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The Crystal Structure of Silver Permanganate*

By E. G. Boonstra†

National Physical Research Laboratory, Council for Scientific and Industrial Research, P.O. Box 395, *Pretoria, South Africa*

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The crystal structure of silver permanganate, $AgMnO_4$, as reported by Sasvari, has been found to be incorrect. A new structure has been determined from three-dimensional X-ray intensity data. Compared with the original structure, the positions of the Ag and Mn atoms are interchanged while altogether new positions have been assigned to the oxygen atoms. Refinement with partial anisotropic thermal motion parameters has decreased R to below 0·09. The tetrahedral permanganate group is regular to within the experimental error, and has an average Mn–O bond length of 1·61 ± 0·01 Å (not corrected for thermal motion).

Introduction

The original determination of the structure of silver permanganate by Sasvari (1938), was based on 140 reflexions obtained from X-ray oscillation photographs about the three crystallographic axes. Assuming regular tetrahedral permanganate groups, packing arguments led to the structure shown in Fig. 1. Although monoclinic (space group $P2_1/n$ with $\beta = 92\frac{1}{2}°$), the structure was considered to be a slight distortion of the orthorhombic barite structure (Wyckoff, 1965), which is also the structure type of the related substance, potassium permanganate (Ramaseshan, Venkatesan & Mani, 1957), shown in Fig. 2.

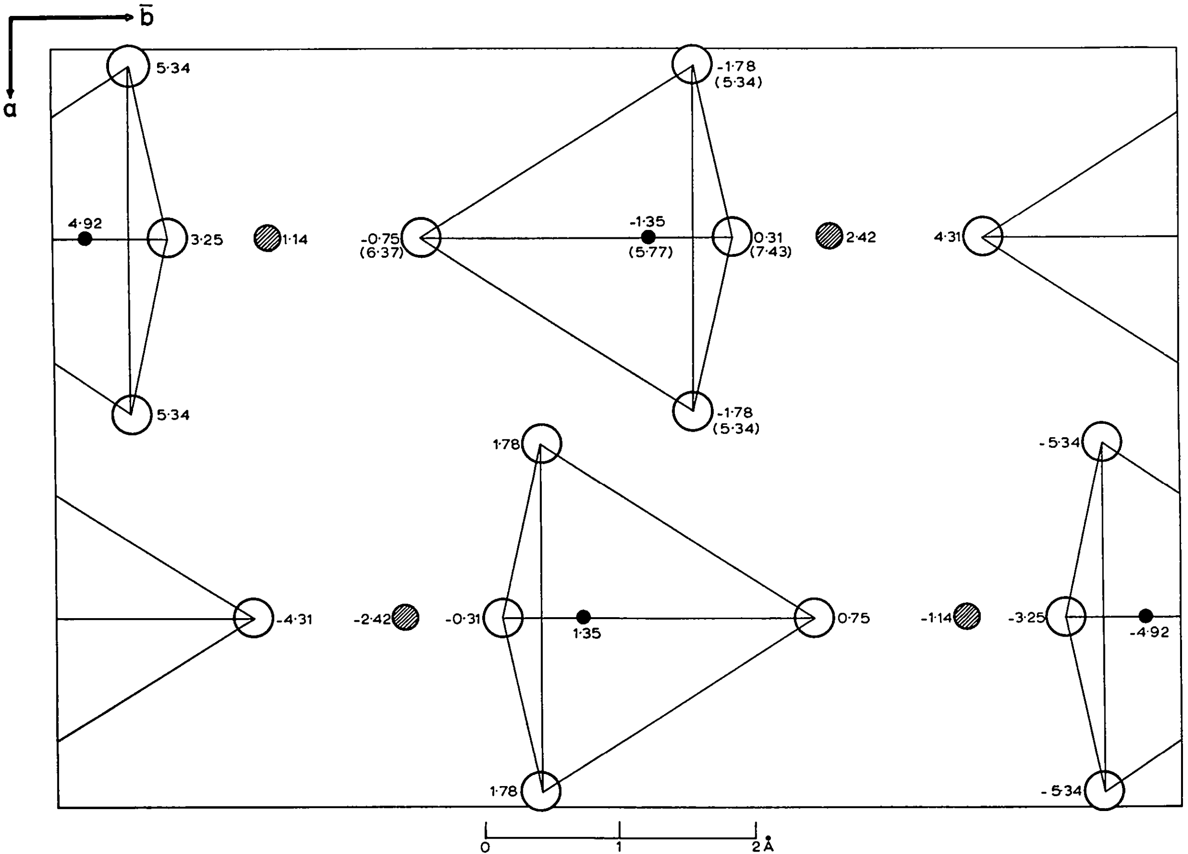

Fig. 1. The structure of silver permanganate, in the [001] projection with z coordinates of the atoms given in Å, after Sasvari. The large open circles represent the oxygen atoms, the small black circles the manganese while the shaded circles represent the silver atoms.

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† Now on a year's leave of absence at the Chemistry Department, University of Maryland, College Park, Maryland, U.S.A.

The *R* value for Sasvari's structure determination of silver permanganate is calculated as 0·34, while the Mn–O distances in the permanganate group vary from 1·4 to 1·8 Å. The structure cannot be refined, showing that serious errors probably exist in the data and the structure. In particular, the method of intensity measurement seems crude by present standards, no allowance was made for absorption corrections, which could be 50% for some reflexions, and the indexing was apparently done on a pseudo-orthorhombic lattice, since no negative indices were assigned.

There is thus considerable doubt as to the correctness of the reported structure. It is not surprising that the positions of the heavy atoms (silver and manganese) agree with those in potassium permanganate, but the oxygen positions seem suspect. The structure was therefore redetermined.

Experimental

Silver permanganate was prepared in the standard manner from silver nitrate and potassium permanganate. Suitable needle-shaped single crystals were selected under a polarizing microscope where they showed oblique extinction. The face development was usually imperfect with prominent striations and pits, so that accurate optical goniometry was not attempted. Crystals were mounted on the goniometer head with the needle direction as the rotation axis.

Herbstein (unpublished) had previously checked the unit cell and space group given by Sasvari. In accordance with the earlier work, the needle direction is chosen as the *c* axis and the space group is $P2_1/n$ (related by transformation to $P2_1/c$, no. 14 in *International Tables for X-ray Crystallography*, 1952) where *b* is the unique monoclinic axis, and β is close to 90°. The cell constants were redetermined and the values used in the present study were $a=5{\cdot}64$, $b=8{\cdot}33$ and $c=7{\cdot}12\pm0{\cdot}02$ Å and $\beta=92{\cdot}25\pm0{\cdot}25°$, where the errors indicate the approximate r.m.s. deviations of different measurements. The corresponding values given by Sasvari were $a=5{\cdot}66$, $b=8{\cdot}27$ and $c=7{\cdot}12$ Å and $\beta=92°29{\cdot}5'$. On the zero-level Weissenberg photograph the absence $I(hk0)=0$ for $k=2n+1$, expected for a barite-type structure, is obeyed only approximately. The structure therefore cannot have symmetry *mg* in the [001] projection, as had been implied. A precession photograph showed clearly that $I(h0l)\neq I(h0\bar{l})$, conflicting with another of Sasvari's simplifying assumptions.

A set of three-dimensional intensity data was collected on equi-inclination Weissenberg photographs with the multiple film technique. Mo $K\alpha$ radiation was used to minimize absorption corrections. The linear absorption

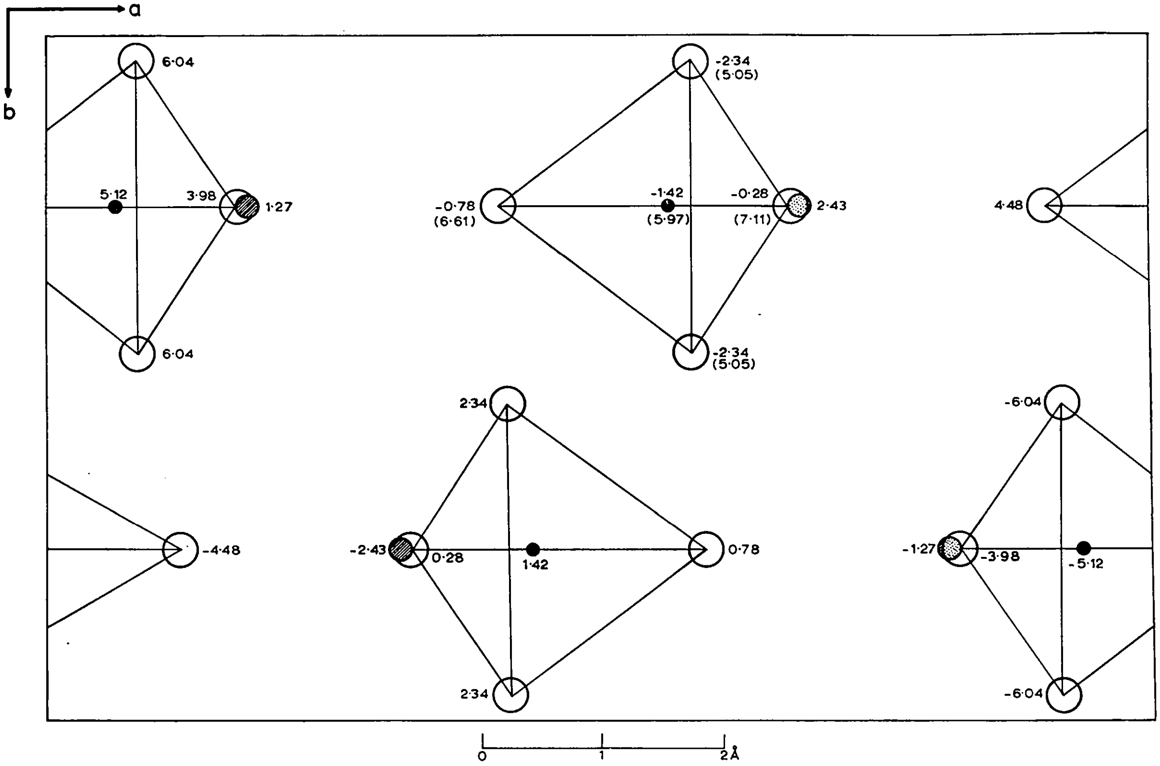

Fig. 2. The structure of potassium permanganate, after Ramaseshan, Venkatesan & Mani, drawn in the [001] projection to facilitate comparison with silver permanganate above. (Same key as for Fig. 1, except that the shaded circles represent the potassium atoms.)

