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A Refinement of the Crystal Structure of Molybdenum Dioxide

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The crystal structure of molybdenum dioxide has been refined using new data. The structure proposed by Magnéli is confirmed, although the space group has been shown to be strictly $P2_1/c$ and not $P2_1$. Least-squares refinement has reached $R = 0.053$ for 1344 visually estimated independent reflections.

In the structure, which consists of Mo—O octahedra linked together by edges and corners, the Mo—O distances are in the range 1.972—2.073 Å ($\sigma\sim$ 0.003 Å). The very short Mo—Mo bond length is found to be 2.5106 Å ($\sigma\sim$ 0.0005 Å).

The known oxides of molybdenum include the dioxide and a series of phases of compositions between $MoO_{2.75}$ and MoO_3. The structures of several of these compounds, including that of the dioxide, were determined by Magnéli.[1] More recently Kihlborg [2] has carried out an accurate structural study of the higher molybdenum oxides in which he refined several known structures and determined a number of new ones.

In 1946 Magnéli [3] reported that the dioxide had a distorted rutile-type structure. A striking feature was the presence of very short metal-metal contacts. The positions of the oxygen atoms, however, were not determined with sufficient accuracy to allow a discussion of the Mo—O bond lengths. This has prompted us to undertake a study, based on new diffraction data, to determine the interatomic distances accurately.

EXPERIMENTAL

Molybdenum dioxide was prepared by the electrolytic reduction of a melt of the composition $K_2O{\cdot}5MoO_3$.[4] The dioxide appeared as rather irregular, brownish violet crystals of relatively large size. The crystal chosen for single-crystal study had the approximate size 0.13 × 0.09 × 0.07 mm. It was rotated about the *b*-axis and Weissenberg photographs were taken with Mo$K\alpha$ radiation using the multiple-film technique. Films of different speeds (Ilford G, B, and C) were used to achieve the desired attenua-

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tion of the spots. Layers $h0l-h9l$ were registered and the intensities of 1381 independent reflections were estimated visually against a calibrated intensity scale.

Most of the calculations were carried out on the computers FACIT EDB and BESK. The Åsbrink-Brändén least-squares program (No. 6023 in *World List of Crystallographic Programs*, (1962)) was used. This employs a block-diagonal matrix approximation and individual isotropic temperature factors. In all cases refinement was continued until the successive shifts were less than 5 % of the respective standard deviations. Atomic scattering factors of Mo^{2+} (Ref. 5) and O^- (Ref. 6) were used. For Mo^{2+} the real part of the anomalous dispersion correction was applied.[7] The absorption corrections were calculated using Werner's program (No. 6019) and a linear absorption coefficient $\mu = 90.6$ cm^{-1}.

X-RAY POWDER DATA

X-Ray powder photographs were taken in a Guinier camera with strictly monochromatised Cu$K\alpha_1$ radiation, using potassium chloride ($a = 6.2919$ Å at 20°C) as an internal standard. The unit-cell dimensions and their standard deviations shown below were obtained by least-squares refinement. The corresponding values obtained by Magnéli *et al.*[8] are shown in brackets.

$$\begin{aligned} a &= 5.6109 \pm 0.0008 \text{ Å} \quad (5.584 \text{ Å}) \\ b &= 4.8562 \pm 0.0006 \text{ Å} \quad (4.842 \text{ Å}) \\ c &= 5.6285 \pm 0.0007 \text{ Å} \quad (5.608 \text{ Å}) \\ \beta &= 120.95° \pm 0.01° \quad (120.94°) \\ V &= 131.52 \pm 0.03 \text{ Å}^3 \quad (130.1 \text{ Å}^3) \end{aligned}$$

Table 1. X-Ray powder data for MoO_2, Cu$K\alpha_1$ radiation ($\lambda = 1.54050$ Å).

I	d(Å)	$\sin^2\theta_{obs}$	h k l	$\sin^2\theta_{calc.}$
vw	4.80	0.02577	1 0 0	0.02562
vs	3.42	0.05072	0 1 1	0.05062
			1 1 0	0.05078
w	2.813	0.07497	1 0 $\bar{2}$	0.07493
m	2.444	0.09931	2 0 $\bar{2}$	0.09925
s	2.429	0.10059	2 1 1	0.10056
			0 2 0	0.10063
m	2.414	0.10184	0 0 2	0.10186
m	2.405	0.10256	2 0 0	0.10250
			1 1 $\bar{1}$	0.10252
w	2.184	0.12441	2 1 $\bar{2}$	0.12440
vw	2.170	0.12595	0 2 1	0.12610
w	2.156	0.12769	2 1 0	0.12765
w	1.8426	0.17475	3 0 $\bar{2}$	0.17481
m	1.8586	0.17551	1 2 $\bar{2}$	0.17556
vw	1.8260	0.17794	1 2 1	0.17800
m	1.7263	0.19909	2 1 $\bar{3}$	0.19917
m	1.7232	0.19979	2 2 $\bar{2}$	0.19988
w	1.7181	0.20099	1 1 $\bar{3}$	0.20113
m	1.7127	0.20225	3 1 $\bar{1}$	0.20241
			0 2 2	0.20249
m	1.7100	0.20290	2 2 0	0.20313
m	1.6980	0.20578	2 2 2	0.20567
vw	1.6040	0.23059	3 0 0	0.23062
w	1.5450	0.24854	3 1 $\bar{3}$	0.24846
w	1.5363	0.25136	1 3 $\bar{1}$	0.25123
w	1.5347	0.25190	0 3 1	0.25189
w	1.5269	0.25446	0 1 $\bar{3}$	0.25433
w	1.4676	0.27545	3 2 $\bar{2}$	0.27544

As can be seen the unit-cell volume is somewhat larger than that previously reported. The X-ray powder pattern is given in Table 1.

SPACE GROUP

The Weissenberg photographs showed the following systematic absences:

$$h0l \text{ with } l \neq 2n$$
$$0k0 \text{ with } k \neq 2n$$

These are characteristic of space group $P2_1/c$ (No. 14). Both these conditions, however, are violated by the presence of a few weak reflections. Thus a Weissenberg photograph about the b-axis with 30 days exposure showed two very weak reflections $50\bar{7}$ and $70\bar{5}$, while a photograph about the a-axis showed a weak reflection 010. The occurrence of the former reflections is the reason why Magnéli chose the space group $P2_1$ (No. 4). The possibility of multiple reflection [9] was not considered at that time.

REFINEMENT OF THE STRUCTURE

In the first stages of refinement the co-ordinates given by Magnéli [3] for space group $P2_1$ were used as the starting point and that space group was assumed to be the correct one. When all 1381 reflections were included the refinement stopped at $R = 0.068$. At this stage the absorption correction was applied and refinement continued to $R = 0.064$. It soon became apparent that some of the strong reflections were suffering from extinction, and when 35 of them were removed the refinement went to $R = 0.052$.

At the end of this refinement two facts emerged. Firstly the atomic positions were extremely close to those compatible with space group $P2_1/c$, and secondly, for the two "forbidden" reflections $50\bar{7}$ and $70\bar{5}$ (the 010 reflection was not measured) the calculated structure factors were negligible compared to the observed values. It therefore seemed likely that the real space group was $P2_1/c$ and the extra reflections were due to multiple reflection. This has been further discussed in a separate publication.[10] The two forbidden reflections were removed and the refinement was continued under identical conditions to the last one, but assuming the centrosymmetric space group. The final R factor was 0.053 and the standard deviations fell to almost half their previous values. Taking into account the smaller number of parameters being refined (12 positional or thermal + 10 scale, against 23 positional or thermal + 10 scale), the slight rise in R is not significant.

Up to this point Cruickshank's weighting scheme [11] had been used. The weighting-scheme analysis, however, showed that the strong reflections were still affected by extinction. If one removed a total of 76 reflections, and continued the refinement R fell to 0.049. We feel, however, that the removal of such a large number of reflections selectively may not be justified. Refinement was therefore continued with only 35 reflections removed, but using Hughes' weighting scheme [12] with $F_{\min} = 21.1$ and $g = 4$ as the constants. The R factor remained constant (0.053), as did also the standard deviations,

but the weighting scheme analysis was improved. We intend to attempt to apply an extinction correction according to Zachariasen [13] by modifying the program of Coppens *et al.*[14]

The final positional and thermal parameters, together with their standard deviations, are shown in Table 2. A weighting-scheme analysis from the final cycle of refinement is shown in Table 3, and a list of observed and calculated structure factors in Table 4.

