THE CRYSTAL STRUCTURE OF POTASSIUM PERMANGANATE

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Abstract

The crystal structure of potassium permanganate was determined from Laue and x-ray single crystal oscillation photographs. It was found that the unit cell is orthorhombic, contains four molecules, and has the dimensions:

$a=9.09$A $\quad b=5.72$A $\quad c=7.41$A

The symmetry of the crystal is $2Di-16$ (V_h^{16}), and the structure may be given by the following parameters, expressed as fractions of the unit cell dimensions:

Four K at $4c$:	$u=0.06$	$v=0.16$	
Four Mn at $4c$:	$u=0.18$	$v=0.67$	
Four O at $4c$:	$u=0.00$	$v=0.61$	
Four O at $4c$:	$u=0.26$	$v=0.49$	
Eight O at $8d$:	$x=0.19$	$y=0.22$	$z=0.80$

The agreement between the observed intensity and the calculated structure amplitude is satisfactory. The crystal, isomorphous with barytes, celestine and anglesite, has a closely similar structure, though the parameters are different. The manganese is surrounded by four oxygen atoms at an average distance of 1.59A, the arrangement being a nearly regular tetrahedron. The average oxygen-to-oxygen distance in a tetrahedron is 2.62A. The smallest distance between oxygens in different tetrahedra is 2.72 A. The potassium is surrounded by nine oxygens at a mean distance of 2.97A.

1. Unit Cell and Space Group

ALTHOUGH the cell size and the space group of potassium permanganate have been reported by James and Wood[1] and by Basche and Mark,[2] no complete structure determination of this crystal has appeared. Since potassium permanganate is isomorphous with the sulphates of strontium, barium and lead, the atomic arrangements must also be analogous.[3]

Crystals of sufficient size and perfection were grown by the slow cooling of an aqueous solution saturated at about thirty-five degrees. From these, both Laue and oscillation photographs were obtained. Laue photographs were taken with the incident beam parallel to the crystallographic axes and were indexed in the usual way by conversion to gnomonic projections. Numerous oscillation photographs (oscillation angle 15° or 30°) around the three principal axes were indexed according to the graphical method described by Bernal.[4]

[1] R. W. James and W. A. Wood, Proc. Roy. Soc. **A109,** 598 (1925).

[2] W. Basche and Z. Mark, Zeits. f. Krist. **64,** 1 (1926).

[3] P. von Groth, Chemische Krystallographie, Vol. 5; Englemann (1908). J. A. Wasastjerna, Phil. Mag. **7,** 2 (1926); Soc. Sci. Fennica (Physico-Math.) **2,** No. 19–30 (1927).

[4] J. D. Bernal, Proc. Roy. Soc. **A113,** 117 (1926).

The following values were found for the lattice dimensions:

$$a = 9.09\text{A} \qquad b = 5.72\text{A} \qquad c = 7.41\text{A}$$

There are four molecules in the unit cell. In agreement with the results of previous investigations, the space group was shown to be $2Di-16$ (V_h^{16}).

2. Determination of the Structure

Since the space group and the number of molecules per unit cell were known, it was possible, by means of the theory of space groups, to list all the arrangements of the twenty four atoms compatible with the symmetry of the crystal. The number of possibilities was limited by some justified assumptions. Because of the isomorphism with the sulphates of strontium, barium and lead, as well as with the perchlorates of potassium, rubidium, caesium and ammonium, the existence of groups MnO_4 in the crystal may well be taken for granted. These MnO_4 groups must of necessity be linked together by the potassium ions. This assumption together with considerations of the intensities showed that only the following distribution of the atoms among the available positions was possible: (See Wyckoff's tables[5]) 4K in $4c(u0v)$; 4Mn in $4c(u0v)$; $4O_I$ in $4c(u0v)$; $4O_{II}$ in $4c(u0v)$ $8O_{III}$ in general positions $8d(xyz)$. There are, therefore, eleven parameters in the structure.