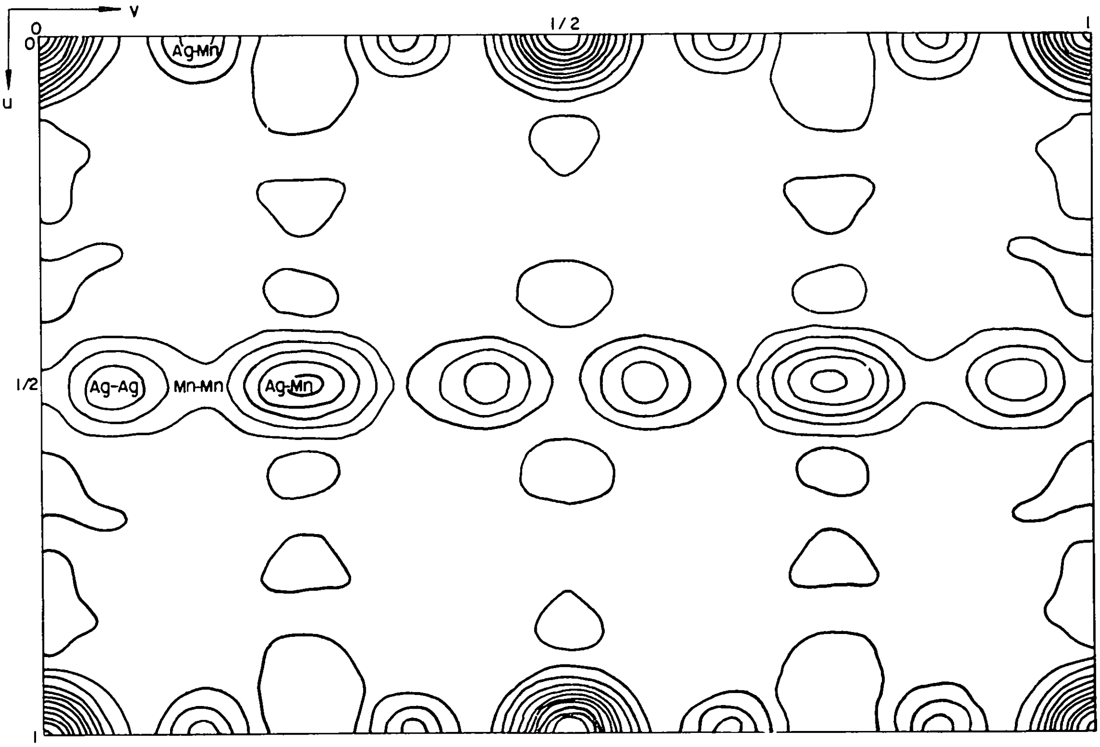

Fig. 3. The Patterson projection $P(uv)$ of silver permanganate. Contours are all positive, and drawn at equal but arbitrary intervals

coefficient of silver permanganate for this radiation is 95 cm^{-1}, and sufficient intensity was available with a crystal diameter somewhat less than 0·3 mm. With this radiation, the interfilm factor is too low to obtain a useful range in intensities. Hence metal foil 0·025 mm thick, was placed between the sheets in the multiple film pack to increase the interfilm factor to a value close to that normally obtained with Cu $K\alpha$ radiation. In order to save time, two cameras, each with its own crystal, were used simultaneously to record the different layer lines. Data from layers $hk0$–10 were used in subsequent calculations. A further two layers $hk11$, 12 were also photographed, but the data from these were not included since the photographs were of poor quality.

In view of the expected pseudo-orthorhombic symmetry of the structure, it was essential to use an indexing scheme that was internally consistent for the different layer lines. It was only necessary to ascertain the correct sign of the h index for each reflexion, since the k and l indices could always be chosen positive in view of the relationships $I(hkl)\equiv I(h\bar{k}l)\equiv I(\bar{h}\bar{k}\bar{l})$. This is naturally done subject to the requirement that $+\mathbf{a}$, $+\mathbf{b}$ and $+\mathbf{c}$ form a right-handed set of axes with $\beta > 90°$. Complicating features were the β angle close to 90°, and the fact that two crystals were used on two cameras for which the directions of spindle rotation relative to carriage movement were in opposite senses. Different cross-checks were used, and at no stage was there any uncertainty about the correct indexing.

The spot intensities were measured by visual comparison with a calibrated wedge. For each three layers, a new wedge was made with the same crystal as had been used in recording the intensity photographs, and thus the spots on the wedge were roughly of the same size as those to be measured. On higher layer lines the extended spots were measured. By interrelating the different wedges, and making a correction for different exposure times, the intensities for the various layers were placed on roughly the same relative scale.

Data processing

The large amount of work involved in processing the data associated with more than 2500 reflexions was done on an IBM 704 computer with the aid of two specially written programs. The first of these was designed to yield a set of measured intensities (on a relative scale) for each layer line from the multiple film measurements. The second program applied the necessary corrections to the intensities to give either corrected intensities or structure factors (F_o^2 or F_o) as required. The standard corrections for equi-inclination Weissenberg photographs are a combined Lorentz–polarization factor (Cochran, 1948), spot-shape factor for higher layer lines (Phillips, 1954), α_1,α_2 splitting factor (Rae & Barker, 1961; Boonstra, 1966), a cylindrical approximation for absorption (*International Tables*, 1959) and an optional scale factor to put all the layers on the same relative or absolute scale.

The *hk*0 data were processed first and the structure investigated in projection because it was hoped that the uncertainty about Sasvari's structure would be cleared up rather quickly. The two-dimensional work proved that Sasvari's structure was incorrect, so that a complete redetermination had to be done. Initially only the data from layers *hk*0–7 were used, but later the extra data *hk*8–10 were included.

The calculations involved in the structure determination were done on an IBM 704 computer with the following standard crystallographic programs:

(i) *MIFR* 1: *Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM* 704 *Computer*. M.I.T. Tech. Rep. Sly, W.G. and Shoemaker, D.P. (1960).

(ii) *ORXLS*: *A Crystallographic Least-Squares Refinement Program for the IBM* 704. O.R.N.L. Rep. No. 59-4-37. Busing, W.R. and Levy, H.A. (1959).

(iii) *ORXFE*: *A Crystallographic Function and Error Program for the IBM* 704. O.R.N.L. Rep. No. 59-12-3. Busing, W.R. & Levy, H.A. (1959).

A simple model of the structure would consist of silver and permanganate ions, Ag^+ and MnO_4^- respectively. In this description, however, the term 'atom' is used to refer to the silver, and to the constituent manganese and oxygen of the permanganate group. The scattering factors used are those for the uncharged atoms, as given in *International Tables for X-ray Crystallography* (1962).

The structure in projection [001]

The Patterson projection $P(u,v)$ shown in Fig. 3 has symmetry *mm*, but contains an additional pseudo-mirror plane at $v = \pm\frac{1}{4}$. This is a result of the pseudo-absence $I(hk0) \simeq 0$ for $k = 2n+1$, which holds strictly for the barite structure. In agreement with Sasvari's structure, it is immediately deduced that $x(\mathrm{Ag})$, $x(\mathrm{Mn}) = \frac{1}{4}$. The assignment of peaks as shown, yields the coordinates $y(\mathrm{Ag}) = 4\frac{1}{4}/120$ and $y(\mathrm{Mn}) = 22\frac{3}{4}/120$, which correspond to Sasvari's structure but with the Ag and Mn positions interchanged. Another possible set of coordinates exists, but this possibility was definitely excluded at a later stage and will not be discussed any further.