Table 2. The structure of MoO_2. The figures in italics are the coordinates given by Magnéli and Andersson [15].

Space group: $P2_1/c$ (No. 14)
Unit-cell dimensions: $a = 5.6109$, $b = 4.8562$, $c = 5.6285$ Å
$\beta = 120° 57'$
Unit-cell content: 4 MoO_2
All atoms in 4(e): xyz; $\bar{x}\bar{y}\bar{z}$; $\bar{x}$, $\frac{1}{2}+y$, $\frac{1}{2}-z$; x, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$ Å^2
	0.232	*0*	*0.017*	
Mo 1	0.23164 ± 0.00005	0.99159 ± 0.00006	0.01644 ± 0.00005	0.181 ± 0.002
	0.11	*0.21*	*0.24*	
O 2	0.1123 ± 0.0006	0.2171 ± 0.0006	0.2335 ± 0.0005	0.370 ± 0.020
	0.39	*0.70*	*0.30*	
O 3	0.3908 ± 0.0006	0.6969 ± 0.0006	0.2987 ± 0.0006	0.339 ± 0.019

Table 3. Weighting-scheme analysis from the last cycle of refinement. w = weighting factor, $\Delta = ||F_{obs}| - |F_{calc}||$.

Interval $\sin\theta$	Number of independent reflections	$\overline{w\Delta^2}$ (normalized)	Interval F_{obs}	Number of independent reflections	$\overline{w\Delta^2}$ (normalized)
0.00—0.46	186	1.38	0— 6	11	1.40
0.46—0.58	195	1.00	6—13	248	1.07
0.58—0.67	162	1.38	13—19	343	1.21
0.67—0.74	157	0.85	19—26	244	1.02
0.74—0.79	142	0.99	26—32	171	0.46
0.79—0.84	116	0.88	32—38	130	0.74
0.84—0.89	114	0.71	38—45	69	1.20
0.89—0.93	111	0.64	45—51	69	0.72
0.93—0.97	97	0.76	51—58	37	1.53
0.97—1.00	64	1.04	> 58	22	1.72

A final difference Fourier ($F_o - F_c$) shows no unusual features and no signs of any significant anisotropy of the thermal vibration. Since the calculated temperature factors of all atoms are very low, and in reality must be positive, any anisotropy must be low in an absolute sense.

The temperature factors of both the molybdenum and oxygen atoms are the lowest reported for any molybdenum oxide. This is consistent with the fact that the dioxide has the highest degree of close packing among them.

If the unit-cell volume is divided by the number of oxygen atoms in the unit cell, the quotient for MoO_2 is 16.44 Å^3 whereas the values for the other oxides range over 16.9—20.5 Å^3.[2]

DISCUSSION OF THE STRUCTURE

The refinement has shown that the structure proposed by Magnéli[3] is correct, and none of the atoms has moved by more than 0.05 Å from the originally proposed positions; the biggest movement is of the molybdenum atoms (0.05 Å). The most significant change is that the structure has been shown to conform strictly to space group $P2_1/c$ and not $P2_1$. Magnéli and Andersson[15] had earlier pointed out that the structure of MoO_2 was very nearly centrosymmetric, and proposed a set of coordinates in that space group.

The structure which consists of Mo—O octahedra joined by corners and edges, is shown in Fig. 1. In a string of octahedra joined by edges, the Mo—Mo distances are alternately shorter and longer than in the metal. The octahedra, all of which are identical, are only moderately distorted (see Fig. 2), the Mo—O distances ranging between 1.972 and 2.073 Å. The greatest distortion occurs along the edge which contains the very short Mo—Mo bond across it. Here the O—O distance is 3.088 Å, compared to the others which are in the range 2.707—2.901 Å. The interatomic distances and angles are shown in Table 5.

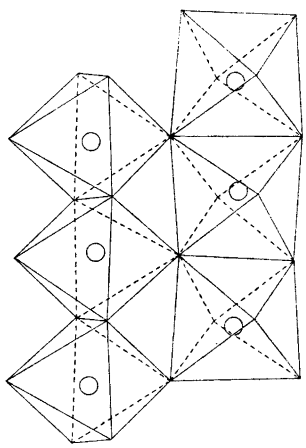

Fig. 1. The structure of MoO_2.

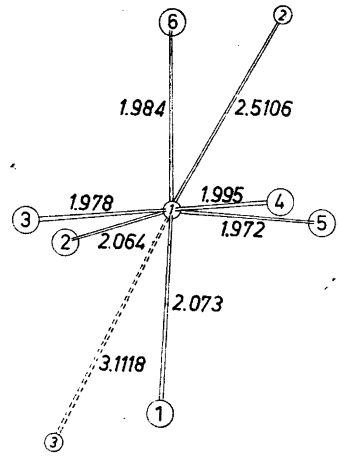

Fig. 2. The coordination about the molybdenum atom showing the short metal-metal bond. The molybdenum atoms (small circles) and oxygen atoms 1, 2, 4, and 6 all lie approximately in a common plane.

Table 4. Observed and calculated structure factors for MoO_2.

