

where $b=2.6$ and $a=1.4$. These values were determined by examining a few reflections over the entire 2θ range and establishing the values which formed the best straight line.

Intensity data was collected for all hkl and $\bar{h}kl$ reflections out to a 2θ value of 100° using Mo$K\alpha$. The data collected for each reflection consisted of a 100 second background count at the beginning of the $\Delta 2\theta$, cumulative count through $\Delta 2\theta$ at 1°/min, 100 second background count at end of $\Delta 2\theta$ and a cumulative count in reverse through $\Delta 2\theta$.

This output data was punched on 8 channel paper tape by the G.E. Automatic Diffractometer in a code which had to be modified by a CDC computer so as to make it useful on the computers FACIT and BESK. The resulting tape was used as data tape for Auto-Galpi [6] which calculated Lorentz and polarization corrected intensities, individual statistical weights and direction cosines of incident and reflected beams. The output of Auto-Galpi was used as the main data tape for AII—G [7] which calculates absorption corrected intensity and data necessary for secondary extinction corrections. The linear absorption coefficient $\mu=81.2$ cm^{-1} was used in calculating absorption factor for each reflection. This factor (A) ranged in value from 0.690 to 0.728 in the formula $I=I_{obs}/A$.

At this point, structure factor least square (SFLS) [8] was started for all reflections using Andersson values, as initial parameters. Atomic scattering factors for un-ionized atoms were used with the real part of the anomalous dispersion correction [9] being applied to the scattering curves.[10] It soon became apparent that many of the very weak structure factors were in error. Therefore, all reflections whose individual statistical weights were below a certain minimum value were eliminated from further least squares. It was noted that many strong reflections were apparently suffering from extinction. In order to perform calculations for correction of secondary extinction according to Zachariasen,[11] it is necessary to remove all strong reflections and perform least-squares refinement until further removal of strong reflections does not lower the standard deviation of the parameters. Using the parameters from the last cycle of such refinements, all structure factors are then calculated. A calculation on a group of the strongest reflections as outlined by Zachariasen gives an average value for a constant (c) used in secondary extinction corrections. The value of (c)

Table 1. The parameters and standard deviations (σ) obtained in the final cycle of the least-squares refinement of VO_2.

Atom	$x \pm 10^5\ \sigma(x)$	$y \pm 10^5\ \sigma(y)$	$z \pm 10^5\ \sigma(z)$	$B \pm (B)$ Å^2
V	0.23947± 5	0.97894± 5	0.02646± 6	0.299± 2
O_1	0.10616±24	0.21185±25	0.20859±27	0.396±11
O_2	0.40051±24	0.70258±26	0.29884±27	0.441±11

Table 2. Normalized weight analysis obtained in the final cycle of the least-squares refinement of VO_2. w=weighting factor, $\Delta = ||F_{obs}| - |F_{calc}||$.

Interval	Number of reflections	$\overline{w\Delta^2}$	Interval F_{obs}	Number of reflections	$\overline{w\Delta^2}$
0.00—0.37	123	1.32	0— 2	0	—
0.37—0.47	112	0.72	2— 5	0	—
0.47—0.54	97	0.88	5— 7	55	0.66
0.54—0.59	100	0.84	7—10	135	0.73
0.59—0.64	90	0.83	10—12	173	1.08
0.64—0.67	91	0.69	12—15	127	0.93
0.67—0.71	84	1.13	15—18	105	1.12
0.71—0.74	82	1.53	18—20	95	1.06
0.74—0.77	84	1.13	20—23	48	0.92
0.77—0.80	1	0.04	23—25	126	1.29

Table 3. Interatomic distances (Å) and standard deviations ($\pm\sigma$ in Å) in VO_2.

V—V		2.61914±39
V—O		1.7628 ±12
		1.8633 ±12
		1.8935 ±12
		2.0149 ±12
		2.0241 ±12
		2.0637 ±12
O—O		2.6934 ±17
	(2×)	2.7131 ±17
	(2×)	2.7209 ±16
		2.6671 ±17
		2.6744 ±16
		2.7412 ±17
		2.7446 ±16
		2.8597 ±16
		2.8933 ±16
		2.5865 ±17
	(2×)	2.7132 ±17
	(2×)	2.7251 ±17

Table 4. Observed and calculated structure factors for VO_2.