In order to find possible oxygen positions, first the *y* and then the *x* coordinates of the heavy atoms were refined, and Fourier and difference Fourier maps calculated. In these maps, the pseudo-symmetry of the heavy atom positions produces two possible peaks for each oxygen atom – the one corresponding to the real, and the other to a ghost atom. Four such pairs were

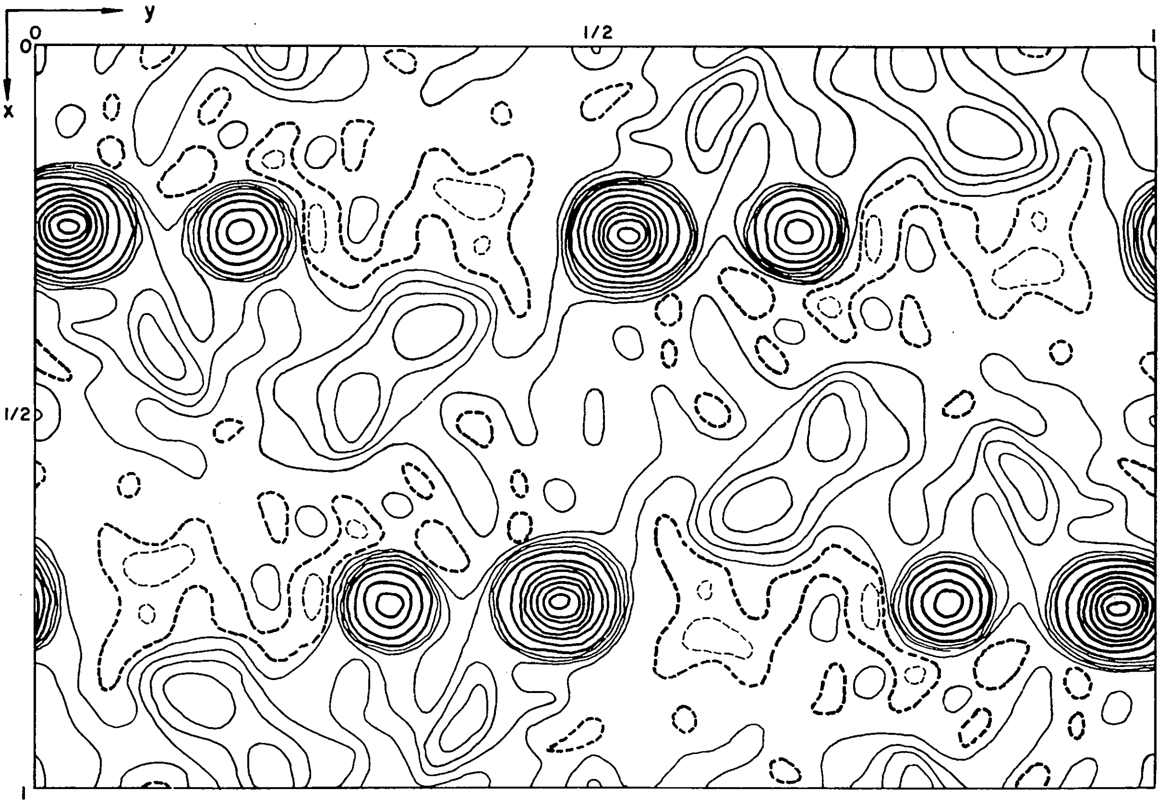

Fig. 4. The final electron density projection $\varrho(xy)$ obtained for silver permanganate by refinement of the two-dimensional trial structure. Contours are at equal but arbitrary intervals with zero level given by thick dotted lines, positive contours by solid lines and negative contours by thinner dotted lines.

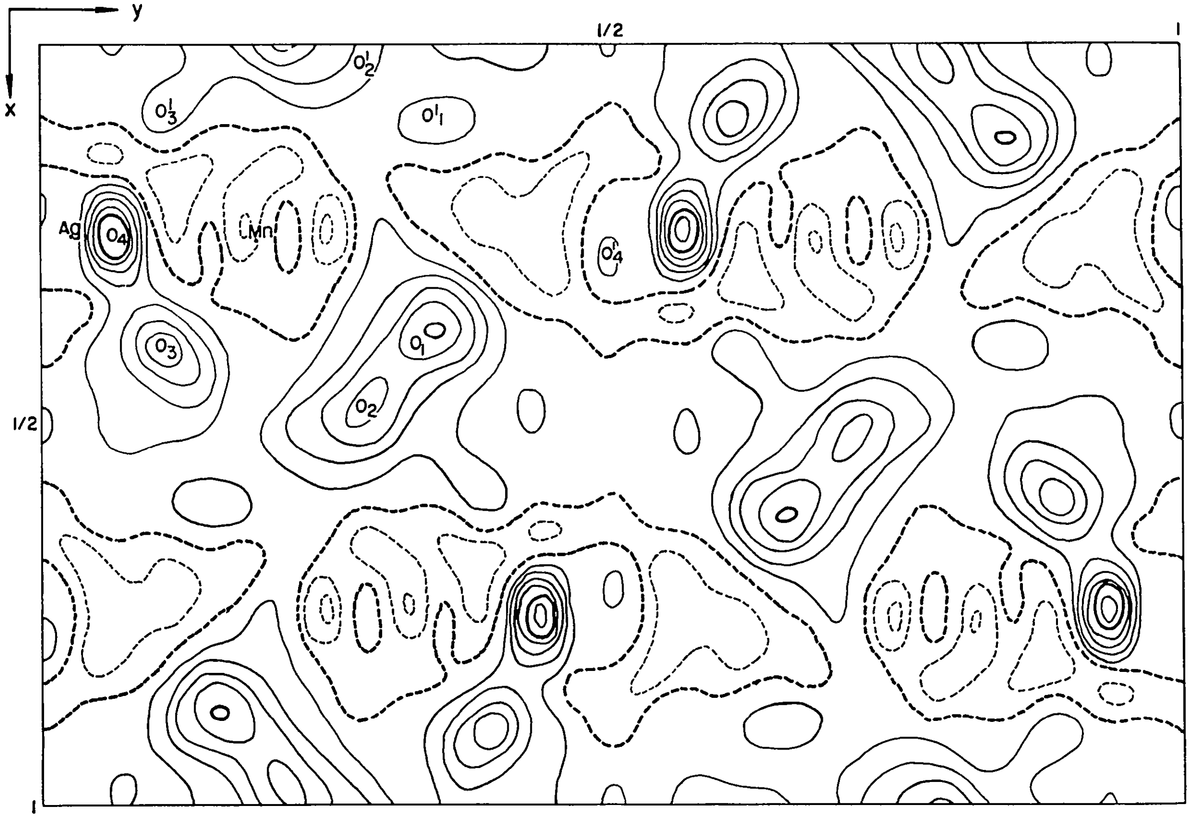

Fig. 5. The difference projection corresponding to Fig. 4, with the Ag and Mn atoms removed to show the oxygen positions O(1)–(4), and the ghost peaks O(1′)–(4′).

observed on the difference map (after removing the heavy atoms) and the real positions selected by considering the peak heights. The structure thus found refined in projection to $R=0{\cdot}21$, and the final electron density maps are shown in Figs. 4 and 5. An oxygen position such as O(1) is obviously preferred to the ghost position O(1′). The only uncertainty was in the correct position O(4), which overlaps with the Ag atom in projection, and here a wrong choice was made. The later refinement showed that the atom O(4) had to be shifted by a small amount in y to the other side of the Ag atom.

In this projection, it is clear that the positions of the silver and manganese atoms are interchanged compared with the structure proposed by Sasvari, and completely new positions are assigned to the oxygen atoms.

The three-dimensional trial structure

The complete trial structure was deduced from the three-dimensional Patterson synthesis $P(uvw)$. The heavy atom positions satisfy the higher orthorhombic pseudo-symmetry and the small departure of β from 90° cannot affect the interpretation of the Patterson synthesis. The Harker peaks yielded the positions of the heavy atoms directly, and by restricting the choice of asymmetric unit, the trial coordinates can without loss of generality be given as

$$x(\mathrm{Ag})=x(\mathrm{Mn})=\tfrac{1}{4}$$
$$y(\mathrm{Ag})=2/60,\ y(\mathrm{Mn})=11/60$$
$$z(\mathrm{Ag})=10/60,\ z(\mathrm{Mn})=-20/60\,.$$

In the unit cell there are four symmetry-related Ag positions, and each oxygen atom in the asymmetric unit hence gives rise to four distinct but related Ag–O vectors, with peaks in $P(uvw)$ at $x(\mathrm{Ag})\pm x(\mathrm{O})$, $y(\mathrm{Ag})\pm y(\mathrm{O})$, $z(\mathrm{Ag})\pm z(\mathrm{O})$; $\frac{1}{2}+x(\mathrm{Ag})\pm x(\mathrm{O})$, $\frac{1}{2}+y(\mathrm{Ag})\pm y(\mathrm{O})$, $\frac{1}{2}+z(\mathrm{Ag})\pm z(\mathrm{O})$. In each set, either the three upper or the three lower signs are taken. Such peaks of roughly the expected height were readily found for the oxygen atoms O(1), (2) and (3). The corresponding but weaker Mn–O peaks could then be found at the predicted positions and yielded shortest Mn–O distances of 1·70, 1·58 and 1·74 Å respectively. The same process could not yield the position of the oxygen atom O(4), and this was finally predicted from the other three oxygen positions by assuming that they, or their symmetry related atoms, form a regular tetrahedral arrangement around the Mn atom. In this way some peaks could be identified, corresponding to a Mn–O distance of 1·74 Å.

Refinement

Refinement of layer line scale factors, positional coordinates and isotropic temperature factor of all the atoms of the trial structure deduced above, was successful and readily yielded an R value of 0·18. Calculations of R for the different layer lines individually, showed conclusively that the indexing of the layers was internally consistent. That the indexing was further correct for the trial structure chosen, was confirmed by calculating interatomic distances in the MnO_4 group for the cases $\beta=92\frac{1}{4}$ and $87\frac{3}{4}°$. The group was clearly more regular with $\beta=92\frac{1}{4}°$, and this removed the last uncertainty about the trial structure.

The scale factors of the layer lines, as applied to the structure factors, varied on a relative basis from 1·0 for the zero layer to about 3·0 for the uppermost layers. The experimental cause of this variation was traced to a fault in the high tension supply of the X-ray generator, which resulted in a gradual increase in output over a period of weeks. The attempt to place the intensities of the different layers on approximately the same scale was therefore unsuccessful. This was the reason for the presence of the severe diffraction ripples observed in the Patterson synthesis, in the **c** direction, which masked most of the interatomic vectors associated with the oxygen atom O(4). A further consequence was that no attempt could be made to do a full anisotropic refinement. Nevertheless, a number of improvements could be introduced and are described briefly.