h	k	l	F_{obs}	F_{calc}
3	0	0	32·9	36·1
4	0	0	53·5	58·8
5	0	0	39·9	41·5
6	0	0	56·9	57·1
7	0	0	43·7	40·5
8	0	0	39·8	37·0
9	0	0	38·7	36·4
10	0	0	14·9	8·9
11	0	0	31·0	29·7
13	0	0	20·0	21·3
1	0	2	10·3	8·0
*2	0	2	80·6	109·8
3	0	2	8·5	7·2
4	0	2	69·4	80·4
5	0	2	24·4	23·0
6	0	2	41·7	40·4
7	0	2	33·0	29·5
8	0	2	28·0	27·6
9	0	2	26·1	25·1
10	0	2	23·3	23·0
11	0	2	20·1	20·3
12	0	2	8·8	8·4
*3	0	2	48·1	62·3
*4	0	2	75·7	101·4
5	0	2	55·9	61·0
6	0	2	42·7	43·4
9	0	4	49·3	53·1
8	0	4	23·9	24·2
*7	0	4	53·3	63·9
6	0	4	28·6	28·8
5	0	4	54·2	62·0
4	0	4	35·7	38·8
*3	0	4	48·1	63·1
*2	0	4	66·5	91·9
1	0	4	49·2	57·0
*0	0	4	72·1	94·3
1	0	4	22·1	22·7
2	0	4	57·9	59·5
4	0	4	53·2	53·5
5	0	4	10·3	6·4
6	0	4	47·5	49·9
7	0	4	15·8	11·8
8	0	4	28·4	28·5
9	0	4	19·5	18·1
10	0	4	13·1	12·7
10	0	6	16·7	11·6
9	0	6	41·3	45·9
8	0	6	9·6	6·6
7	0	6	55·1	59·6
6	0	6	24·1	24·2
5	0	6	66·0	73·2
4	0	6	40·5	42·8
3	0	6	52·8	59·5
2	0	6	35·6	37·1
1	0	6	38·4	39·4
0	0	6	47·4	49·9
1	0	6	31·3	32·7
2	0	6	57·9	59·8
3	0	6	25·2	17·8
4	0	6	42·8	43·4
6	0	6	30·0	28·1
7	0	6	9·9	7·3
8	0	6	26·1	25·1
9	0	6	5·8	5·7
12	0	8	26·2	24·4
11	0	8	31·9	31·9
10	0	8	15·6	12·4
9	0	8	44·4	50·4
7	0	8	51·2	52·1
6	0	8	9·6	4·1
5	0	8	49·4	49·9
4	0	8	15·2	14·0
3	0	8	54·7	57·3
2	0	8	34·0	35·0
1	0	8	47·2	48·3
0	0	8	32·9	33·1
1	0	8	26·1	24·5
2	0	8	29·0	28·8
3	0	8	17·1	14·5
4	0	8	31·9	32·3
5	0	8	14·2	11·3
6	0	8	25·6	27·2
12	0	10	23·6	20·7
11	0	10	23·5	23·8
10	0	10	24·9	25·5
9	0	10	28·1	29·2
8	0	10	20·8	16·9
7	0	10	42·9	46·5
5	0	10	45·7	50·5
3	0	10	33·7	36·9
2	0	10	8·8	8·3
1	0	10	31·3	33·0
0	0	10	20·4	20·4
1	0	10	30·9	31·8
2	0	10	24·6	23·1
3	0	10	18·9	17·1
4	0	10	17·0	17·7
5	0	10	6·5	5·0
12	0	12	23·7	23·3
11	0	12	21·5	20·2
10	0	12	21·7	19·6
9	0	12	27·9	28·6
8	0	12	21·2	19·3
7	0	12	24·3	25·0
6	0	12	18·7	14·8
5	0	12	30·4	30·8
3	0	12	35·8	37·8
1	0	12	26·5	27·3
0	0	12	11·0	6·8
1	0	12	16·0	16·3
2	0	12	10·7	10·6
12	0	14	19·5	21·2
11	0	14	7·2	5·2
10	0	14	20·6	21·9
9	0	14	15·0	12·7
8	0	14	17·7	17·5
7	0	14	25·3	25·3
6	0	14	13·4	12·9
5	0	14	21·3	22·0
4	0	14	10·7	8·8
3	0	14	15·7	17·3
7	0	2	50·9	52·5
8	0	2	14·9	13·5
9	0	2	46·7	45·4
10	0	2	16·4	12·5
11	0	2	35·6	35·8
13	0	2	23·9	24·7
14	0	2	9·8	8·8
11	0	4	35·3	36·4
12	0	4	16·9	13·7
13	0	4	26·0	25·8
14	0	4	10·0	8·3
11	0	6	38·5	39·6
13	0	6	27·1	27·2
14	0	6	17·5	15·6
15	0	6	13·7	13·5
13	0	8	18·7	17·6
14	0	8	19·7	21·1
15	0	8	13·6	13·7
13	0	10	22·3	20·1
14	0	10	18·3	18·7
15	0	10	8·7	7·4
14	0	12	20·7	23·1
** 5	0	7	5·2	0·0
** 7	0	5	4·5	0·0
3	1	0	6·1	5·1
4	1	0	10·6	9·0
6	1	0	15·1	12·8
*2	1	1	134·7	114·2
3	1	1	20·7	20·4
4	1	1	64·6	71·2
5	1	1	34·2	31·7
6	1	1	50·0	47·6
7	1	1	36·6	34·3
8	1	1	31·6	32·6
9	1	1	31·1	30·4
10	1	1	17·8	16·9
11	1	1	24·9	24·9
2	1	1	41·1	47·9
*4	1	1	65·2	78·5
6	1	2	12·7	11·0
1	1	2	12·4	12·0
2	1	2	19·2	19·1
4	1	2	9·3	8·5
7	1	3	58·2	57·9
6	1	3	37·0	35·3
5	1	3	56·5	62·1
*4	1	3	57·9	68·2
*3	1	3	52·3	63·4
*2	1	3	62·3	100·1
1	1	3	41·4	47·0
*0	1	3	65·0	92·0
1	1	3	16·5	15·9
*2	1	3	67·5	78·2
4	1	3	67·1	65·9
5	1	3	14·7	13·7
6	1	3	47·0	46·4
7	1	3	22·7	20·2
8	1	3	28·7	27·9
9	1	3	22·1	21·3
10	1	3	18·8	17·4
11	1	3	17·9	17·8
9	1	5	53·5	49·8
8	1	5	10·2	8·6
7	1	5	60·6	62·4
6	1	5	28·0	27·5
5	1	5	64·0	68·1
4	1	5	42·7	41·6
3	1	5	54·3	60·3
2	1	5	51·3	57·7
1	1	5	43·5	46·2
0	1	5	62·7	68·2
1	1	5	29·1	28·8
2	1	5	62·6	60·6
3	1	5	10·0	9·3
4	1	5	47·9	47·7
6	1	5	34·8	37·9
8	1	5	25·8	27·1
9	1	5	11·0	11·3
10	1	5	15·3	15·8
6	1	4	17·3	16·4
3	1	4	13·3	11·7
2	1	4	16·0	14·7
0	1	4	15·6	15·2
2	1	4	8·2	7·8
4	1	6	13·7	12·6
3	1	6	7·7	5·7
2	1	6	9·2	9·0
11	1	7	35·3	36·2
10	1	7	15·0	11·6
9	1	7	46·0	48·2
7	1	7	56·7	55·4
6	1	7	9·8	8·5
5	1	7	59·8	60·9
4	1	7	27·3	27·0
3	1	7	57·1	58·9
2	1	7	38·8	36·8
1	1	7	46·2	44·2
0	1	7	42·5	40·2
1	1	7	27·0	28·2
2	1	7	40·0	42·3
3	1	7	18·8	16·6
4	1	7	34·8	37·8
6	1	7	27·6	27·8
8	1	7	19·0	20·1
12	1	9	23·9	22·6
11	1	9	27·7	27·5
10	1	9	19·5	19·8
9	1	9	38·6	39·6
8	1	9	12·8	11·1
7	1	9	50·5	49·7
5	1	9	51·2	50·1
3	1	9	47·0	46·0
2	1	9	21·3	19·8
1	1	9	38·0	40·5
0	1	9	27·3	26·4
1	1	9	29·6	29·0
2	1	9	27·4	25·8
3	1	9	15·1	15·8
4	1	9	23·4	23·9
5	1	9	7·4	8·0
6	1	9	19·7	21·0
12	1	11	23·4	22·1
11	1	11	24·1	22·3
10	1	11	23·4	22·3
9	1	11	29·4	28·6
8	1	11	20·2	18·6
7	1	11	33·1	34·6
5	1	11	39·1	40·2
3	1	11	35·6	37·8
1	1	11	27·9	29·6
0	1	11	14·7	12·4
1	1	11	23·4	23·3
2	1	11	15·4	16·0
3	1	11	16·1	16·9
12	1	13	22·5	22·4
11	1	13	12·2	12·0
10	1	13	22·0	21·2
9	1	13	21·9	20·8
8	1	13	18·4	18·3
7	1	13	26·1	25·3
6	1	13	15·3	13·7
5	1	13	26·6	25·6
3	1	13	27·8	26·4
1	1	13	23·5	24·4
11	1	15	6·8	6·9
10	1	15	18·4	19·5
9	1	15	9·5	10·1
8	1	15	16·9	17·1
7	1	15	14·2	15·5
6	1	15	12·3	13·0
5	1	15	17·7	19·0
1	1	1	50·1	50·5
6	1	1	55·7	51·7
7	1	1	48·3	46·8
8	1	1	27·8	25·8
9	1	1	39·4	40·8
10	1	1	8·2	10·3
11	1	1	30·9	32·4
13	1	1	21·7	23·0
8	1	3	20·6	19·0
9	1	3	48·3	49·2
11	1	3	37·1	36·5
13	1	3	25·1	25·4
14	1	3	9·8	8·8
11	1	5	37·3	37·8
13	1	5	25·5	26·6
14	1	5	11·8	11·6
15	1	5	15·0	16·1
12	1	7	17·5	16·5
13	1	7	22·6	22·6
14	1	7	18·0	18·7
15	1	7	12·5	13·4
13	1	9	18·8	18·8
14	1	9	19·9	19·7
15	1	9	11·6	10·8
13	1	11	12·6	12·6
14	1	11	20·2	21·3
3	2	0	28·0	30·5
*4	2	0	67·6	87·7

* Reflections removed from refinement because of extinction.