H	K	L	FOBS	FCALC
0	0	2	25.83	27.34
0	0	4	40.36	42.01
0	0	6	17.50	17.15
1	0	2	14.34 -	15.14
1	0	4	19.64 -	20.05
1	0	6	23.00 -	22.75
1	0	8	17.14 -	17.40
2	0	0	55.26 -	55.69
2	0	4	14.12 -	13.91
2	0	6	24.22 -	24.40
3	0	0	12.1[illegible] -	12.25
3	0	2	7.05	7.41
3	0	4	10.95	11.63
3	0	6	16.27	15.97
3	0	8	15.91	15.33
4	0	0	23.69	24.13
4	0	2	39.31	39.94
4	0	4	24.22	24.63
4	0	6	9.53	9.92
5	0	0	11.67	11.93
5	0	4	8.47 -	9.06
5	0	6	9.53 -	9.35
6	0	0	37.67 -	38.06
6	0	2	13.95 -	15.02
7	0	4	26.70 -	28.70
7	0	0	9.89 -	10.23
8	0	0	23.86	24.00
8	0	2	19.64	19.95
9	0	0	11.31	12.23
0	1	2	18.39 -	17.36
0	1	3	38.03	39.05
0	1	4	19.31	20.69
0	1	5	23.70	23.39
0	1	6	8.30 -	8.22
0	1	7	7.94	7.21
0	1	8	9.00	8.96
1	1	0	9.72	8.92
1	1	2	9.19	9.15
1	1	3	17.06 -	18.01
1	1	5	21.92 -	21.43
1	1	7	20.13 -	19.75
1	1	9	13.44 -	16.96
2	1	0	37.14 -	36.31
2	1	2	13.77	14.24
2	1	3	33.97 -	35.66
2	1	5	21.22 -	20.36
2	1	7	11.67 -	12.06
3	1	3	9.00	9.59
3	1	5	14.12	14.19
3	1	7	15.55	16.01
4	1	0	11.37 -	12.45
4	1	1	34.14	34.04
4	1	2	12.91	12.95
4	1	3	30.81	30.32
4	1	4	3.33 -	3.43
4	1	5	13.27	16.42
4	1	6	7.50	7.40
4	1	7	11.50	11.50
5	1	5	9.00 -	9.22
6	1	0	9.72	9.91
6	1	1	24.50 -	25.15
6	1	3	21.75 -	21.77
6	1	5	15.91 -	17.20
7	1	1	20.36	21.79
7	1	2	7.77 -	7.61
8	1	3	14.24	15.73
9	1	1	7.53	7.29
0	2	0	23.70	23.04
0	2	1	17.50 -	16.32
0	2	3	13.08	13.67
0	2	4	23.51	22.42
0	2	5	12.91	13.07
0	2	8	9.30	9.24
0	2	9	6.87	7.71
1	2	1	16.61	16.91
1	2	2	12.02 -	11.83
1	2	3	9.36	9.04
1	2	4	19.93 -	19.97
1	2	6	18.22 -	18.10
1	2	8	20.16 -	19.15
2	2	1	7.53 -	7.33
2	2	2	27.53 -	27.04
2	2	4	37.33 -	36.59
2	2	5	10.03 -	9.93
2	2	6	7.05 -	7.19
2	2	8	9.53 -	9.57
3	2	0	7.41 -	7.57
3	2	1	10.42 -	10.24
3	2	3	8.47 -	8.96
3	2	4	12.91	12.65
3	2	6	14.30	14.68
4	2	0	50.06	51.31
4	2	2	24.53	25.06
4	2	4	20.33	20.77
4	2	6	17.50	17.72
5	2	0	10.61	10.93
5	2	1	7.23	7.44
5	2	6	10.95 -	11.67
6	2	0	17.50 -	17.92
6	2	2	31.14 -	31.31
6	2	4	11.31 -	12.24
7	2	0	11.67 -	12.09
7	2	1	6.70 -	6.75
8	2	0	14.48	15.20
8	2	2	16.80	17.30
9	2	0	9.53	9.79
10	2	0	13.56 -	13.79
0	3	1	40.33	40.90
0	3	2	13.77	14.52
0	3	3	42.64	42.87
0	3	5	10.03	9.33
0	3	6	16.90	15.60
0	3	7	15.19	14.16
1	3	0	20.69	21.26
1	3	2	15.19	14.72
1	3	3	15.37 -	15.40
1	3	4	10.73	10.54
1	3	5	16.44 -	16.21
1	3	7	13.56 -	13.05
2	3	0	17.69	18.50
2	3	1	27.05 -	26.69
2	3	2	10.61 -	10.97
2	3	3	33.23 -	32.50
2	3	5	13.75 -	13.70
2	3	8	10.61 -	9.32
3	3	0	14.66 -	14.72
3	3	2	14.30 -	13.36
3	3	3	7.58	7.98
3	3	4	7.05 -	7.53
3	3	5	12.91	13.31
3	3	6	7.41 -	6.72
3	3	7	12.72	12.43
4	3	1	36.97	37.41
4	3	3	16.03	15.79
4	3	4	9.72	9.89
4	3	5	21.39	21.55
5	3	0	9.72	10.27
5	3	2	10.95	10.61
5	3	4	7.41	7.34
5	3	5	3.30 -	3.39
6	3	1	25.11 -	25.64
6	3	3	18.32 -	17.94
6	3	5	11.50 -	11.13
7	3	0	9.00 -	9.19
7	3	2	6.70 -	6.63