On inspecting the listing of F_o and F_c (observed and calculated structure factors respectively), it was found that the strongest reflexions had F_o values consistently low compared with F_c. This was attributed to extinction and/or overexposure on the film, and a total of 20 such reflexions were excluded from the refinement. Absorption corrections, varying on a relative scale up to 6% on the zero layer, and up to 10% on the seventh layer, were applied to the observed structure factors. These small but systematic corrections should make the values obtained for the temperature factors more meaningful physically (Srivastava & Lingafelter, 1966). Dispersion corrections were included in the scattering factors of Ag and Mn (*International Tables*, 1962), only the real term being used as recommended by Ramaseshan, Venkatesan & Mani (1957).

Up to this stage unobserved reflexions were assigned a structure factor value corresponding to $I_{\text{unobs}}=\frac{1}{3}I_{\text{min}}$ (Hamilton, 1955) before correction (De Vries, 1965). With the short wavelength used, reflexions were not observed above about $2\theta=90°$, and even below this value roughly half of the reflexions were unobserved. It is clearly incorrect to give all unobserved spots the same I_{unobs} value, independent of 2θ. The apparent contradiction arises because it is not generally appreciated that Hamilton's formula is based on an approximation which is only valid if I_{min} is small compared with I_{av} (the average intensity of the reflexions at the angle of diffraction corresponding to the unobserved reflexion). The formula should therefore not be used in regions of the film where there are a large number of unobserved reflexions, or where the observed intensities are weak. It was therefore rather arbitrarily decided to include only those unobserved reflexions which occur at $\sin\theta/\lambda$ values less than about half the maximum value corresponding to observed reflexions. In this way 95% of the unobserved reflexions were excluded from the refinement. This led to a considerable reduction in R (about 0·08), with no significant changes in the atomic positions.

In the later stages of the refinement, a weighting scheme (based on the usual assumption $w=1/\sigma^2$) was introduced. Initially an estimate of σ was obtained by using the method of Hughes (1941). Later an experimental method of obtaining σ was used, and although this gave a slightly lower R value there were no significant changes in parameters. In this scheme, each reflexion is treated on merit and the e.s.d. is obtained from the measured intensity values on the films of the multiple film pack, and from the intensity wedge used. The most important effect of weighting was a marked increase in the atomic temperature factors, coupled with an increase in layer line scale factors. The atomic parameters obtained with isotropic refinement and corresponding to an R value of 0·104 for the *hk*0–10 data are given in Table 1.

By repeating the refinement firstly with only the *hk*0–4 data, and secondly with *hk*0–7 data, it was clearly shown that the oxygen atom O(4) was most susceptible to the effect of series termination. Changes in atomic coordinates were minimal, but $\sigma(z)$ for O(4) was always considerably bigger than for the other oxygen atoms, and there were noticeable differences in temperature factors. The temperature factors for the other three oxygen atoms were virtually identical and the average varied from $2·08\pm0·15$, $2·23\pm0·11$ to $2·11\pm0·10$ with cut-off after the fourth, seventh and tenth layer respectively, showing no significant trend.

Table 1. *Atomic parameters for silver permanganate, obtained from isotropic refinement with* $R=0·104$ *and based on* 1439 *hk*0–10 *reflexions, as fractional coordinates* $\times 10^4$

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B	$\sigma(B)$
Ag	2439	0001	0328	0001	1647	0001	1·82	0·02
Mn	2573	0002	1868	0002	6608	0001	1·22	0·02
O(1)	3829	0013	3492	0010	5921	0008	2·05	0·10
O(2)	−0139	0014	2233	0010	7153	0008	2·17	0·10
O(3)	4044	0014	1190	0010	8445	0008	2·12	0·10
O(4)	2520	0019	0590	0013	4963	0011	2·97	0·14

Table 2. *Observed and calculated structure factors* (F_o *and* F_c) *on* 10× *absolute scale, corresponding to partial anisotropic refinement with* $R=0{\cdot}087$