From considerations of the intensities of reflections occurring at large glancing angles (where the influence of the oxygens becomes negligible) the parameters for potassium and manganese were determined. The values obtained agree very well with those given for Ba and S in $BaSO_4$. (Compare James and Wood.[1])

The intensities of reflections from about fifty planes with simple indices were used for the determination of the seven oxygen parameters. Some simplification was obtained by the conception of tetrahedral MnO_4 groups with dimensions somewhat larger than those of the SO_4 group; further, all arrangements were rejected if they gave an oxygen-to-oxygen distance considerably less than 2.5A. In this way a set of approximate parameter values was easily derived. Then a series of changes in the parameter values was made so as progressively to better the agreement between observed and calculated intensities, until by this process of trial and error a satisfactory agreement was obtained. The final set of parameter values is given in the Table I. In Table II the calculated values of the structure amplitude are compared with the

Table I. *Parameter values.*
(Given in fractions of the length of the unit cell sides)

Potassium:	$u=0.06$	$v=0.16$	
Manganese:	$u=0.18$	$v=0.67$	
Oxygen_{I}:	$u=0.00$	$v=0.61$	
$\text{Oxygen}_{\text{II}}$:	$u=0.26$	$v=0.49$	
$\text{Oxygen}_{\text{III}}$:	$x=0.19$	$y=0.22$	$z=0.80$

[5] R. W. G. Wyckoff, Analytical Expression of the Results of the Theory of Space Groups, Carnegie Institute of Washington, 1930.

TABLE II. *Calculated and observed values of the structure amplitude.*

hkl	sin θ	*F* (calculated)	Intensity (observed)
101	0.0618	49.4	M
200	0.0782	53.4	M
011	0.0784	51.05	M
201	0.0917	59.5	M
002	0.0960	60.4	M
210	0.1001	107.6	VVS
102	0.1036	92.8	S
202	0.1230	20.5	M
020	0.1248	134.4	VVS
301	0.1266	7.7	W
400	0.1573	34.3	MW
302	0.1517	5.6	VW
122	0.1621	92.9	S
401	0.1635	137.1	VVS
203	0.1640	25.2	M
303	0.1860	68.3	S
004	0.1917	43.7	M
123	0.1940	46.4	M
104	0.1960	50.0	M
420	0.2000	21.3	W
501	0.2010	22.0	W
230	0.2030	68.8	M
114	0.2056	60.4	M
204	0.2076	37.2	W
132	0.2105	66.1	M
141	0.2238	27.6	W
304	0.2249	6.5	W
133	0.2350	1.8	VVW
124	0.2324	63.7	M
610	0.2430	55.0	M
600	0.2440	41.2	MW
601	0.2441	16.7	W
105	0.2441	13.3	W
040	0.2470	123.5	VVS
015	0.2480	23.8	W
233	0.2490	7.9	VVW
513	0.251	60.1	MS
205	0.253	9.2	W
414	0.255	2.6	VVW
240	0.261	19.4	W
602	0.263	34.4	MW
241	0.265	25.3	W
620	0.266	10.1	VW
142	0.269	56.0	MW
134	0.271	65.5	M
125	0.273	51.0	M
531	0.275	30.0	W
440	0.295	10.9	W

observed intensities. The agreement is as good as can be expected for a structure having eleven parameters. The *F*-curves shown in Table III were used in calculating structure amplitudes. The observed intensities are rated as very strong, (VS); strong, (S); medium, (M); weak, (W), and very weak (VW).