7	3	4	7.41 -	7.49
8	3	0	9.53 -	9.34
8	3	1	11.31	11.70
9	3	1	7.53	7.37
0	4	0	44.73	46.24
0	4	1	19.31	20.15
0	4	2	25.47	23.91
0	4	4	23.34	23.37
0	4	5	12.36	11.43
0	4	6	12.91	11.63
0	4	7	13.42	12.92
1	4	1	13.56	13.54
1	4	2	10.03 -	9.78
1	4	3	15.37	15.06
1	4	4	12.55 -	12.36
1	4	5	9.30	9.74
1	4	6	17.14 -	16.67
1	4	8	14.12 -	13.93
2	4	0	30.06 -	30.73
2	4	1	7.05	7.14
2	4	2	33.23 -	32.63
2	4	3	15.55 -	15.19
2	4	4	14.43 -	14.44
2	4	6	15.37 -	15.34
2	4	7	13.42 -	12.76
3	4	0	6.87 -	7.00
3	4	1	17.33 -	17.41
3	4	3	10.95 -	11.50
3	4	4	9.30	9.51
3	4	5	10.42 -	9.73
3	4	6	10.61	11.27
4	4	0	20.33	20.54
4	4	1	8.47 -	8.50
4	4	2	24.75	25.30
4	4	4	18.39	17.72
4	4	5	7.53	8.00
4	4	6	9.19	9.37
5	4	0	6.37	6.64
5	4	1	13.42	13.22
5	4	3	11.50	11.57
6	4	0	23.51 -	23.46
6	4	2	14.43 -	14.66
6	4	4	17.50 -	17.36
7	4	0	7.53 -	8.25
7	4	1	9.19 -	8.91
7	4	3	9.53 -	9.77
8	4	0	15.91	16.79
8	4	2	14.34	14.79
9	4	0	9.36	9.67
9	4	1	8.83	8.30
0	5	1	30.42	30.23
0	5	3	12.02	11.49
0	5	4	13.08	12.42
0	5	5	23.17	22.44
0	5	6	10.08	9.44
0	5	8	12.02	11.84
1	5	0	19.64	19.29
1	5	2	19.09	18.39
1	5	3	9.12 -	8.19
1	5	4	13.95	13.41
1	5	5	13.77 -	13.62
1	5	7	13.08 -	12.73
2	5	1	34.50 -	34.94
2	5	3	14.84 -	14.85
2	5	4	7.53 -	7.97
2	5	5	12.19 -	12.00
2	5	6	10.42 -	9.58
2	5	7	11.31 -	11.04
3	5	0	19.28 -	19.74
3	5	2	14.34 -	14.46
3	5	4	13.42 -	13.28
3	5	5	8.47	8.20
3	5	6	6.87 -	7.15
4	5	1	12.36	12.73
4	5	3	26.00	25.47
5	5	0	14.48	15.05
5	5	2	14.12	13.92
5	5	4	9.39	10.00
6	5	1	12.19 -	13.02
6	5	3	12.91 -	13.64
7	5	0	9.89 -	10.24
7	5	2	12.02 -	11.95
8	5	1	18.92	19.26
9	5	0	9.36	8.70
0	6	0	21.05	20.59
0	6	1	7.58 -	8.00
0	6	2	17.36	17.71
0	6	3	16.27	15.68
0	6	4	14.66	13.23
0	6	5	11.31	10.29
0	6	6	7.94	7.89
0	6	7	10.31	9.21
1	6	1	19.31	19.53
1	6	3	16.97	16.38
1	6	4	10.42 -	10.44
1	6	5	10.03	9.33
1	6	6	10.08 -	10.15
1	6	7	7.05	6.79
2	6	0	19.45 -	18.32
2	6	2	17.69 -	17.63
2	6	4	13.03 -	12.70
2	6	5	16.30 -	16.58
2	6	6	9.19 -	8.27
3	6	1	17.14 -	16.93
3	6	3	16.61 -	15.34
3	6	5	10.42 -	10.12
4	6	0	15.19	16.23
4	6	2	16.03	15.23
4	6	4	11.31	12.28
5	6	1	15.37	15.53
5	6	3	12.02	12.09
6	6	0	13.42 -	13.83
6	6	1	10.03	10.03
6	6	2	12.72 -	12.57
6	6	3	7.94 -	7.45
7	6	1	12.36 -	13.18
8	6	0	10.61	10.38
0	7	1	12.02	11.89
0	7	3	18.92	18.31
0	7	4	13.25	12.83
0	7	5	10.95	10.22
1	7	0	21.22	20.59
1	7	2	18.22	17.87
1	7	4	12.36	12.59
1	7	5	10.25	9.45
2	7	3	15.02 -	15.10
2	7	4	8.12 -	8.06
2	7	5	10.61 -	8.92
3	7	0	15.91 -	16.28
3	7	2	13.22 -	13.12
3	7	4	12.72 -	12.30
3	7	5	7.53	7.10
4	7	1	18.39	18.15
5	7	0	15.37	15.49
5	7	2	13.77	13.60
6	7	0	7.53	7.15
6	7	1	12.91 -	13.30
7	7	0	13.42 -	13.50
0	8	1	9.19	9.77
0	8	2	13.42	13.32
0	8	5	12.55	12.35
1	8	1	18.92	19.23
1	8	3	14.48	14.15
1	8	5	12.02	11.81
2	8	0	11.14 -	11.43
2	8	3	10.61 -	11.05