h	k	Fo	Fc
l 0			
0	0	0	4140*
2	0	1507	-2146*
4	0	1282	1469*
6	0	924	-923
8	0	574	569
10	0	236	-265
1	1	20-	-18
2	1	453	430
3	1	34-	30
4	1	40-	18
5	1	46-	-0
0	2	699	763*
1	2	1095	-1351
2	2	994	-1074
3	2	914	952
4	2	509	477
5	2	633	-611
6	2	380	-363
7	2	336	349
8	2	167	163
9	2	151	-171
1	3	130	-106
2	3	156	152
3	3	108	-91
4	3	43-	27
5	3	98	84
7	3	124	-119
0	4	616	659
1	4	506	-481
2	4	690	-683
3	4	214	168
4	4	711	691
5	4	162	-163
6	4	240	-247
8	4	141	193
1	5	196	181
2	5	175	-168
3	5	86	74
4	5	48-	-24
0	6	587	599
1	6	1064	-1183*
2	6	595	-563
3	6	955	1014*
4	6	366	340
5	6	599	-610
6	6	285	-299
7	6	418	425
8	6	149	169
9	6	229	-251
1	7	45-	-26
2	7	47-	1
3	7	123	-135
0	8	352	-364
1	8	510	-544
2	8	426	436
3	8	544	533
4	8	350	-336
5	8	387	-394
6	8	217	198
7	8	181	201
8	8	160	-121
9	8	166	-151
1	10	144	-145
3	10	126	91
0	12	218	-201
1	12	318	-319
2	12	141	155
3	12	231	238
4	12	151	-138
5	12	194	-200
7	12	166	160
0	14	223	-210
2	14	227	217
4	14	165	-175
l = 1			
-9	0	147	167
-7	0	145	-156
-5	0	391	381
-3	0	782	-795
-1	0	0	495*
1	0	0	-458*
3	0	561	493
5	0	322	-319
-7	1	172	173
-6	1	165	-172
-5	1	46-	-23
-4	1	191	199
-3	1	511	466
-2	1	251	-239
-1	1	418	-393
0	1	0	647*
1	1	431	425
2	1	447	-428
3	1	34-	53
4	1	199	196
5	1	175	167
6	1	268	-270
8	1	164	173
-9	2	211	236
-7	2	443	-461
-6	2	107	78
-5	2	788	750
-4	2	82	-82
-3	2	1165	-1167*
-2	2	94	-80
-1	2	1441	1648*
0	2	154	130
1	2	1406	-1680*
2	2	391	364
3	2	1273	1303*
4	2	101	86
5	2	737	-723
7	2	487	508
9	2	217	-273
-8	3	215	217
-7	3	193	-205
-6	3	386	-372
-5	3	273	261
-4	3	631	621
-3	3	391	-382
-2	3	803	-811
-1	3	91	89
0	3	623	642
1	3	668	-660
2	3	727	-734
3	3	197	180
4	3	621	632
5	3	205	-200
6	3	222	-236
7	3	123	104
8	3	137	164
-9	4	153	131
-8	4	281	-283
-7	4	270	-274
-6	4	437	423
-5	4	419	370
-4	4	830	-838
-3	4	414	-394
-2	4	1067	1102*
-1	4	782	801
0	4	1172	-1356*
1	4	814	-856
2	4	992	1056*
3	4	406	396
4	4	913	-939
5	4	358	-358
6	4	483	544
7	4	199	205
8	4	283	-341
9	4	154	-128
10	4	162	208
-9	5	156	157
-7	5	204	-203
-6	5	117	107
-5	5	258	259
-4	5	95	-63
-3	5	341	-333
-2	5	39-	-48
-1	5	656	681
0	5	72	-52
1	5	316	-292
2	5	40-	-54
3	5	331	324
4	5	117	119
5	5	214	-224
7	5	186	176
-8	6	147	-121
-6	6	212	234
-4	6	213	-217
-3	6	46-	-34
-2	6	510	516
-1	6	41-	11
0	6	379	-375
1	6	154	164
2	6	301	302
3	6	46-	-84
4	6	242	-223
6	6	213	231
-3	7	145	-131
-2	7	148	-152
-1	7	45-	67
0	7	279	293
1	7	90	-83
2	7	94	-126
3	7	145	150
4	7	108	103
5	7	168	-156
-8	8	157	-176
-6	8	252	247
-5	8	124	148
-4	8	361	-363
-3	8	272	-251
-2	8	342	353
-1	8	209	193
0	8	578	-583
1	8	250	-239
2	8	406	416
3	8	249	253
4	8	326	-328
5	8	153	-150
6	8	193	211
-7	9	152	-165
-5	9	302	286
-3	9	302	-326
-1	9	311	329
1	9	350	-375
3	9	328	324
5	9	188	-210
7	9	152	139
-6	10	258	234
-4	10	277	-315
-3	10	251	255
-2	10	423	429
-1	10	295	-297
0	10	370	-376
1	10	250	250
2	10	410	465
3	10	217	-254
4	10	303	-321
5	10	203	227
6	10	234	236
7	10	159	-161
8	10	163	-158
-4	11	171	-178
-2	11	202	198
-1	11	126	116
0	11	197	-199
1	11	126	-131
2	11	158	152
-1	12	136	-141
-1	12	167	178
0	14	155	-106
l 2			
-8	0	203	-197
-6	0	256	273
-4	0	598	-550
-2	0	529	498
0	0	0	-1103*
2	0	655	651
4	0	736	-754
6	0	363	382
8	0	245	-264
-10	1	131	136
-9	1	234	259
-8	1	203	-229
-7	1	417	-402
-6	1	381	357
-5	1	728	676
-4	1	570	-537
-3	1	1281	-1307*
-2	1	810	787
-1	1	1308	1408*
0	1	777	-1091*
1	1	1197	-1318*
2	1	713	725
3	1	1223	1254*
4	1	580	-568
5	1	746	-782
6	1	225	234
7	1	346	401
8	1	206	-210
9	1	189	-252
11	1	70	142
-7	2	100	107
-6	2	216	221
-4	2	118	-132
-3	2	244	235
-2	2	504	479
-1	2	701	-738
0	2	97	-82
1	2	151	149
2	2	270	242
3	2	216	-207
4	2	80	-46
5	2	334	352
6	2	90	111
7	2	189	-219
-6	3	117	123
-5	3	186	166
-4	3	263	-236
-3	3	33-	29
-2	3	468	438
-1	3	464	456
0	3	277	-265
1	3	566	-518
2	3	476	463
3	3	233	216
4	3	276	-256
5	3	153	-152
6	3	158	182
7	3	169	192
8	3	115	-84
-6	4	120	114
-4	4	285	-335
-3	4	67	62
-2	4	259	235
-1	4	111	88
0	4	464	-449
1	4	29-	38
2	4	263	237
3	4	78	48
4	4	210	-198
6	4	109	102
-9	5	128	166
-7	5	309	-334
-6	5	178	206
-5	5	435	441
-4	5	383	-371
-3	5	651	-677
-2	5	459	435
-1	5	782	798
0	5	519	-501
1	5	923	-1011
2	5	437	408
3	5	558	586
4	5	438	-419
5	5	471	-465
6	5	250	245
7	5	296	301
8	5	120	-145
9	5	129	-173
-7	6	144	130
-6	6	156	163
-5	6	255	-269
-4	6	228	-210
-3	6	318	310
-2	6	281	249
-1	6	321	-292
0	6	278	-249
1	6	480	465
2	6	440	420
3	6	512	-501
4	6	201	-201
5	6	186	221
6	6	118	123
7	6	174	-224
-8	7	292	-283
-6	7	448	485
-4	7	623	-609
-2	7	736	788
-1	7	40-	-17
0	7	966	-983*
1	7	180	182
2	7	790	835
4	7	563	-566
6	7	416	449
8	7	243	-274
-7	8	121	106
-5	8	133	-147
-3	8	245	226
-1	8	271	-274
0	8	81	86
1	8	237	262
2	8	163	-193
3	8	157	-161
4	8	124	126
5	8	181	194
-5	9	168	-181
-3	9	136	150
-2	9	106	119
-1	9	270	-253
0	9	163	-165
1	9	188	178
2	9	170	171
3	9	166	-181
4	9	119	-117
-3	10	119	103
-1	10	137	-144
-6	11	128	117
-4	11	243	-205
-2	11	256	261
0	11	199	-211
2	11	216	228
4	11	216	-243
6	11	129	133
-3	12	119	131
-1	12	160	-137
1	12	175	170
3	12	138	-142
-5	13	151	-186
-3	13	222	215
-2	13	143	114
-1	13	262	-261
0	13	140	-123
1	13	245	237
2	13	124	121
3	13	221	-223
l 3			
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-7	0	108	96
-5	0	108	-103
-3	0	33-	2
-1	0	20-	32
1	0	391	400
3	0	271	266
5	0	99	-92
-8	1	233	-240
-7	1	125	-121
-6	1	457	453
-5	1	154	132
-4	1	665	-610
-3	1	400	-346
-2	1	835	908
-1	1	0	-31*
0	1	0	-1351*
1	1	505	-529
2	1	964	1078*
3	1	314	304
4	1	605	-617
5	1	112	-140
6	1	448	437
8	1	214	-246
-6	2	97	-83
-4	2	163	144
-3	2	126	-130
-2	2	86	49
-1	2	68	80
0	2	201	-151
1	2	202	-203
2	2	177	-187
3	2	95	-87
4	2	41-	-27
-10	3	199	218
-9	3	175	-144
-8	3	368	-356
-7	3	338	321
-6	3	569	536
-5	3	432	-404
-4	3	960	-970
-3	3	797	758
-2	3	1268	1453*
-1	3	871	-976
0	3	1249	-1501*
1	3	969	1095*
2	3	1085	1269*
3	3	598	-606
4	3	983	-1073
5	3	535	545
6	3	574	618
7	3	306	-315
8	3	380	-388
9	3	177	166
10	3	200	213
-6	4	145	125
-4	4	149	-136
-3	4	119	103
-2	4	250	218
-1	4	33-	64
0	4	32-	50
1	4	108	-140
2	4	117	74
3	4	40-	29
-9	5	195	-198
-7	5	310	316
-5	5	605	-584
-3	5	709	724
-2	5	38-	19
-1	5	886	-947
0	5	168	159
1	5	915	1030*
2	5	85	64
3	5	854	-914
5	5	477	484
7	5	336	-350
9	5	180	226
-5	6	117	-74
-2	6	152	-146
-1	6	164	-138
0	6	39-	-19
1	6	40-	-6
2	6	42-	40
-5	7	163	-158
-4	7	139	-112
-3	7	297	300
-1	7	250	-250
0	7	243	-232
1	7	273	268
2	7	159	142
3	7	274	-268
4	7	129	-135
5	7	205	190
-7	9	248	261
-5	9	384	-383
-3	9	525	528
-1	9	592	-641
1	9	549	593
3	9	478	-512
5	9	389	431
7	9	297	-297
-4	10	120	-37
5	10	129	-29
-6	11	195	-211
-5	11	134	-103
-4	11	277	255
-2	11	310	-323
-1	11	134	-135
0	11	332	359
1	11	134	150
2	11	337	-362
4	11	280	268
6	11	179	-216
l 4			
-10	0	170	161
-8	0	246	-239
-6	0	529	521
-4	0	469	-503
-2	0	568	680*
0	0	0	-981*
2	0	789	945*
4	0	392	-376
6	0	357	349
8	0	248	-242
10	0	99	105
-11	1	91	105
-10	1	74	-68
-9	1	181	-198
-8	1	111	97
-7	1	358	329
-6	1	220	-198
-5	1	525	-531
-4	1	457	476
-3	1	735	860*
-2	1	336	-360
-1	1	689	-1036*
0	1	0	590*
1	1	963	1125*
2	1	564	-644*
3	1	765	-861
4	1	520	551
5	1	536	564
6	1	227	-208
7	1	397	-385