** Probable Renninger reflections.

h	k	l	F_{obs}	F_{calc}
5	2	0	37·5	39·4
6	2	0	38·6	42·7
7	2	0	41·6	40·1
8	2	0	25·2	22·6
9	2	0	33·6	34·6
10	2	0	19·9	18·7
11	2	0	26·9	27·5
12	2	0	5·9	6·8
13	2	0	19·7	21·1
2	2	1	5·5	4·1
3	2	1	8·1	8·3
1	2	2	10·4	8·7
*2	2	2	61·4	77·9
3	2	2	15·3	14·1
4	2	2	54·3	57·7
5	2	2	23·5	21·0
6	2	2	52·0	53·5
7	2	2	24·9	24·1
8	2	2	34·6	32·7
9	2	2	25·1	25·9
10	2	2	12·0	11·9
11	2	2	22·1	22·0
12	2	2	7·4	7·4
*3	2	2	37·4	50·8
*4	2	2	42·7	51·0
*5	2	2	44·9	52·6
6	2	2	41·9	44·4
6	2	3	6·3	5·3
5	2	3	6·9	6·0
4	2	3	4·3	3·5
3	2	3	12·7	11·8
2	2	3	12·5	11·8
1	2	3	7·0	6·4
0	2	3	13·0	12·4
1	2	3	6·9	6·6
2	2	3	6·9	5·6
3	2	3	9·3	9·8
7	2	4	55·9	57·1
6	2	4	32·3	33·8
5	2	4	59·4	68·2
*4	2	4	53·1	66·3
*3	2	4	46·7	60·0
*2	2	4	48·2	60·8
1	2	4	33·6	36·6
*0	2	4	52·8	64·3
1	2	4	24·2	23·6
*2	2	4	65·7	76·0
3	2	4	9·4	8·0
4	2	4	51·9	58·3
5	2	4	13·0	9·9
6	2	4	32·7	34·5
7	2	4	15·9	16·1
8	2	4	26·7	27·0
9	2	4	13·6	13·7
10	2	4	20·1	20·4
6	2	5	10·2	10·1
4	2	5	13·3	12·1
1	2	5	11·4	10·6
1	2	5	6·2	6·6
2	2	5	7·7	6·9
9	2	6	50·9	52·2
8	2	6	11·9	8·4
7	2	6	55·6	58·4
6	2	6	12·9	10·7
5	2	6	51·0	56·1
4	2	6	26·7	25·6
3	2	6	52·3	59·3
2	2	6	49·4	53·9
1	2	6	45·7	50·2
0	2	6	52·3	54·2
1	2	6	25·9	24·7
2	2	5	41·2	42·0
3	2	6	12·7	9·6
4	2	6	39·8	41·6
6	2	6	35·5	36·7
8	2	6	21·2	21·6
9	2	6	9·5	10·7
8	2	7	8·7	8·2
2	2	7	9·5	10·0
11	2	8	32·8	31·7
10	2	8	22·2	19·4
9	2	8	36·7	37·7
8	2	8	14·3	12·5
7	2	8	50·2	53·0
6	2	8	8·4	8·5
5	2	8	57·1	60·2
4	2	8	17·2	17·9
3	2	8	46·8	46·9
2	2	8	22·0	20·1
1	2	8	41·0	37·0
0	2	8	32·7	32·2
1	2	8	31·6	33·0
2	2	8	36·0	37·4
3	2	8	19·7	18·2
6	2	8	21·8	21·1
4	2	8	28·2	28·0
12	2	10	25·7	24·1
11	2	10	26·9	25·7
10	2	10	18·2	17·2
9	2	10	35·4	38·2
8	2	10	15·2	13·9
7	2	10	35·1	37·2
6	2	10	13·3	10·8
5	2	10	36·8	39·6
3	2	10	43·0	46·2
2	2	10	17·1	15·8
1	2	10	34·8	36·3
0	2	10	18·1	16·6
1	2	10	22·0	20·6
2	2	10	17·8	17·6
3	2	10	17·6	16·1
4	2	10	20·5	20·5
12	2	12	23·2	21·5
11	2	12	14·3	13·4
10	2	12	25·9	23·9
9	2	12	21·5	20·5
8	2	12	19·9	17·9
7	2	12	34·7	34·0
6	2	12	8·2	9·4
5	2	12	34·0	33·6
3	2	12	25·5	25·6
1	2	12	27·0	26·4
0	2	12	8·8	9·2
1	2	12	23·3	24·3
2	2	12	11·8	11·7
7	2	14	16·7	14·7
10	2	14	19·2	18·9
9	2	14	16·7	16·1
8	2	14	18·1	18·1
7	2	14	15·8	14·7
6	2	14	14·2	14·1
5	2	14	22·0	21·8
4	2	14	8·4	7·1
3	2	14	24·4	25·4
5	2	1	8·5	7·5
7	2	2	49·5	52·2
8	2	2	34·5	31·0
9	2	2	42·8	44·6
11	2	2	33·2	33·3
13	2	2	22·6	23·8
8	2	3	11·3	10·9
9	2	4	45·1	46·6
11	2	4	37·9	38·2
13	2	4	26·5	26·2
14	2	4	12·1	11·9
11	2	6	34·3	34·8
12	2	6	21·3	19·0
13	2	6	24·5	22·3
14	2	6	15·8	14·8
15	2	6	15·8	16·1
12	2	8	16·5	15·4
13	2	8	24·2	23·6
14	2	8	17·3	17·5
15	2	8	11·3	10·7
13	2	10	12·6	11·3
14	2	10	21·7	22·4
15	2	10	7·8	7·8
13	2	12	12·7	12·5
14	2	12	18·7	18·5
12	2	14	18·5	20·0
2	3	0	18·9	19·8
3	3	0	11·0	10·5
4	3	0	5·6	1·6
*2	3	1	54·8	72·4
3	3	1	21·0	21·5
4	3	1	63·2	71·0
5	3	1	29·9	27·2
6	3	1	49·9	50·8
7	3	1	30·2	29·7
8	3	1	24·4	23·5
9	3	1	31·2	29·8
10	3	1	15·1	13·1
11	3	1	22·4	23·9
12	3	1	10·5	9·5
*2	3	1	71·8	108·6
3	3	1	32·8	36·5
*4	3	1	55·3	64·4
5	3	1	40·4	42·5
6	3	2	17·2	16·7
5	3	2	9·6	8·4
4	3	2	9·2	9·7
3	3	2	16·5	15·7
2	3	2	11·9	9·8
1	3	2	13·4	13·0
0	3	2	10·6	8·9
1	3	2	11·6	10·2
2	3	2	11·6	9·9
3	3	2	14·8	13·1
4	3	2	10·1	8·1
5	3	2	12·0	10·3
8	3	3	18·0	16·8
7	3	3	50·5	52·8
6	3	3	39·5	44·1
*5	3	3	49·6	59·0
4	3	3	47·8	52·7
3	3	3	41·9	49·0
*2	3	3	50·1	62·0
1	3	3	31·5	32·3
*0	3	3	63·1	88·5
1	3	3	19·5	18·7
*2	3	3	65·2	78·1
4	3	3	48·0	50·7
5	3	3	17·6	16·3
6	3	3	40·4	39·9
7	3	3	19·4	18·8
8	3	3	32·8	32·2
9	3	3	18·7	17·3
10	3	3	14·8	16·1
11	3	3	15·9	17·4
5	3	4	6·4	5·9
4	3	4	14·9	13·2
2	3	4	17·0	17·5
1	3	4	13·5	12·8
1	3	4	15·6	14·4
9	3	5	48·3	49·2
7	3	5	49·7	53·2
6	3	5	17·5	15·4
5	3	5	51·0	56·9
4	3	5	44·3	45·8
*3	3	5	51·4	59·8
2	3	5	53·1	58·6
1	3	5	40·3	42·3
0	3	5	46·1	50·1
1	3	5	22·0	19·6
2	3	5	48·6	52·8
3	3	5	12·2	9·5
4	3	5	48·6	51·6
6	3	5	34·2	34·4
7	3	5	8·6	10·2
8	3	5	21·9	20·7
9	3	5	13·1	12·7
4	3	6	9·0	4·1
6	3	6	14·6	14·9
3	3	6	10·2	10·5
0	3	6	11·6	11·3
11	3	7	29·5	30·1
10	3	7	18·7	15·8
9	3	7	42·3	42·1
7	3	7	52·9	56·8
6	3	7	13·5	11·8
5	3	7	53·2	55·8
4	3	7	17·8	16·0
3	3	7	45·7	46·2
2	3	7	34·8	32·1
1	3	7	40·9	42·5
0	3	7	45·7	44·5
1	3	7	33·4	31·3
2	3	7	38·2	37·6
3	3	7	14·5	12·0
4	3	7	32·5	30·1
6	3	7	28·1	28·3
4	3	8	14·4	12·7
12	3	9	19·5	17·4
11	3	9	32·0	30·3
10	3	9	19·0	16·3
9	3	9	37·2	36·2
8	3	9	17·8	15·8
7	3	9	38·4	39·4
5	3	9	49·1	48·9
4	3	9	14·9	12·7
3	3	9	45·6	48·0
2	3	9	18·8	16·3
1	3	9	31·0	32·7
0	3	9	21·1	20·2
1	3	9	23·5	23·6
2	3	9	26·6	26·7
3	3	9	19·2	19·2
4	3	9	24·3	24·3
5	3	9	9·2	8·4
12	3	11	24·6	23·8
11	3	11	17·9	15·9
10	3	11	22·0	20·2
9	3	11	30·8	29·4
8	3	11	16·7	13·6
7	3	11	37·0	36·8
6	3	11	12·8	10·5
5	3	11	33·0	32·2
3	3	11	31·7	32·1
2	3	11	11·1	8·4
1	3	11	32·5	32·9
0	3	11	14·8	12·9
1	3	11	23·7	22·3
2	3	11	13·6	12·7
3	3	11	10·9	11·7
12	3	13	18·8	19·2
11	3	13	15·2	14·6
10	3	13	21·4	21·2
9	3	13	14·4	14·9
8	3	13	17·7	18·3
7	3	13	20·0	21·4
6	3	13	10·3	10·8
5	3	13	29·1	29·1
3	3	13	24·8	24·8
1	3	13	18·1	18·3
9	3	15	12·7	14·0
8	3	15	15·9	16·3
7	3	15	13·2	14·3
6	3	15	12·2	13·3
6	3	1	37·3	35·1
7	3	1	44·1	44·6