Table 4. Continued.

H	K	L	FOBS	FCALC
2	8	4	10.78	10.79
3	8	1	18.03	17.66
3	8	3	14.30	14.40
4	8	0	12.19	12.40
4	8	2	6.87	7.17
5	8	1	13.77	13.77
0	9	1	8.66	8.10
0	9	2	8.30	8.29
1	9	0	16.80	16.69
1	9	2	15.72	15.69
2	9	1	10.61	10.40
3	9	0	17.69	17.19
-1	0	2	27.05	26.48
-1	0	4	32.91	32.71
-1	0	6	26.00	26.00
-1	0	8	22.64	22.79
-1	0	10	17.50	17.35
-2	0	0	55.90	55.69
-2	0	2	49.89	43.74
-2	0	4	54.31	53.34
-2	0	8	10.95	11.40
-2	0	10	7.94	8.04
-3	0	0	12.36	12.85
-3	0	2	29.47	30.41
-3	0	4	36.61	36.62
-3	0	6	30.95	30.92
-3	0	8	26.36	26.23
-3	0	10	17.50	17.21
-4	0	0	23.69	24.13
-4	0	4	7.94	7.77
-4	0	6	16.44	16.50
-4	0	10	12.19	12.01
-5	0	0	11.83	11.93
-5	0	2	24.75	25.50
-5	0	4	32.37	34.07
-5	0	6	31.97	32.20
-5	0	8	25.11	25.02
-5	0	10	18.92	19.58
-6	0	0	37.50	38.06
-6	0	2	21.92	22.08
-6	0	4	12.36	12.49
-6	0	6	15.02	15.62
-6	0	8	14.12	14.24
-7	0	0	9.53	10.23
-7	0	2	22.45	22.74
-7	0	4	26.70	27.53
-7	0	6	29.00	23.47
-7	0	8	23.86	23.45
-7	0	10	17.50	17.80
-8	0	0	23.17	24.00
-8	0	2	7.41	7.84
-8	0	4	21.22	21.56
-8	0	6	7.94	7.94
-8	0	10	10.73	10.29
-9	0	0	11.33	12.23
-9	0	2	13.39	13.35
-9	0	4	22.11	22.70
-9	0	6	24.41	24.26
-9	0	8	20.50	20.47
-9	0	10	13.77	14.51
-10	0	2	16.08	16.85
-10	0	10	19.93	19.28
-11	0	2	12.72	14.38
-11	0	4	18.92	20.01
-11	0	6	18.03	18.87
-11	0	8	17.69	16.76
-11	0	10	10.61	11.39
-12	0	3	13.50	14.47
-1	1	0	9.10	8.92
-1	1	1	16.97	16.20
-1	1	2	8.30	8.14
-1	1	3	31.48	30.46
-1	1	5	29.19	28.18
-1	1	7	25.11	24.18
-1	1	9	20.69	20.12
-2	1	0	33.20	36.31
-2	1	1	50.73	53.16
-2	1	2	43.53	41.32
-2	1	3	53.95	52.56
-2	1	4	10.73	10.96
-2	1	5	20.50	19.87
-2	1	7	7.53	6.93
-2	1	8	6.37	6.86
-3	1	1	21.05	21.51
-3	1	3	34.14	33.91
-3	1	5	33.42	33.07
-3	1	7	29.00	28.03
-3	1	9	21.05	21.13
-3	1	11	14.84	14.80
-4	1	0	11.83	12.48
-4	1	1	43.70	44.89
-4	1	3	35.55	36.25
-4	1	5	13.77	13.72
-4	1	6	16.08	17.15
-4	1	7	7.94	7.27
-4	1	10	7.05	8.10
-4	1	11	7.41	7.65
-5	1	1	17.69	18.35
-5	1	3	29.00	29.95
-5	1	5	32.91	33.11
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-6	1	0	9.89	9.91
-6	1	1	29.89	30.70
-6	1	2	10.78	11.47
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-6	1	4	17.36	18.54
-6	1	5	14.12	14.13
-6	1	9	6.87	7.44
-6	1	11	10.25	9.64
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-7	1	11	13.08	13.16
-8	1	0	7.05	6.35
-8	1	1	16.27	16.64
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-8	1	3	14.12	14.46
-8	1	8	10.61	11.00
-8	1	9	7.05	7.04
-9	1	11	14.48	14.05
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-9	1	3	20.50	20.60
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-9	1	7	21.92	22.46
-9	1	9	18.97	17.33
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-10	1	1	11.14	11.91
-10	1	2	7.94	7.38
-10	1	8	10.00	10.14
-10	1	6	10.42	10.69
-10	1	9	11.67	11.30
-11	1	1	11.31	12.84
-11	1	3	15.72	17.14
-11	1	5	19.28	19.57
-11	1	7	17.36	17.37
-11	1	9	13.08	14.01
-1	2	1	15.19	15.09
-1	2	2	23.34	22.82
-1	2	3	11.14	10.41
-1	2	4	26.17	25.56
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-1	2	8	21.75	21.15
-1	2	10	15.91	15.43
-2	2	0	61.22	61.64
-2	2	5	15.19	15.20
-2	2	4	15.91	15.24