8	1	219	224
9	1	229	229
10	1	118	-120
11	1	98	-118
-9	2	132	-116
-7	2	195	170
-5	2	314	-289
-4	2	158	-149
-3	2	391	379
-2	2	62	77
-1	2	319	-366
0	2	201	-242
1	2	390	417
2	2	151	135
3	2	255	-217
4	2	248	-232
5	2	246	225
6	2	149	150
7	2	131	-119
8	2	102	-105
9	2	72	53
-9	3	72	-80
-8	3	68	70
-7	3	124	128
-6	3	159	-159
-5	3	242	-248
-4	3	256	252
-3	3	228	213
-2	3	264	-295
-1	3	278	-289
0	3	148	152
1	3	213	208
2	3	430	-454
3	3	262	-227
4	3	190	168
5	3	141	115
6	3	138	-132
8	3	69	64
-6	4	89	88
-4	4	161	-172
-3	4	134	-128
-2	4	394	438
-1	4	15-	30
0	4	101	-125
1	4	16-	-14
2	4	236	248
3	4	62	-41
4	4	303	-309
6	4	169	177
7	4	56	-73
8	4	70	-81
-9	5	122	-115
-8	5	163	149
-7	5	275	252
-6	5	182	-189
-5	5	314	-291
-4	5	257	243
-3	5	492	497
-2	5	385	-405
-1	5	580	-637
0	5	511	553
1	5	614	652
2	5	251	-229
3	5	471	-471
4	5	291	280
5	5	435	422
6	5	216	-206
7	5	278	-266
8	5	112	123
9	5	121	147
-9	6	149	-144
-8	6	118	-103
-7	6	239	218
-6	6	158	150
-5	6	274	-265
-4	6	220	-227
-3	6	415	420
-2	6	214	242
-1	6	416	-414
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1	6	435	450
2	6	263	301
3	6	353	-338
4	6	211	-212
5	6	288	279
6	6	124	136
7	6	113	-125
8	6	80	-102
9	6	104	116
-8	7	196	197
-6	7	351	-330
-4	7	460	445
-2	7	598	-648
-1	7	39	-38
0	7	676	707
1	7	21-	-59
2	7	622	-651
3	7	57	57
4	7	522	523
6	7	389	-405
8	7	241	248
-8	8	126	116
-7	8	94	80
-6	8	145	-125
-5	8	143	-147
-4	8	218	183
-3	8	228	231
-2	8	237	-215
-1	8	265	-274
0	8	172	118
1	8	156	155
2	8	127	-80
3	8	252	-256
4	8	160	109
5	8	191	174
7	8	136	-120
-6	9	106	-92
-5	9	81	80
-4	9	158	154
-3	9	65	-83
-2	9	126	-115
-1	9	219	236
0	9	116	101
1	9	134	-147
2	9	150	-145
3	9	128	132
4	9	84	86
5	9	145	-151
7	9	102	113
1	10	112	122
-6	11	137	-116
-4	11	178	159
-2	11	211	-191
0	11	237	209
2	11	221	-187
4	11	163	158
6	11	98	-111
-5	12	131	-127
-4	12	71	57
-3	12	117	120
-2	12	77	-71
-1	12	173	-180
0	12	102	76
1	12	182	187
2	12	69	-71
3	12	139	-157
5	12	73	87
-5	13	147	145
-4	13	90	75
-3	13	169	-169
-2	13	129	-103
-1	13	169	174
0	13	112	102
1	13	203	-203
2	13	101	-97
3	13	205	219
4	13	90	71
5	13	134	-144
-4	14	118	111
-2	14	128	-113
0	14	131	119
2	14	104	-98
4	14	105	83
l 5			
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-3	0	273	284
-1	0	404	-458*
1	0	141	110
3	0	378	-400
5	0	256	219
7	0	165	-178
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-6	1	135	-146
-5	1	23	4
-4	1	207	204
-3	1	167	135
-2	1	308	-332
-1	1	64	75
0	1	173	180
1	1	172	145
2	1	166	-150
3	1	179	-169
4	1	213	206
5	1	108	97
6	1	128	-126
7	1	68	-70
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2	2	99	-88
3	2	702	-787
4	2	57	55
5	2	591	621
7	2	348	-347
9	2	239	244
11	2	101	-117
-8	3	82	90
-7	3	98	-94
-6	3	176	-165
-4	3	260	237
-3	3	162	-164
-2	3	250	-243
-1	3	192	214
0	3	476	520
1	3	184	-204
2	3	404	-414
3	3	133	145
4	3	270	279
5	3	181	-184
6	3	230	-214
7	3	96	120
8	3	203	195
10	3	81	-92
-10	4	184	-169
-8	4	274	261
-7	4	160	166
-6	4	443	-417
-5	4	303	-302
-4	4	519	568
-3	4	241	242
-2	4	718	-854*
-1	4	418	-463
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1	4	430	489
2	4	657	-757
3	4	406	-414
4	4	585	610
5	4	259	232
6	4	406	-415
7	4	212	-215
8	4	252	250
9	4	80	103
10	4	134	-138
-6	5	107	-95
-5	5	158	167
-4	5	118	100
-3	5	178	-210
-2	5	112	-81
-1	5	171	183
0	5	19-	-1
1	5	189	-201
2	5	127	-105
3	5	249	285
4	5	55	-77
5	5	175	-190
7	5	106	131
-8	6	66	79
-6	6	106	-104
-5	6	111	94
-4	6	179	170
-3	6	67	-46
-2	6	205	-201
-1	6	47	39
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1	6	41	-43
2	6	211	-198
3	6	94	84
4	6	190	173
6	6	196	-186
8	6	79	93
-7	7	75	-85
-6	7	61	-35
-5	7	115	124
-4	7	149	103
-3	7	109	-107
-2	7	144	-94
-1	7	61	74
0	7	131	94
1	7	133	-135
2	7	69	-18
3	7	58	55
4	7	167	126
-9	8	80	-75
-8	8	93	96
-7	8	78	78
-6	8	225	-208
-5	8	138	-130
-4	8	264	236
-3	8	213	209
-2	8	298	-303
-1	8	204	-212
0	8	322	337
1	8	155	175
2	8	373	-379
3	8	203	-203
4	8	261	262
5	8	132	134
6	8	180	-182
8	8	134	141
-7	9	101	-90
-5	9	128	104
-3	9	175	-147
-2	9	63	-50
-1	9	249	229
0	0	51	15
1	9	230	-228
3	9	205	191
5	9	160	-153
7	9	123	125
-9	10	92	86
-8	10	154	139
-7	10	130	-120
-6	10	203	-174
-5	10	163	150
-4	10	299	281
-3	10	238	-206
-2	10	318	-324
-1	10	269	255
0	10	349	338
1	10	241	-221
2	10	321	-329
3	10	180	166
4	10	285	295
5	10	165	-158
6	10	178	-191
7	10	124	110
8	10	136	128
-5	11	66	58
-3	11	106	-87
-2	11	74	97
-1	11	110	90
2	11	105	124
3	11	63	49
4	11	90	-120
5	11	66	-47
6	11	79	116
-5	12	114	91
-3	12	134	-126
-1	12	140	124
1	12	145	-117
3	12	135	133
5	12	79	-76
-4	14	68	71
0	14	79	96
-5	16	82	85
-3	16	99	-101
-1	16	113	128
1	16	113	-113
3	16	85	101
5	16	75	-85
l 6			
-10	0	200	-186
-8	0	312	301
-6	0	599	-566
-4	0	763	774
-2	0	1057	-1107*
0	0	0	1224*
2	0	987	-1136*
4	0	833	907
6	0	588	-601
8	0	352	370
10	0	194	-216
12	0	95	128
-8	1	73	70
-6	1	134	-123
-5	1	45	-34
-4	1	76	65
-3	1	150	135
-2	1	196	-173
-1	1	148	-156
0	1	39	23
1	1	14-	-14
2	1	139	-145
3	1	64	-60
4	1	22-	-25
5	1	83	88
-9	2	126	121
-8	2	134	134
-7	2	252	-239
-6	2	166	-176
-5	2	297	282
-4	2	305	295
-3	2	420	-409
-2	2	333	-362
-1	2	631	689
0	2	429	479
1	2	584	-674
2	2	367	-370
3	2	370	379
4	2	285	275
5	2	379	-392
6	2	219	-211
7	2	270	267
8	2	112	111
9	2	127	-141
11	2	64	80
-9	3	66	73
-5	3	64	51
-4	3	22-	12
-3	3	137	-116
-2	3	18-	18
-1	3	133	120
0	3	89	46
1	3	66	93
2	3	18-	65
3	3	21-	-28
4	3	91	72
-10	4	78	-79
-8	4	116	119
-6	4	211	-192
-5	4	105	108
-4	4	268	275
-3	4	120	-116
-2	4	404	-398
-1	4	166	164
0	4	371	393
1	4	109	-103
2	4	417	-410
3	4	178	170
4	4	304	289
5	4	69	-58
6	4	200	-194
8	4	144	152
10	4	66	-74
-5	5	82	-101
-3	5	23-	41
-2	5	76	-52
-1	5	20-	-81
0	5	20-	-29
1	5	52	113
2	5	21-	-17
3	5	23-	-53
6	5	69	-52
-11	6	85	-88
-9	6	158	153
-8	6	105	103
-7	6	274	-248
-6	6	172	-164
-5	6	408	398
-4	6	294	280
-3	6	572	-601
-2	6	295	-291
-1	6	529	558
0	6	292	299
1	6	625	-684
2	6	329	-339
3	6	591	601
4	6	297	294
5	6	411	-449
6	6	183	-177
7	6	278	266
8	6	106	124
9	6	184	-198
10	6	65	-89
11	6	92	103
-8	7	66	54
-6	7	83	-88
-5	7	109	84
-4	7	125	111
-2	7	47	-44
-1	7	69	14
0	7	106	114
1	7	101	-54
2	7	72	-78
-10	8	64	55
-9	8	78	95
-8	8	90	-83
-7	8	150	-150
-6	8	126	116
-5	8	221	230
-4	8	216	-198
-3	8	272	-269
-2	8	244	244
-1	8	375	397
0	8	242	-252
1	8	330	-338
2	8	253	273
3	8	330	322
4	8	234	-215
5	8	224	-222
6	8	132	139
7	8	172	186
8	8	110	-119
9	8	89	-95
10	8	63	70
-7	9	66	-51
-5	9	62	45
-4	9	70	-58
-3	9	95	-57
-2	9	54	44
-1	9	72	25
1	9	72	-27
-3	10	82	-75
-1	10	92	79
1	10	116	-101
5	10	76	-68
-7	12	105	-94
-6	12	78	75
-5	12	148	151
-4	12	77	-71
-3	12	166	-174
-2	12	113	110
-1	12	196	206
0	12	135	-131
1	12	191	-194
2	12	103	97
3	12	182	205
4	12	78	-91
5	12	128	-150
6	12	67	77
7	12	100	117
-8	14	58	-66
-6	14	76	83
-4	14	112	-113
-2	14	142	144
0	14	162	-168
2	14	134	145
4	14	106	-119
6	14	86	107
8	14	57	-71
l 7			
-9	0	70	83
-7	0	105	-119
-5	0	254	242
-3	0	180	-171
-1	0	271	271
1	0	282	-271
3	0	272	255
5	0	45	-37
7	0	87	96
-9	1	81	-70
-7	1	79	69
-6	1	102	-109
-5	1	177	-145
-4	1	141	146
-3	1	194	170
-2	1	105	-113
-1	1	144	-134
0	1	207	226
1	1	118	134
2	1	237	-229