h	k	l	F_{obs}	F_{calc}
8	3	1	28·8	28·2
9	3	1	35·9	38·1
10	3	1	17·4	15·1
11	3	1	28·3	28·8
13	3	1	19·7	21·9
9	3	3	41·4	42·7
11	3	3	32·4	34·6
13	3	3	23·5	24·9
11	3	5	35·4	36·1
12	3	5	8·6	10·0
13	3	5	22·2	22·4
14	3	5	14·4	15·5
12	3	7	17·4	17·9
13	3	7	23·5	23·5
14	3	7	12·9	13·3
15	3	7	11·5	13·9
13	3	9	16·2	15·2
14	3	9	19·0	21·0
15	3	9	6·2	7·3
13	3	11	12·1	11·1
14	3	11	17·5	19·3
*2	4	0	61·0	76·7
3	4	0	27·7	27·1
4	4	0	53·4	54·4
5	4	0	30·7	30·7
6	4	0	44·7	44·2
7	4	0	34·4	34·0
8	4	0	28·7	28·2
9	4	0	33·9	32·7
11	4	0	25·5	25·1
8	4	1	17·1	14·9
6	4	1	11·5	11·9
5	4	1	10·1	9·6
4	4	1	7·2	4·5
3	4	1	17·7	17·0
1	4	1	15·3	14·7
2	4	1	8·4	7·3
3	4	1	16·3	15·7
4	4	1	14·6	13·9
5	4	1	12·2	12·5
9	4	2	35·3	37·0
8	4	2	18·4	15·1
7	4	2	43·1	45·6
6	4	2	35·4	35·7
5	4	2	47·1	48·7
4	4	2	56·8	62·8
3	4	2	37·8	38·0
2	4	2	65·7	71·7
1	4	2	24·2	22·5
0	4	2	66·1	70·6
1	4	2	11·4	10·0
*2	4	2	62·0	74·1
3	4	2	8·5	7·4
4	4	2	56·3	61·0
5	4	2	23·4	21·3
6	4	2	37·3	38·2
7	4	2	24·9	23·5
8	4	2	26·4	24·8
9	4	2	22·5	20·7
10	4	2	18·8	17·3
11	4	2	18·6	19·0
6	4	3	12·0	12·0
4	4	3	22·3	22·4
3	4	3	10·5	9·4
1	4	3	18·3	18·6
1	4	3	16·7	16·9
2	4	3	11·1	9·1
3	4	3	9·5	9·4
11	4	4	30·9	32·9
9	4	4	45·6	45·2
8	4	4	18·4	15·6
7	4	4	50·1	50·0
6	4	4	27·4	26·1
5	4	4	48·2	50·5
4	4	4	37·7	37·7
3	4	4	44·7	50·9
*2	4	4	51·4	59·9
1	4	4	36·7	38·2
0	4	4	61·7	66·7
1	4	4	15·7	15·8
2	4	4	52·1	54·3
4	4	4	43·7	45·8
6	4	4	38·4	39·0
7	4	4	13·9	12·2
8	4	4	25·7	25·1
9	4	4	15·2	15·5
10	4	4	12·8	13·2
13	4	6	23·4	23·4
11	4	6	30·9	31·8
9	4	6	39·2	40·3
7	4	6	49·1	52·2
6	4	6	18·0	15·8
5	4	6	55·6	56·4
4	4	6	32·1	31·9
3	4	6	45·1	46·6
2	4	6	36·3	35·9
1	4	6	39·3	36·4
0	4	6	42·7	41·6
1	4	6	28·8	27·4
2	4	6	45·5	46·3
4	4	6	36·5	38·1
6	4	6	27·0	26·5
8	4	6	19·0	20·6
8	4	5	19·2	17·4
5	4	5	10·3	10·3
3	4	5	12·3	10·8
2	4	5	18·0	17·7
0	4	5	12·3	10·7
1	4	5	12·2	11·7
3	4	5	14·0	14·3
6	4	7	17·0	16·8
4	4	7	15·4	13·6
1	4	7	14·7	12·6
14	4	8	17·0	17·0
13	4	8	16·4	16·7
12	4	8	20·6	19·4
11	4	8	29·2	28·9
10	4	8	13·8	13·3
9	4	8	38·3	40·1
7	4	8	40·1	43·2
5	4	8	45·4	45·7
4	4	8	13·8	11·4
3	4	8	46·2	47·5
2	4	8	25·2	25·9
1	4	8	36·4	37·4
0	4	8	29·2	29·6
1	4	8	22·5	22·5
2	4	8	28·7	26·7
3	4	8	15·8	14·5
4	4	8	26·7	26·1
6	4	8	21·7	23·0
14	4	10	15·8	18·2
13	4	10	14·8	15·4
12	4	10	18·3	18·1
11	4	10	21·5	20·3
10	4	10	21·0	19·6
9	4	10	28·5	28·0
8	4	10	16·7	15·2
7	4	10	38·2	38·6
5	4	10	37·7	40·0
3	4	10	32·9	33·6
1	4	10	30·4	30·2
0	4	10	18·2	15·6
1	4	10	24·6	25·0
2	4	10	20·4	19·6
3	4	10	13·5	14·2
4	4	10	17·2	17·1
13	4	12	7·3	6·8
12	4	12	20·7	21·2
11	4	12	17·7	16·5
10	4	12	17·9	18·3
9	4	12	22·7	22·4
8	4	12	15·4	15·1
7	4	12	25·2	23·7
6	4	12	11·0	12·0
5	4	12	26·6	28·1
3	4	12	29·2	30·0
1	4	12	22·8	23·3
1	4	12	15·6	16·6
10	4	14	18·6	19·1
9	4	14	13·5	13·0
8	4	14	16·6	16·6
7	4	14	19·2	19·6
6	4	14	11·8	10·9
5	4	14	18·0	19·2
4	4	14	6·6	6·7
3	4	14	16·3	17·5
11	4	2	30·2	30·2
13	4	2	21·6	22·8
13	4	4	19·4	21·7
14	4	6	13·8	14·1
3	5	0	19·4	20·2
4	5	0	8·2	8·0
5	5	0	13·9	13·7
6	5	0	9·0	10·3
9	5	1	31·3	32·1
8	5	1	17·5	17·3
7	5	1	34·7	35·9
6	5	1	47·8	45·3
5	5	1	35·4	36·8
4	5	1	53·5	54·3
3	5	1	30·9	29·1
2	5	1	53·5	52·4
2	5	1	73·0	78·0
3	5	1	14·6	13·6
4	5	1	48·4	47·6
5	5	1	24·4	24·8
6	5	1	31·3	32·0
7	5	1	27·1	26·9
8	5	1	28·8	29·7
9	5	1	23·1	23·3
10	5	1	15·7	15·3
11	5	1	20·7	20·4
4	5	2	10·1	10·1
3	5	2	12·5	12·6
2	5	2	12·4	11·1
1	5	2	22·4	21·9
1	5	2	18·8	19·8
3	5	2	11·2	12·3
11	5	3	29·2	29·3
10	5	3	9·3	9·9
9	5	3	41·5	39·6
8	5	3	16·9	15·3
7	5	3	43·9	43·1
6	5	3	19·4	19·3
5	5	3	43·3	43·0
4	5	3	48·9	47·8
3	5	3	43·7	42·5
2	5	3	71·5	68·6
1	5	3	30·6	29·5
0	5	3	53·5	54·9
1	5	3	9·1	8·5
2	5	3	49·7	50·8
4	5	3	53·9	55·3
6	5	3	35·7	38·3
7	5	3	16·7	16·6
8	5	3	17·3	18·4
9	5	3	17·6	18·5
10	5	3	13·4	14·1
6	5	4	14·3	15·3
5	5	4	11·6	11·2
4	5	4	12·8	12·8
3	5	4	14·2	14·1
2	5	4	7·7	7·4
1	5	4	9·9	11·1
0	5	4	8·5	7·3
1	5	4	13·6	14·3
3	5	4	16·6	16·0
13	5	5	22·6	22·8
12	5	5	8·8	8·7
11	5	5	28·4	28·9
9	5	5	36·4	37·5
7	5	5	50·8	50·1
6	5	5	26·7	26·1
5	5	5	48·6	50·7
4	5	5	28·1	25·9
3	5	5	38·7	39·4
2	5	5	36·2	36·7
1	5	5	34·0	33·7
0	5	5	54·7	55·5
1	5	5	27·1	24·9
2	5	5	47·5	48·3
4	5	5	31·5	32·7
6	5	5	29·6	30·2
8	5	5	23·3	25·0
9	5	5	7·7	8·3
14	5	7	17·7	18·1
13	5	7	17·6	17·2
12	5	7	12·8	11·9
11	5	7	31·8	31·1
9	5	7	39·5	38·4
7	5	7	40·3	39·3
5	5	7	48·6	47·1
4	5	7	26·1	25·1
3	5	7	48·7	48·6
2	5	7	30·0	29·6
1	5	7	31·9	32·0
0	5	7	27·2	26·5
1	5	7	20·2	19·1
2	5	7	32·8	33·5
3	5	7	15·1	15·6
4	5	7	33·1	33·3
14	5	9	13·5	14·3
13	5	9	17·3	15·7
12	5	9	20·5	20·2
11	5	9	20·4	18·9
10	5	9	18·0	17·5
9	5	9	33·2	32·0
7	5	9	41·0	42·6
5	5	9	36·9	36·9
3	5	9	33·0	32·9
2	5	9	17·0	15·9
1	5	9	33·7	35·1
0	5	9	23·3	23·7
1	5	9	24·8	24·6
2	5	9	19·9	19·4
4	5	9	18·4	17·9
5	5	9	5·9	6·3
13	5	11	10·8	11·0
12	5	11	17·0	16·1
11	5	11	21·1	20·8
10	5	11	20·0	17·5
9	5	11	21·7	20·8
8	5	11	17·6	17·1
7	5	11	26·5	24·9
5	5	11	33·9	35·3
3	5	11	30·4	31·6
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1	5	11	18·9	18·8
2	5	11	13·3	14·3
12	5	13	16·8	19·6
11	5	13	7·6	7·8
10	5	13	17·2	16·9
9	5	13	19·7	19·8
8	5	13	12·8	13·7
7	5	13	22·4	21·7
6	5	13	11·1	11·9
5	5	13	17·8	17·4
3	5	13	22·2	21·6