-2	2	6	24.41	23.87
-2	2	7	11.33	12.24
-3	2	0	7.77	7.57
-3	2	1	12.19	12.21
-3	2	2	26.00	26.16
-3	2	3	10.95	10.32
-3	2	4	31.31	30.56
-3	2	6	29.89	29.16
-3	2	8	22.81	22.08
-3	2	10	13.75	13.36
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-4	2	1	14.84	15.38
-4	2	2	16.44	16.39
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-7	2	6	25.28	25.53
-7	2	8	22.28	22.56
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-8	2	0	14.66	15.20
-8	2	2	23.34	23.21
-8	2	6	8.30	8.41
-8	2	7	9.00	9.33
-8	2	8	9.00	9.32
-8	2	10	12.19	11.63
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-9	2	8	19.64	19.22
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-10	2	8	12.72	12.91
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-11	2	6	17.69	13.77
-11	2	8	14.84	15.17
-12	2	5	7.23	7.60
-12	2	6	9.19	9.25
-1	3	0	21.05	21.26
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-1	3	2	15.91	15.73
-1	3	3	19.81	19.70
-1	3	4	12.36	11.90
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-2	3	1	59.45	61.24
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-2	3	3	19.93	19.11
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-2	3	6	9.00	8.58
-2	3	7	6.37	7.34
-2	3	10	10.73	10.21
-3	3	0	14.43	14.72
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-3	3	4	9.36	8.96
-3	3	5	27.41	26.93
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-3	3	9	10.91	10.23
-4	3	1	28.30	28.45
-4	3	2	7.77	8.34
-4	3	3	22.11	21.77
-4	3	4	17.14	17.27
-4	3	5	21.22	21.59
-4	3	6	15.55	15.43
-5	3	0	10.42	10.27
-5	3	1	14.84	15.07
-5	3	2	11.31	11.31
-5	3	3	23.36	23.36
-5	3	5	26.00	25.52
-5	3	7	24.41	24.07
-5	3	9	19.64	19.20
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-6	3	1	14.30	15.06
-6	3	2	16.27	16.52
-6	3	3	26.87	27.26
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-6	3	11	12.55	12.55
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-7	3	1	13.95	14.50
-7	3	2	7.05	6.77
-7	3	3	19.64	19.35
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-7	3	7	22.45	22.42
-7	3	9	16.97	17.05
-7	3	11	11.67	12.07
-8	3	0	9.10	9.34
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-8	3	3	9.53	9.76
-8	3	4	8.33	8.72
-8	3	6	12.72	12.92
-8	3	9	13.50	13.72
-9	3	10	10.25	10.65
-9	3	1	11.14	11.33
-9	3	3	18.39	18.55
-9	3	5	20.36	20.54
-9	3	7	19.22	19.90
-9	3	9	15.02	15.50
-10	3	1	12.36	13.20
-10	3	4	12.72	12.86
-10	3	5	7.05	7.24
-10	3	7	9.53	9.22
-10	3	8	9.00	9.97
-10	3	9	6.37	7.13
-11	3	3	15.19	15.51
-11	3	5	15.55	16.27
-11	3	7	15.55	16.21
-11	3	9	11.33	12.24
-1	4	1	20.36	20.36
-1	4	2	12.72	12.25
-1	4	3	16.61	15.90
-1	4	4	13.28	13.50
-1	4	5	8.12	7.76
-1	4	6	13.98	13.42
-1	4	8	13.80	16.33
-2	4	0	30.78	30.73
-2	4	2	27.53	27.34
-2	4	4	25.64	24.89
-2	4	5	22.45	22.15
-2	4	9	14.12	14.09
-3	4	0	6.37	7.00
-3	4	1	17.14	17.29
-3	4	2	14.43	14.47
-3	4	3	12.91	12.30
-3	4	4	23.34	22.86
-3	4	5	8.30	9.17
-3	4	6	20.50	20.23
-3	4	8	20.33	19.55
-3	4	10	13.77	13.65
-4	4	0	20.50	20.54
-4	4	2	31.31	31.13
-4	4	3	23.51	23.84
-4	4	4	10.73	10.75
-4	4	6	9.47	9.25
-4	4	7	14.30	13.34
-4	4	9	12.91	12.61
-4	4	10	7.53	7.30
-5	4	0	6.87	6.64