* Marks reflexions given zero weight and F_{obs} values followed by minus sign are unobserved reflexions included in refinement.

Table 2 (*cont.*)

h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc	h	k	Fo	Fc
3	1	165	-166	-2	4	451	433	0	8	221	-220	-2	0	230	271	-1	4	59	-93	-5	9	92	-78	-7	3	143	126	-4	11	150	130	2	3	80	-81
4	1	163	168	-1	4	354	356	1	8	155	-133	0	0	0	-242*	0	4	138	-115	-3	9	111	81	-6	3	280	257	-2	11	176	-149	-4	4	72	-62
5	1	53	81	0	4	490	-535	2	8	204	200	2	0	159	149	2	4	180	149	-1	9	140	-129	-5	3	193	-172	0	11	185	175	-2	4	75	101
6	1	132	-131	1	4	195	-188	3	8	148	132	4	0	266	-261	4	4	72	-63	1	9	131	122	-4	3	354	-342	2	11	132	-148	0	4	66	-91
8	1	86	101	2	4	503	516	4	8	201	-204	6	0	198	188	-9	5	122	102	2	9	85	59	-3	3	221	224	4	11	150	151	2	4	100	121
-10	2	60	21	3	4	262	249	5	8	77	-68	8	0	109	-121	-7	5	193	-167	3	9	102	-78	-2	3	388	423	6	11	100	-113	4	4	76	-83
-9	2	104	121	4	4	406	-411	6	8	124	133	-10	1	104	85	-6	5	128	120	-3	10	86	68	-1	3	278	-300					-6	5	86	-84
-7	2	254	-227	5	4	216	-201	7	8	71	75	-9	1	141	136	-5	5	269	246	-1	10	71	-52	0	3	406	-472	ℓ = 10				-5	5	114	-103
-5	2	363	316	6	4	276	298	8	8	60	-82	-8	1	118	-104	-4	5	101	-96	-6	11	77	74	1	3	289	317					-4	5	89	91
-4	2	85	-99	7	4	114	125	-7	9	118	-121	-7	1	224	-212	-3	5	279	-288	-4	11	104	-99	2	3	474	516*	-8	0	133	-124	-3	5	185	154
-3	2	567	-527	8	4	194	-229	-5	9	149	170	-6	1	206	182	-2	5	195	183	-2	11	118	129	3	3	251	-234	-6	0	204	192	-2	5	126	-120
-2	2	35	35	10	4	103	130	-3	9	211	-212	-5	1	317	316	-1	5	341	382	0	11	116	-134	4	3	368	-370	-4	0	260	-253	-1	5	198	-190
-1	2	543	531	-8	5	59	-45	-1	9	251	266	-4	1	270	-259	0	5	221	-228	2	11	125	138	5	3	226	220	-2	0	285	307	0	5	99	110
0	2	48	47	-7	5	139	-132	1	9	217	-252	-3	1	420	-440	1	5	355	-396	4	11	104	-111	6	3	286	277	0	0	0	-304*	1	5	203	192
1	2	638	-642	-6	5	118	87	3	9	168	187	-2	1	343	367	2	5	202	198	-1	12	94	-74	7	3	146	-137	2	0	285	302	2	5	127	-132
2	2	46	39	-5	5	213	195	5	9	142	-170	-1	1	387	516*	3	5	291	297	1	12	76	42	8	3	196	-206	4	0	232	-228	3	5	183	-159
3	2	527	495	-4	5	76	-33	7	9	100	121	0	1	0	-233*	4	5	134	-112	-5	13	104	-105	-6	4	109	81	6	0	205	201	4	5	110	95
5	2	425	-434	-3	5	285	-259	-6	10	123	114	1	1	464	-535*	5	5	262	-271	-3	13	159	143	-4	4	113	-93	8	0	90	-102	5	5	192	164
7	2	247	254	-2	5	79	52	-5	10	80	-79	2	1	364	367	6	5	159	139	-1	13	122	-137	-2	4	144	118	-7	1	129	109	7	5	105	-104
9	2	173	-182	-1	5	227	222	-4	10	177	-186	3	1	453	471	7	5	166	181	0	13	95	-84	-1	4	52	-27	-6	1	96	-70	-7	6	89	86
11	2	77	98	0	5	73	-29	-3	10	88	101	4	1	266	-264	-4	6	88	-53	1	13	134	135	0	4	121	-103	-5	1	195	-191	-5	6	159	-143
-10	3	94	-103	1	5	256	-248	-2	10	178	194	5	1	345	-346	-3	6	112	129	3	13	121	-144	2	4	98	67	-4	1	89	84	-4	6	94	-114
-9	3	71	77	2	5	61	38	-1	10	143	-149	6	1	182	178	-2	6	150	96	ℓ = 9				-7	5	135	127	-3	1	247	235	-3	6	179	181
-8	3	175	171	3	5	288	274	0	10	212	-220	7	1	248	238	-1	6	87	-102					-5	5	208	-204	-2	1	155	-159	-2	6	127	129
-7	3	105	-111	5	5	170	-157	1	10	149	175	8	1	94	-100	0	6	152	-93	-5	0	90	-105	-3	5	297	306	-1	1	222	-245	-1	6	187	-195
-6	3	246	-226	7	5	96	95	2	10	238	237	9	1	160	-158	1	6	179	184	5	0	71	-45	-1	5	306	-335	0	1	0	144*	0	6	93	-121
-5	3	204	174	-8	6	81	-92	3	10	134	-135	-6	2	76	91	2	6	125	78	-8	1	86	-100	1	5	313	313	1	1	285	305	1	6	156	153
-4	3	316	298	-6	6	99	113	4	10	164	-181	-4	2	115	-123	3	6	118	-121	-6	1	145	150	3	5	328	-323	2	1	191	-179	2	6	85	116
-3	3	189	-164	-4	6	121	-132	5	10	93	117	-3	2	45	62	4	6	128	-77	-5	1	79	64	5	5	253	243	3	1	277	-276	3	6	214	-188
-2	3	475	-490	-2	6	187	186	6	10	133	146	-2	2	102	113	5	6	117	129	-4	1	212	-217	7	5	167	-172	4	1	142	129	4	6	98	-125
-1	3	275	249	0	6	215	-233	7	10	82	-104	-1	2	64	-76	6	6	100	69	-3	1	134	-122	-5	6	93	-55	5	1	210	192	5	6	119	133
0	3	383	424	2	6	128	157	8	10	91	-103	0	2	94	-104	7	6	90	-103	-2	1	269	302	-3	6	140	74	6	1	117	-131	-6	7	104	-106
1	3	254	-254	3	6	53	-72	-6	11	114	108	1	2	86	115	-10	7	99	90	-1	1	82	88	-1	6	73	-16	8	1	105	91	-4	7	162	151
2	3	355	-385	4	6	109	-117	-4	11	144	-145	2	2	105	108	-8	7	185	-161	0	1	0	-329*	1	6	74	24	7	1	151	-140	-4	8	128	96
3	3	161	141	6	6	94	105	-2	11	126	122	3	2	108	-121	-6	7	275	236	1	1	107	-104	-3	7	85	91	-7	2	134	101	-2	7	209	-213
4	3	295	310	-4	7	50	60	0	11	174	-153	4	2	54	-41	-4	7	342	-323	2	1	267	256	-2	7	94	99	-5	2	151	-133	0	7	240	241
5	3	141	-136	-2	7	44	-77	2	11	118	117	5	2	116	116	-2	7	390	388	3	1	126	107	-1	7	67	-76	-3	2	128	106	2	7	221	-206
6	3	230	-244	0	7	43	68	4	11	103	-106	-4	3	147	-141	0	7	458	-452	4	1	267	-246	0	7	67	-54	-1	2	170	-182	2	8	113	-81
7	3	108	102	2	7	95	-151	6	11	60	57	-3	3	64	-74	2	7	399	395	5	1	97	-113	1	7	92	104	0	2	53	-72	4	8	88	66
8	3	122	134	3	7	74	64	-3	12	60	78	-2	3	99	101	4	7	354	-339	6	1	190	184	3	7	102	-90	1	2	198	193	4	7	214	209
9	3	61	-59	4	7	51	65	-1	12	59	-83	-1	3	74	75	6	7	267	250	8	1	87	-96	-7	9	138	125	3	2	122	-112	6	7	163	-164
-10	4	60	73	5	7	55	-68	1	12	59	88	0	3	121	-126	8	7	160	-170	-5	2	108	93	-5	9	192	-179	5	2	110	84	-6	8	89	-71
-9	4	71	79	-8	8	71	-78	-2	14	60	58	1	3	74	-75	-5	8	90	-94	-3	2	63	-71	-3	9	256	212	7	2	89	-84	-3	8	98	86
-8	4	130	-127	-6	8	141	125	0	14	61	-55	2	3	135	111	-3	8	66	59	-1	2	99	113	-1	9	285	-267	-4	3	93	92	-2	8	131	-105
-7	4	112	-111	-5	8	106	78	2	14	60	45	3	3	103	105	-2	8	63	15	0	2	48	76	1	9	288	284	-3	3	83	82	-1	8	93	-89
-6	4	247	246	-4	8	179	-180					4	3	169	-156	-1	8	76	-97	1	2	52	-55	3	9	260	-246	-2	3	55	-64	0	8	107	87
-5	4	199	178	-3	8	110	-88	ℓ = 8				5	3	98	-83	1	8	91	102	3	2	78	95	5	9	188	200	-1	3	124	-125	1	8	120	119
-4	4	351	-320	-2	8	244	250	-6	0	63	73	-6	4	113	92	3	8	107	-118	4	2	65	-36	7	9	149	-145	0	3	91	104				
-3	4	253	-231	-1	8	127	94	-4	0	109	-109	-4	4	129	-111	-7	9	77	74	-8	3	148	-148	-6	11	101	-84	1	3	54	50				
												-2	4	84	54																				

Table 3. *Positional parameters obtained from partial anisotropic refinement with $R=0{\cdot}087$, as fractional coordinates* $\times 10^4$

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Ag	2494	0001	0327	0001	1647	0001
Mn	2572	0002	1867	0001	6608	0001
O(1)	3840	0011	3497	0008	5923	0006
O(2)	−0145	0011	2226	0008	7156	0007
O(3)	4050	0012	1189	0008	8444	0007
O(4)	2554	0017	0594	0010	4971	0009

Table 4. *Thermal motion obtained from partial anisotropic refinement, represented as mean square amplitude tensor* U_{ij} (Å$^2 \times 10^4$)

	U_{11}	$\sigma(U_{11})$	U_{22}	$\sigma(U_{22})$	U_{12}	$\sigma(U_{12})$	U_{33}*	U_{13}*	U_{23}*
Ag	0196	0003	0274	0003	0031	0002	0227	−0009	0·0
Mn	0151	0004	0162	0004	−0003	0003	0152	−0006	0·0
O(1)	0263	0028	0251	0027	−0071	0023	0256	−0010	0·0
O(2)	0219	0025	0308	0032	0068	0024	0271	−0011	0·0
O(3)	0266	0027	0271	0029	0065	0024	0264	−0010	0·0
O(4)	0489	0048	0289	0037	−0032	0036	0370	−0015	0·0

* Not refined.