TABLE III. *F-curve values used for potassium permanganate structure.*[6]

Sin θ/λ	O	K	Fe
0.1	8.0	16.9	22.6
0.2	5.8	13.0	18.0
0.3	3.7	10.5	14.9
0.4	2.5	8.6	12.5
0.5	1.7	7.2	10.7
0.6	1.1	6.0	9.3
0.7	0.7	5.1	8.2
0.8	0.5	4.3	7.2
0.9	0.4	3.7	6.3
1.0	0.3	3.1	5.6

3. DISCUSSION OF THE STRUCTURE

In Fig. 1 is given a projection of the structure on the *c*-face. It is true that some use has been made of atomic distances in deriving the approximate

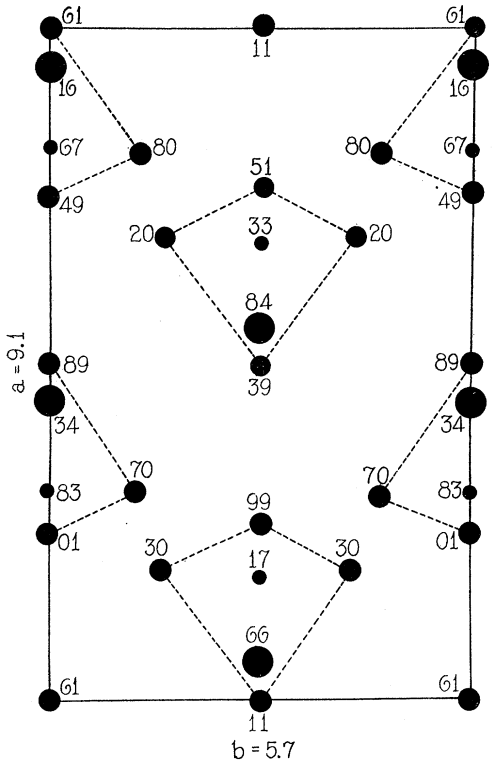

Fig. 1. Crystal structure of potassium permanganate projected on *c*-face. Large circles are potassium, medium circles are oxygen and small circles are manganese.

parameter values. The more accurate evaluation of the positions was, however, made on the basis of intensities alone.

Manganese is surrounded by four oxygens (one O_I, one O_{II}, and two O_{III})

[6] The values are taken from: W. L. Bragg and J. West, Zeits. f. Krist. **69**, 118 (1928).

forming a nearly regular tetrahedron. The manganese-to-oxygen distances are: Two O at 1.58A; one O at 1.68A, and one at 1.52A, the average being 1.59A. The oxygen-to-oxygen distances in the tetrahedron are:

$O_I - O_{III} = 2.62A$ $O_{III} - O_{III} = 2.53A$ $O_{III} - O_{II} = 2.70A$

$O_I - O_{II} = 2.54A$

The average O to O distance is 2.62A.

For comparison it may be remarked that the silicon-to-oxygen distance in the SiO_4 group is given as 1.54–1.64A;[7] the sulphur-to-oxygen distance in the SO_4 group is 1.5A;[8] the phosphorus-to-oxygen distance in the PO_4 group is 1.56A;[9] and chlorine-to-oxygen distance in ClO_4 is 1.56A.[10]

In $KMnO_4$, potassium is surrounded by nine oxygens at a mean distance of 2.97A; one at 3.37A; two at 2.93A; two at 2.96A; one at 2.94A; one at 3.05A; and two at 2.79A. The potassium-to-oxygen distance in other crystals with coordination number nine is reported as 2.96A and 2.94A.[11]

The smallest distance between oxygens belonging to different tetrahedra is 2.72A.

In conclusion I wish to express my most sincere thanks to Dr. W. H. Zachariasen for his interest and assistance in this investigation.

[7] W. L. Bragg, Zeits. f. Krist. **74,** 237 (1930).

[8] A. J. Bradley, Phil. Mag. **49,** 1225 (1925); R. W. James and W. A. Wood, ibid.

[9] J. West, Zeits. f. Krist. **74,** 306 (1930).

[10] W. H. Zachariasen, Zeits. f. Krist. **73,** 2, 141 (1930).

[11] W. H. Zachariasen, Norske, Vid. Akad. Skr. Mat.-Nat. Kl. No. 4 Oslo, 1928, p. 97, Zeits. f. Krist. **71,** 501 (1929).