Table 4. Continued.

H	K	L	FOBS	FCALC
- 5	4	1	11.83 -	12.24
- 5	4	2	16.97	17.11
- 5	4	3	10.61 -	11.10
- 5	4	4	21.39	21.07
- 5	4	6	22.45	21.32
- 5	4	8	19.81	19.35
- 5	4	10	13.42	13.40
- 6	4	0	23.17 -	23.46
- 6	4	1	12.36 -	12.24
- 6	4	2	15.91 -	16.31
- 6	4	3	10.42 -	11.10
- 6	4	4	9.89 -	9.92
- 6	4	5	6.37 -	7.33
- 6	4	6	7.23 -	7.51
- 6	4	7	19.64 -	19.43
- 6	4	8	7.59	6.99
- 7	4	0	3.12 -	3.25
- 7	4	1	10.06	10.70
- 7	4	2	16.27 -	16.12
- 7	4	3	7.58	7.04
- 7	4	4	18.75 -	18.66
- 7	4	6	21.39 -	21.52
- 7	4	8	16.97 -	16.30
- 7	4	10	13.42 -	13.63
- 8	4	0	15.91	16.79
- 8	4	1	11.31	11.35
- 8	4	2	8.66	8.39
- 8	4	4	12.19	11.79
- 8	4	5	10.92	10.08
- 8	4	9	9.53	9.42
- 8	4	10	8.66 -	8.30
- 9	4	0	9.53	9.37
- 9	4	1	6.37 -	7.05
- 9	4	2	13.42	13.04
- 9	4	4	18.03	17.84
- 9	4	6	17.69	17.79
- 9	4	8	15.10	15.33
- 9	4	10	11.50	11.61
- 10	4	2	10.61 -	10.73
- 10	4	3	10.95 -	11.37
- 10	4	5	9.19 -	9.30
- 10	4	9	11.50 -	12.30
- 11	4	4	14.66 -	15.10
- 11	4	6	13.59 -	14.02
- 11	4	8	13.95 -	13.43
- 1	5	0	19.45 -	19.20
- 1	5	2	20.16 -	20.29
- 1	5	3	13.95	13.23
- 1	5	4	11.50 -	11.10
- 1	5	5	17.14	16.03
- 1	5	6	8.47 -	8.04
- 1	5	7	14.43	14.53
- 2	5	1	11.31 -	10.61
- 2	5	2	11.33 -	11.80
- 2	5	3	30.06 -	30.31
- 2	5	4	11.31 -	10.70
- 2	5	5	7.77 -	7.42
- 2	5	6	13.42 -	13.72
- 2	5	8	13.42 -	12.44
- 3	5	0	18.45	17.74
- 3	5	0	18.45	19.74
- 3	5	0	18.45	18.74
- 3	5	1	9.53 -	9.28
- 3	5	2	15.19	15.29
- 3	5	3	15.19 -	15.18
- 3	5	4	12.02	11.55
- 3	5	5	17.69 -	17.27
- 3	5	7	18.75 -	17.32
- 3	5	9	13.59 -	13.82
- 4	5	1	23.51	23.31
- 4	5	2	9.89	10.13
- 4	5	3	19.23	19.30
- 4	5	4	11.67	12.22
- 4	5	6	16.97	16.20
- 4	5	7	11.31	11.00
- 4	5	8	10.73	10.72
- 4	5	9	10.25 -	9.00
- 5	5	0	15.37 -	15.05
- 5	5	1	9.19	9.21
- 5	5	2	11.83 -	11.96
- 5	5	3	16.03	15.74
- 5	5	4	10.95 -	10.34
- 5	5	5	19.09	18.55
- 5	5	7	18.22	17.59
- 5	5	9	13.42	13.57
- 6	5	1	23.51 -	24.07
- 6	5	2	7.58 -	7.96
- 6	5	4	15.02 -	15.50
- 6	5	5	14.12 -	14.31
- 6	5	6	12.72 -	12.80
- 6	5	8	12.02 -	12.55
- 6	5	10	10.42 -	9.60
- 7	5	0	10.06	10.24
- 7	5	1	10.25 -	9.96
- 7	5	2	10.95	10.93
- 7	5	3	15.19 -	15.56
- 7	5	5	17.33 -	16.97
- 7	5	7	16.44 -	15.33
- 7	5	9	13.25 -	13.64
- 8	5	2	10.25	10.43
- 8	5	3	10.25	10.73
- 8	5	4	12.36	12.35
- 8	5	6	11.14	11.6
- 8	5	7	7.41 -	7.75
- 8	5	8	13.06	12.92
- 9	5	0	7.58 -	8.70