h	k	l	F_{obs}	F_{calc}
11	5	1	25·3	26·3
13	5	3	20·0	20·1
6	5	7	21·3	21·5
2	5	0	60·1	58·1
3	6	0	17·4	17·2
4	6	0	41·8	46·9
5	6	0	28·3	29·9
6	6	0	34·3	34·2
7	6	0	28·5	28·7
8	6	0	21·3	20·9
9	6	0	25·6	23·4
10	6	0	10·5	10·1
11	6	0	20·6	21·6
5	5	1	13·0	12·6
4	6	1	21·3	19·9
3	5	1	17·8	16·7
3	6	1	15·9	16·1
5	6	1	13·9	13·4
6	6	1	13·9	12·8
11	6	2	25·6	25·7
9	6	2	34·7	34·4
8	5	2	17·2	15·8
7	6	2	34·1	34·5
6	6	2	31·8	29·9
5	6	2	32·6	33·6
4	5	2	43·7	43·9
3	6	2	34·2	34·0
2	5	2	59·0	53·4
0	6	2	62·8	58·5
2	6	2	51·2	55·1
3	6	2	8·9	7·4
4	6	2	45·1	45·3
5	5	2	13·3	12·3
6	6	2	33·2	32·8
7	6	2	21·2	19·6
8	5	2	22·7	22·4
9	6	2	21·9	20·4
10	6	2	12·1	13·1
8	6	3	20·7	19·6
6	5	3	11·8	12·7
5	6	3	12·8	12·8
3	6	3	16·5	15·0
2	6	3	15·0	14·3
1	5	3	13·7	14·3
0	6	3	14·9	14·2
1	5	3	16·3	17·5
3	6	3	19·8	18·6
13	6	4	19·1	21·0
11	6	4	26·5	26·0
9	6	4	33·1	33·6
8	6	4	10·0	9·6
7	6	4	44·4	43·8
6	6	4	21·1	20·0
5	6	4	41·7	43·5
4	5	4	33·1	34·3
3	6	4	35·7	33·9
2	6	4	45·4	45·7
1	6	4	28·3	27·5
0	5	4	44·4	47·7
1	6	4	18·7	18·2
2	6	4	46·1	45·2
4	6	4	38·1	40·3
6	6	4	31·3	30·4
8	6	4	20·3	19·6
9	6	4	9·5	10·9
6	6	5	18·4	17·9
4	6	5	21·3	20·7
3	6	5	10·4	11·0
1	6	5	17·0	18·0
13	6	6	16·8	17·4
12	6	6	11·4	10·2
11	6	6	28·2	28·5
9	6	6	36·0	35·7
7	6	6	38·6	38·5
6	6	6	13·9	13·0
5	6	6	45·7	43·3
4	6	6	21·8	21·2
3	6	6	43·2	42·4
2	6	6	30·1	29·9
1	6	6	27·9	29·6
0	6	6	37·8	37·4
1	6	6	17·0	17·8
2	6	6	32·7	35·8
3	6	6	11·7	10·9
4	6	6	28·5	29·2
6	6	6	23·5	24·1
8	6	7	17·3	16·6
2	6	7	16·6	17·5
1	6	7	12·6	13·0
13	6	8	16·1	15·9
12	6	8	14·0	13·9
11	6	8	20·7	21·6
10	6	8	11·0	10·5
9	6	8	31·3	31·4
7	6	8	37·8	39·0
5	6	8	36·1	37·9
4	6	8	13·6	13·1
3	6	8	33·9	34·7
2	6	8	20·1	19·4
1	6	8	31·1	31·2
0	6	8	23·1	21·4
1	6	8	21·9	21·7
2	6	8	24·7	24·4
3	6	8	8·2	10·7
4	6	8	22·3	23·5
6	6	9	16·5	16·0
13	6	10	11·9	11·9
12	6	10	17·5	17·8
11	6	10	19·7	19·4
10	6	10	15·5	16·2
9	6	10	24·1	24·0
7	6	10	29·5	28·9
5	6	10	34·8	33·1
3	6	10	30·3	30·7
2	6	10	10·0	9·3
1	6	10	24·0	24·2
0	6	10	14·9	15·0
1	6	10	20·1	19·0
2	6	10	14·4	14·3
3	6	10	13·1	13·3
12	6	12	14·8	15·5
11	6	12	11·7	12·0
10	6	12	15·4	16·2
9	6	12	19·6	18·6
8	6	12	15·2	15·3
7	6	12	22·7	22·1
5	6	12	22·0	23·0
3	6	12	21·6	23·3
1	6	12	20·7	20·8
3	7	0	14·0	14·4
4	7	0	8·3	9·1
5	7	0	11·9	12·7
6	7	0	11·6	11·5
7	7	0	12·8	12·3
10	7	1	12·2	11·4
9	7	1	27·6	25·7
8	7	1	22·9	19·7
7	7	1	29·0	27·6
6	7	1	22·2	21·2
5	7	1	25·9	27·8
4	7	1	41·1	38·6
3	7	1	25·3	23·1
2	7	1	44·5	41·3
3	7	1	10·3	10·5
4	7	1	45·5	45·1
5	7	1	17·1	17·1
6	7	1	34·8	35·0
7	7	1	21·1	21·7
8	7	1	14·3	15·1
9	7	1	20·1	20·5
10	7	1	7·6	8·6
10	7	2	12·2	11·6
8	7	2	13·2	12·1
6	7	2	8·8	10·0
5	7	2	15·3	15·3
4	7	2	12·4	12·4
3	7	2	19·7	18·7
1	7	2	18·2	18·9
3	7	2	19·7	21·0
11	7	3	23·9	22·8
9	7	3	31·1	29·4
8	7	3	11·8	10·6
7	7	3	35·2	36·2
6	7	3	30·4	29·8
5	7	3	35·4	35·0
4	7	3	34·5	32·3
3	7	3	28·7	27·3
2	7	3	39·4	35·1
1	7	3	20·5	21·2
0	7	3	55·9	51·2
1	7	3	11·8	11·8
2	7	3	48·2	50·1
4	7	3	30·5	32·4
5	7	3	12·2	10·9
6	7	3	25·3	25·8
7	7	3	11·4	11·4
8	7	3	23·0	23·4
9	7	3	11·0	12·6
8	7	4	14·9	14·4
6	7	4	15·0	16·4
4	7	4	10·5	11·4
3	7	4	12·8	13·6
2	7	4	9·7	9·9
1	7	4	18·3	19·7
0	7	4	9·8	10·1
1	7	4	12·4	14·9
5	7	4	15·0	13·9
11	7	5	27·5	26·2
9	7	5	33·4	32·1
7	7	5	33·8	33·6
5	7	5	37·6	38·1
4	7	5	28·4	28·6
3	7	5	42·4	37·8
2	7	5	39·4	38·0
1	7	5	23·5	24·4
0	7	5	30·0	31·4
2	7	5	31·7	33·2
4	7	5	33·0	35·8
6	7	5	22·0	24·5
7	7	5	8·3	8·3
8	7	5	12·3	14·0
5	7	6	15·5	14·2
4	7	6	15·9	17·2
2	7	6	11·6	11·5
1	7	6	13·9	14·8
13	7	7	15·9	16·3
12	7	7	12·9	12·2
11	7	7	20·9	19·7
10	7	7	15·4	12·2
9	7	7	32·5	29·6
7	7	7	37·6	38·6
5	7	7	33·7	34·8
3	7	7	29·7	29·8
2	7	7	21·7	19·5
1	7	7	28·5	29·9
0	7	7	28·8	30·6
1	7	7	20·5	20·9
2	7	7	25·9	26·5
4	7	7	19·8	19·9
6	7	7	19·1	19·9
8	7	8	14·7	14·2
6	7	8	13·2	12·1
13	7	9	12·3	12·4
12	7	9	13·4	12·4
11	7	9	24·2	22·0
10	7	9	11·2	9·9
9	7	9	24·5	23·6
7	7	9	26·3	26·0
5	7	9	35·0	34·5
3	7	9	31·1	32·4
2	7	9	12·7	12·2
1	7	9	20·6	20·8
0	7	9	14·1	12·8
1	7	9	15·9	16·7
2	7	9	17·4	18·1
3	7	9	14·5	14·6
6	7	10	13·6	12·9
12	7	11	16·3	17·2
11	7	11	10·2	10·7
10	7	11	15·4	15·4
9	7	11	22·8	21·7
7	7	11	25·7	25·7
5	7	11	21·3	21·0
3	7	11	21·5	22·5
1	7	11	23·2	24·3
0	7	11	10·2	10·2
9	7	13	8·3	9·7
8	7	13	11·7	13·8
7	7	13	14·9	15·3
6	7	13	8·4	8·5
5	7	13	20·4	21·9
11	7	1	19·4	21·5
2	8	0	35·4	43·6
3	8	0	16·6	15·9
4	8	0	36·1	39·1
5	8	0	15·5	15·7
6	8	0	20·7	23·5
7	8	0	19·8	21·3
8	8	0	13·0	13·8
9	8	0	20·5	22·3
10	8	0	9·8	10·3
8	8	1	15·6	14·8
7	8	1	9·7	9·2
6	8	1	14·4	13·1
5	8	1	16·8	15·3
3	8	1	16·8	16·2
3	8	1	18·0	19·2
5	8	1	11·0	12·1
10	8	1	8·4	10·3
9	8	2	24·5	22·4
8	8	2	18·7	15·7
7	8	2	29·7	29·5
6	8	2	23·7	24·2
5	8	2	29·1	29·1
4	8	2	29·7	27·8
3	8	2	21·3	19·0
2	8	2	42·7	41·5
0	8	2	45·7	46·7
1	8	2	7·6	7·6
2	8	2	35·3	37·7
4	8	2	30·3	32·0
5	8	2	15·4	14·5
6	8	2	28·1	28·6
7	8	2	13·1	13·2
8	8	2	15·5	17·7
9	8	2	12·0	13·2
10	8	3	12·7	12·1
6	8	3	15·1	13·6
4	8	3	18·0	18·8
3	8	3	17·2	16·4
2	8	3	8·1	7·9
1	8	3	17·2	20·0
1	8	3	15·4	15·9
3	8	3	14·3	14·5
5	8	3	14·5	15·0
11	8	4	23·1	23·2
9	8	4	29·5	28·1
7	8	4	28·7	28·0
6	8	4	20·8	18·1
5	8	4	32·1	31·6