For O(4) however, the corresponding figures were 3·86 ± 0·28, 3·22 ± 0·18 and 2·97 ± 0·14, and revealed a marked dependence on cut-off. No physical significance can therefore at this stage be attached to the apparently higher thermal motion of O(4), which might be due to a termination effect.

Since the layer lines were not properly scaled experimentally, refinement with full anisotropic temperature factors would be meaningless (Lingafelter & Donohue, 1963). The introduction of anisotropic thermal motion in projection is however justified, and hence only the terms b_{11}, b_{22} and b_{12} in the temperature factor $\exp(-b_{11}h^2-2b_{12}hk\ \ldots)$ were refined. The refinement was terminated at $R=0{\cdot}087$, and the corresponding set of F_o and F_c values (10 times absolute scale) are given in Table 2, while the positional and thermal parameters are given in Tables 3 and 4 respectively. As recommended by Cruickshank (1965), the thermal motion is given in terms of the mean square amplitude tensor U_{ij} where $b_{ij}=2\pi^2 U_{ij}a_i^* a_j^*$.

Discussion

The new structure as redetermined here and shown in Fig. 6, is clearly very different from the earlier structure proposed by Sasvari. The positions of the Ag and Mn atoms are interchanged almost exactly, and completely new positions assigned to the oxygen atoms. Silver permanganate cannot be regarded as having a slightly deformed barite structure, because although there is a formal correspondence in the heavy atom positions, the orientation of the oxygen tetrahedron is quite different.

The thermal parameters obtained indicate that the motion of the Mn atom is small and isotropic, whereas that of the Ag atom is decidedly anisotropic. This seems reasonable since the Mn atom is at the center of the large permanganate group, while the smaller Ag atom is relatively free. This agrees with results obtained for $CsMnO_4$ (Prout & Nassimbeni, 1966). More recently in an accurate refinement of the structure of $KMnO_4$, Palenik (1967) also found that the motion of the Mn atom is nearly isotropic, and that the permanganate group can be considered as a rigid body.

Bond lengths and angles found in the present study for the permanganate group are given in Table 5. The observed departures from regularity are mostly associated with O(4) and are probably due to the series termination effect. Within the experimental errors, the permanganate group is a regular tetrahedron with an

Table 5. *Bond lengths and angles in the permanganate group*

R = 0·087 with partial anisotropic refinement, no correction for thermal motion.

	Distance	e.s.d.
Mn–O(1)	1·612 Å	0·010 Å
–O(2)	1·631	0·008
–O(3)	1·625	0·007
–O(4)	1·571	0·008
Av. Mn–O	1·610	0·004
O(1)–O(2)	2·670	0·011
–O(3)	2·621	0·009
–O(4)	2·591	0·012
O(2)–O(3)	2·656	0·010
–O(4)	2·602	0·012
O(3)–O(4)	2·630	0·011
Av. O–O	2·628	0·007

	Angle	e.s.d.
O(1)–Mn–O(2)	110·9°	0·4°
–O(3)	108·1	0·3
–O(4)	109·0	0·4
O(2)–Mn–O(3)	109·3	0·3
–O(4)	108·7	0·4
O(3)–Mn–O(4)	110·8	0·4
Av. O–Mn–O	109·5	0·2

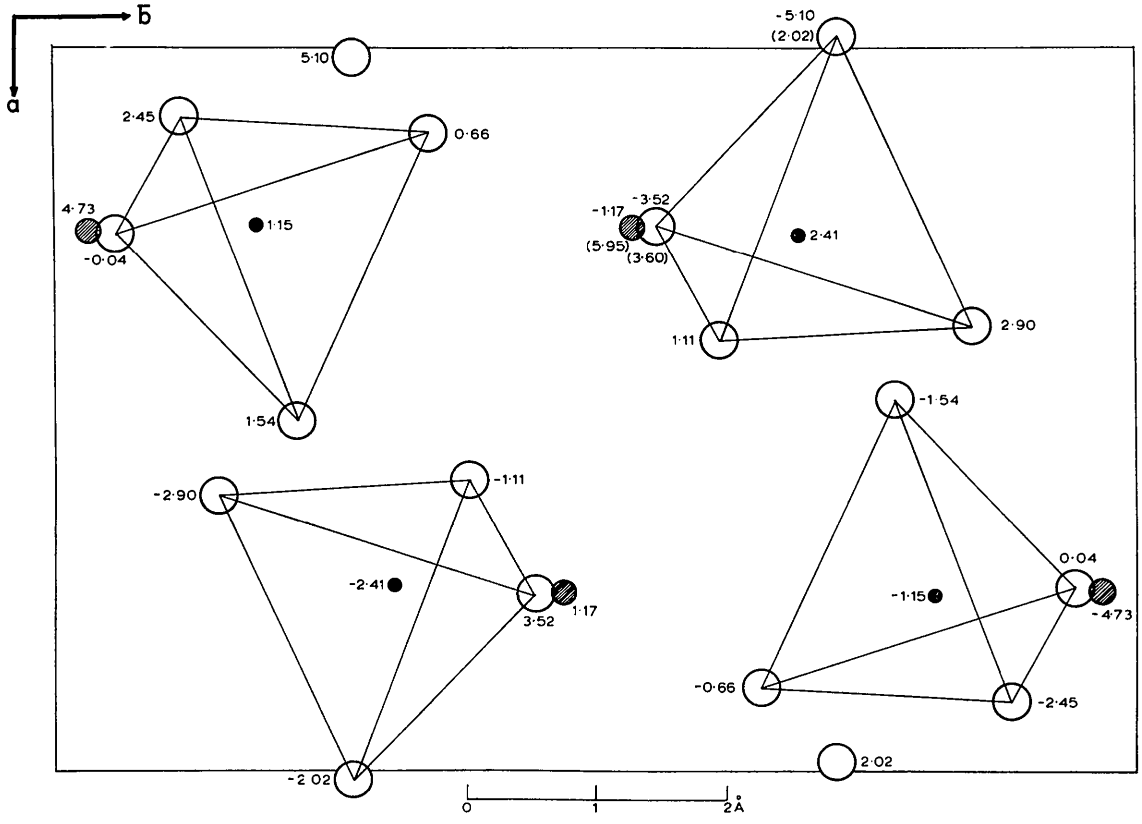

Fig. 6. The new structure of silver permanganate in [001] projection for comparison with Figs. 1 and 2, using the same key as Fig. 1.

average Mn–O bond length of 1·61 ± 0·01 Å. The e.s.d. is here set at a somewhat higher value to allow for the effect of some possible systematic errors. This bond length is in close agreement with the result of 1·629 Å found in $KMnO_4$ by Palenik after applying a correction of 0·022 Å for anisotropic motion. Such a correction cannot be made in the present study on account of the incomplete thermal motion data.

The structure as seen in the [001] projection seems to consist of stacks of MnO_4 tetrahedra and rows of Ag atoms extending in the **c** direction. The difference in z coordinates of the Ag and Mn atoms closest in projection is almost exactly $\frac{1}{2}$, and leads to a regular zigzag Ag–Mn–Ag–Mn chain running in the **c** direction. This description probably has no significance since there are closer Ag–Mn (and Ag–O) approaches in other directions. Each Ag atom is in fact surrounded by seven MnO_4 groups with Ag–Mn distances varying between 3·51 and 3·81 Å, and corresponding close Ag–O approaches between 2·33 and 2·67 Å. The shortest Ag–Ag and Mn–Mn distances are 3·63 and 4·33 Å respectively, while the closest approaches between oxygen atoms in different permanganate groups vary from 2·81 to 3·06 Å. The shortest Ag–O and non-bonded O–O distances are markedly shorter than the corresponding distances in $KMnO_4$ (2·62 and 3·06 Å respectively). The present structure is clearly more compact since the molecular volume of $AgMnO_4$ is about 15% smaller than that of $KMnO_4$. The closer approaches found in $AgMnO_4$ compared to $KMnO_4$ can probably be attributed to the fact that $AgMnO_4$ is not a truly ionic compound, but contains a measure of covalent bonding. Unfortunately, accurate data for similar permanganates are not available.

The investigation of the structural aspects of the thermal decomposition of silver permanganate, which led to this structure determination, was undertaken at the suggestion, and under the initial guidance of Dr F. H. Herbstein. In the present work, helpful discussions with Dr G. Gafner are gratefully acknowledged.

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The Crystal Structure of Cd_3As_2

BY G. A. STEIGMANN AND J. GOODYEAR
Physics Department, The University of Hull, England

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A Weissenberg study of the structure of Cd_3As_2 has shown that the unit cell is tetragonal ($a = 12·67 \pm 0·01$ Å, $c = 25·48 \pm 0·02$ Å, $Z = 32$, space group $I4_1cd$). Arsenic ions are approximately cubic close-packed and Cd ions are tetrahedrally coordinated. The main difference between the present structure and that proposed by von Stackelberg & Paulus lies in the disposition of the vacant tetrahedral sites. Both structures are geometrically related to the fluorite structure.

Introduction

The crystal structure of Cd_3As_2 was determined by von Stackelberg & Paulus (1935) as tetragonal ($a = 8·95$, $c = 12·65$ Å, space group $P4_2/nmc$) with As ions approximately in a cubic close-packed array. Cd ions were tetrahedrally coordinated and each As ion was surrounded by Cd ions at six of the eight corners of a distorted cube, the two vacant sites being at diagonally opposite corners of a cube face.

In the same paper von Stackelberg & Paulus also reported the crystal structure of Zn_3As_2 as being the