- 9	5	1	10.61	10.30
- 9	5	2	8.12 -	7.21
- 9	5	3	12.36	12.75
- 9	5	5	15.91	15.55
- 9	5	7	14.43	14.60
- 9	5	9	11.67	11.53
- 10	5	2	9.00 -	9.71
- 10	5	3	10.95 -	10.91
- 10	5	4	8.93 -	9.09
- 10	5	6	12.02 -	12.35
- 10	5	8	8.47 -	8.51
- 1	6	1	10.99 -	10.34
- 1	6	2	8.47	8.21
- 1	6	3	15.55 -	15.34
- 1	6	4	12.19	11.93
- 1	6	5	11.31 -	10.96
- 1	6	6	11.33	11.35
- 1	6	8	13.42	12.96
- 2	6	0	19.28 -	19.02
- 2	6	2	17.39 -	17.06
- 2	6	3	17.33 -	17.05
- 2	6	4	12.36 -	12.65
- 2	6	7	22.11 -	21.15
- 3	6	1	13.22	13.24
- 3	6	2	11.14 -	11.01
- 3	6	3	14.43	14.11
- 3	6	4	12.36 -	11.55
- 3	6	5	9.00	8.93
- 3	6	6	16.03 -	15.35
- 3	6	8	12.19 -	12.32
- 4	6	0	15.91	16.20
- 4	6	1	16.30	17.39
- 4	6	2	15.55	15.19
- 4	6	4	9.00	9.95
- 4	6	5	20.33	20.93
- 4	6	7	13.42	13.25
- 4	6	9	8.72	9.23
- 5	6	0	6.37	6.74
- 5	6	1	15.03 -	14.34
- 5	6	2	9.00	9.01
- 5	6	3	11.33 -	11.42
- 5	6	4	14.63	14.45
- 5	6	5	7.22 -	6.53
- 5	6	6	15.72	15.05
- 5	6	8	12.55	12.13
- 6	6	0	13.25 -	13.83
- 6	6	2	11.14 -	11.50
- 6	6	3	12.36 -	12.44
- 6	6	4	7.41 -	7.50
- 6	6	5	19.64	19.43
- 6	6	7	7.58 -	7.14
- 6	6	9	13.56 -	17.72
- 7	6	1	10.42	10.53
- 7	6	2	9.72 -	9.87
- 7	6	3	9.18	9.21
- 7	6	4	14.43 -	14.49
- 7	6	6	13.03 -	12.61
- 7	6	8	13.59 -	13.38
- 8	6	0	10.42	10.33
- 8	6	2	7.58	8.43
- 8	6	3	18.92	19.07
- 8	6	7	18.03	17.49
- 9	6	2	10.25	10.77
- 9	6	4	10.42	11.07
- 9	6	6	12.72	12.35
- 10	6	5	11.67 -	11.56
- 1	7	0	21.39 -	20.50
- 1	7	2	16.27 -	15.94
- 1	7	3	8.47	8.11
- 1	7	4	15.19 -	14.63
- 1	7	5	9.36	8.72
- 1	7	7	11.14	10.85
- 2	7	1	23.00 -	22.93
- 2	7	2	11.50 -	11.30
- 2	7	4	11.14 -	11.05
- 2	7	5	10.42 -	10.46
- 2	7	6	15.19 -	14.27
- 3	7	0	16.03	15.23
- 3	7	2	16.97	17.19
- 3	7	3	8.83 -	8.54
- 3	7	4	11.67	11.47
- 3	7	5	11.33 -	11.10
- 3	7	7	11.31 -	10.66
- 4	7	1	9.53	9.97
- 4	7	2	10.06	10.04
- 4	7	3	8.37	7.23
- 4	7	4	12.72	12.50
- 4	7	5	11.50	11.59
- 4	7	6	16.97	17.14
- 4	7	8	12.19	11.33
- 5	7	0	15.55 -	15.41
- 5	7	1	7.23	6.55
- 5	7	2	14.66 -	14.56
- 5	7	3	8.47	8.77
- 5	7	4	7.94 -	7.52
- 5	7	5	11.67	11.82
- 5	7	7	10.25	10.25
- 6	7	0	7.41 -	7.15
- 6	7	2	8.63 -	8.47
- 6	7	3	14.04 -	15.05
- 6	7	4	16.06 -	15.32
- 6	7	6	13.42 -	13.40
- 6	7	8	14.20 -	13.42
- 7	7	0	13.59	13.50
- 7	7	2	8.66	9.10
- 7	7	3	10.25 -	9.51
- 7	7	4	7.41	7.41
- 7	7	5	11.11 -	10.73
- 7	7	7	10.25 -	10.33