h	k	l	F_{obs}	F_{calc}
4	8	4	29·7	28·3
3	8	4	34·4	31·5
2	8	4	31·1	29·2
1	8	4	18·8	18·9
0	8	4	33·3	34·4
2	8	4	37·0	38·5
4	8	4	30·3	29·9
6	8	4	20·9	20·4
7	8	4	10·4	10·3
8	8	4	14·7	17·1
10	8	5	11·7	11·0
8	8	5	20·4	17·9
6	8	5	13·9	13·2
5	8	5	12·0	10·5
2	8	5	15·4	15·1
1	8	5	15·3	15·9
3	8	5	15·2	14·7
7	8	5	6·4	7·8
12	8	6	11·4	10·2
11	8	6	19·0	18·5
9	8	6	29·1	27·5
7	8	6	35·2	34·1
5	8	6	29·2	30·4
4	8	6	17·6	16·0
3	8	6	27·0	27·3
2	8	6	26·3	27·2
1	8	6	26·7	26·1
0	8	6	26·6	26·4
1	8	6	15·9	16·1
2	8	6	24·1	24·0
4	8	6	23·4	25·2
6	8	6	19·3	20·8
12	8	7	10·2	10·5
10	8	7	10·2	9·3
6	8	7	17·4	16·6
4	8	7	17·2	15·9
5	8	7	9·3	11·0
12	8	8	11·3	10·5
11	8	8	22·0	20·2
10	8	8	12·2	11·7
9	8	8	24·4	22·0
7	8	8	28·4	26·8
5	8	8	32·9	32·6
3	8	8	26·6	28·0
2	8	8	13·0	11·8
1	8	8	18·4	19·7
0	8	8	19·8	19·9
1	8	8	15·8	16·9
2	8	8	18·9	20·2
3	8	8	11·5	11·7
4	8	8	14·9	15·5
8	8	9	14·2	13·2
2	8	9	12·5	13·6
11	8	10	15·1	13·7
10	8	10	10·4	9·9
9	8	10	24·6	21·9
8	8	10	10·3	10·1
7	8	10	24·9	22·9
5	8	10	23·0	22·0
3	8	10	24·1	24·7
1	8	10	22·1	21·9
0	8	10	8·7	8·3
1	8	10	14·3	13·3
6	8	11	11·4	11·7
9	8	12	11·2	12·2
8	8	12	9·9	8·8
7	8	12	20·8	18·9
5	8	12	6·7	6·6
5	8	12	19·8	20·4
11	8	2	17·7	19·3
0	9	3	30·9	32·0
0	9	5	29·4	29·0
0	9	6	12·0	12·2
0	9	7	17·2	16·9
0	9	9	14·8	14·1
1	9	5	12·6	12·4
1	9	4	17·5	17·9
1	9	2	18·3	18·3
1	9	3	13·5	12·2
1	9	4	13·7	12·6
1	9	5	23·4	21·6
1	9	6	11·7	12·4
1	9	7	17·3	17·1
1	9	9	20·7	21·1
2	9	7	18·0	18·2
2	9	5	26·9	28·5
2	9	3	27·9	28·9
2	9	1	36·8	39·7
2	9	4	14·6	13·8
2	9	5	21·0	20·4
2	9	6	10·3	11·1
2	9	7	19·3	18·4
2	9	8	9·4	10·1
2	9	9	7·3	7·4
2	9	10	9·5	11·8
3	9	6	10·5	11·5
3	9	4	14·3	16·0
3	9	2	13·3	13·9
3	9	1	12·2	10·9
3	9	0	18·2	19·7
3	9	1	14·1	13·0
3	9	2	14·9	14·8
3	9	3	23·8	23·9
3	9	4	11·0	11·7
3	9	5	22·7	22·7
3	9	6	12·6	11·8
3	9	7	26·6	26·0
3	9	9	22·4	21·4
3	9	11	18·2	18·3
4	9	5	20·9	20·8
4	9	3	29·0	29·8
4	9	1	26·8	28·0
4	9	1	30·5	29·6
4	9	3	26·0	24·7
4	9	4	15·9	16·1
4	9	5	17·1	16·8
4	9	6	10·6	10·1
4	9	7	12·9	12·3
4	9	8	15·4	16·1
4	9	10	8·3	9·2
5	9	6	11·6	12·0
5	9	2	14·9	14·4
5	9	1	14·8	14·2
5	9	0	13·3	14·0
5	9	1	18·0	18·7
5	9	3	27·5	26·9
5	9	4	12·3	12·0
5	9	5	25·2	25·4
5	9	7	30·1	29·2
5	9	9	21·9	20·9
5	9	11	18·5	21·3
6	9	5	17·8	17·5
6	9	3	22·5	23·0
6	9	1	20·8	19·4
6	9	1	25·3	24·0
6	9	2	16·5	16·7
6	9	3	14·0	12·6
6	9	4	10·1	10·1
5	9	5	15·7	14·0
6	9	6	16·5	16·3
6	9	8	12·4	13·0
6	9	10	8·3	9·4
7	9	4	7·3	8·5
7	9	3	12·5	11·8
7	9	2	10·0	11·1
7	9	1	13·6	13·2
7	9	1	25·4	23·5
7	9	2	10·8	9·2
7	9	3	25·0	22·8
7	9	5	32·6	29·2
7	9	7	26·2	23·8
7	9	9	27·6	23·7
7	9	10	6·1	5·7
7	9	11	16·9	16·8
8	9	1	16·8	16·5
8	9	0	10·9	11·9
8	9	1	11·4	10·9
8	9	2	10·7	10·8
8	9	3	11·3	9·3
8	9	4	11·6	11·9
8	9	6	16·7	15·6
8	9	8	8·7	8·8
8	9	10	10·5	11·9
8	9	11	10·2	9·9
8	9	3	11·6	12·7
9	9	1	13·9	15·1
9	9	1	19·7	19·7
9	9	3	23·7	21·8
9	9	5	27·3	24·5
9	9	7	22·0	20·7
9	9	9	24·1	20·7
10	9	4	12·8	14·2
10	9	6	7·8	8·2
10	9	8	8·0	10·6
10	9	9	10·0	11·6
11	9	3	17·3	20·0
11	9	5	15·5	16·7
11	9	7	19·0	19·1
3	9	7	9·5	9·9
4	9	7	16·7	20·0
1	9	9	12·0	13·5