- 8	7	2	10.61	11.55
- 8	7	4	12.55	12.11
- 8	7	6	13.06	12.37
- 1	8	1	17.69 -	17.40
- 1	8	3	15.72 -	15.93
- 1	8	5	10.25 -	9.90
- 1	8	6	9.36	8.84
- 2	8	0	11.14 -	11.43
- 2	8	2	10.25 -	10.33
- 2	8	3	7.23 -	6.94
- 2	8	5	19.31 -	18.31
- 2	8	6	7.23 -	7.11
- 3	8	1	16.61	15.79
- 3	8	2	14.12	14.53
- 3	8	4	8.83 -	8.30
- 3	8	5	6.37	7.27
- 4	8	0	12.72	12.40
- 4	8	2	17.36	17.92
- 4	8	4	8.00	8.09
- 4	8	5	10.73	10.42
- 5	8	1	15.55 -	15.10
- 5	8	2	7.23	8.92
- 5	8	3	11.31 -	10.61
- 5	8	4	7.77	7.19
- 5	8	5	7.23 -	6.41
- 5	8	6	8.47	7.36
- 6	8	1	11.50 -	10.92
- 6	8	2	8.37 -	7.80
- 6	8	3	12.72 -	12.42
- 6	8	5	11.14 -	11.38
- 7	8	3	7.41	7.53
- 7	8	4	8.37 -	8.65
- 1	9	0	13.97 -	13.99
- 1	9	2	17.36 -	16.82
- 1	9	4	11.31 -	10.83
- 2	9	0	7.58 -	7.19
- 2	9	3	9.89 -	9.09
- 2	9	4	15.02 -	14.52
- 3	9	0	17.50	17.19
- 3	9	2	13.95	13.63
- 3	9	4	9.89	10.21
- 4	9	1	7.05	6.89
- 4	9	2	9.19	9.09
- 4	9	4	14.34	15.14
- 5	9	2	11.50 -	11.31

obtained for this crystal of VO_2 was 0.413×10^{-2}. With this constant, secondary extinction correction was applied to all reflections used in least squares refinement by a program called Ringvrak.[6] These corrected structure factors were then refined to an R value of 0.028 where

$$R = \sum||F_o|-|F_c||/\sum|F_o|$$

The seven strongest reflections showed random error. A final least squares refinement was carried out with these reflections removed and changing to Hughes' weighting scheme. The R value dropped to 0.026 and gave the best standard deviation for the parameters. The final parameters including isotropic temperature factor with standard deviations are given in Table 1. The weight analysis of the structure factors compared to magnitude and $\sin\theta$ value is given in Table 2 for this final cycle of refinement. Interatomic distances and angles with standard deviations were then calculated [12] using these final atomic positional parameters and are presented in Table 3. The observed and calculated structure factors of the 864 reflections included in the last cycle of refinement are listed in Table 4.

The present investigation has not changed the general picture of the structure reported in Ref. 1 but gives a substantial improvement of the atomic parameters.

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