(Although many reflections quoted here have k negative those actually measured were equivalent reflections with k positive.)

The short metal-metal bond length found is 2.5106 Å, close to the value reported by Magnéli.[1] The only other molybdenum oxide in which metal-metal bonding occurs is $Mo_{17}O_{47}$, in which Kihlborg [16,17] found a pair of metal atoms 2.626 Å apart. For comparison the Mo—Mo distance in the metal is 2.725 Å.[18] Similarly a short contact of 2.60 Å is found between tungsten atoms in $W_{18}O_{49}$.[19]

Structural studies have been carried out on other related rutile-type oxides, for example a recent accurate investigation by Kierkegaard and Longo on VO_2 using diffractometer data has shown the V—V distance to be 2.6191 Å.[20] Marinder [21] has in his study of NbO_2 found the Nb—Nb distance to be 2.802 Å indicating a metal-metal interaction. A further example of metal-metal bonding in oxides is found in low—Ti_3O_5.[22]

Table 5. Interatomic distances and angles in MoO_2. The numbering of atoms is the same as is used in Fig. 2.

$Mo_1 - O_1$	2.073 Å	σ = 0.003 Å*	$Mo_1 - Mo_2$	2.5106 Å	σ = 0.0005 Å
$- O_2$	2.064		$- Mo_3$	3.1118	
$- O_3$	1.978		All other Mo — Mo		> 3.664
$- O_4$	1.995				
$- O_5$	1.972				
$- O_6$	1.984				
Average	2.011				
			$Mo_2-Mo_1-Mo_3$	172.6°	
O_1-O_2	2.727 Å	σ = 0.004 Å	$O_1-Mo_1-O_2$	82.5°	σ = 0.15°
$-O_3$	2.897		$O_1-Mo_1-O_3$	91.3	
$-O_4$	2.887		$O_1-Mo_1-O_4$	90.4	
$-O_5$	2.707		$O_1-Mo_1-O_5$	84.0	
O_2-O_3	2.861		$O_2-Mo_1-O_3$	90.1	
$-O_5$	2.723		$O_2-Mo_1-O_5$	84.8	
$-O_6$	2.736		$O_2-Mo_1-O_6$	85.0	
O_3-O_4	2.893		$O_3-Mo_1-O_4$	93.5	
$-O_6$	2.901		$O_3-Mo_1-O_6$	94.2	
O_4-O_5	2.832		$O_4-Mo_1-O_5$	91.1	
$-O_6$	3.088		$O_4-Mo_1-O_6$	101.8	
O_5-O_6	2.786		$O_5-Mo_1-O_6$	89.5	
Average	2.837				

* The standard deviations take into account the uncertainty in the unit-cell dimensions.

Molybdenum-molybdenum bonding also exists in oxides of the formula $A_2^{II}Mo_3^{IV}O_8$ (Ref. 23) where A = Mg, Mn, Fe, Co, Ni, Zn, and Cd and also probably in $LiScMo_3O_8$. [24] In $Zn_2Mo_3O_8$ the molybdenum atoms occur in clusters of three and a recent refinement [25] shows the Mo—Mo distances to be 2.524 Å. Thus the Mo—Mo bond in molybdenum dioxide is the shortest found in oxides, however, it is not the shortest known, as Lawton and Mason [26] have found for molybdenum(II) acetate, $Mo_2(O_2CCH_3)_4$, the remarkably short metal-metal distance of 2.11 Å.

In recent years there has been a great rise in interest in metal-metal bonding, and very many examples have been found of transition metal and other metal complexes containing such bonds.[27–29]

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