of thermal ʟ ɔvement in particular planes. The accuracy claimed in this work is not enough for the discrepancy between the tin–chlorine separation found and the values quoted in the literature (Pauling, 1939) to be taken as significant. An attempt is being made to find an isomorphous crystal with a lighter atom replacing the tin so that the hydrazinium ion position may be found more accurately.

The work was begun in the Physics Department, University of Cape Town, and completed in the Crystallographic Laboratory, Cavendish Laboratory, Cambridge. I wish to thank Prof. R. W. James (who introduced me to crystallography) for help and encouragement and Dr W. Cochran for frequent and valuable advice.

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The Crystal Structure of Mg₆MnO₈

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The structure of Mg_6MnO_8 is found to be of a simple new type. It is cubic, with $a_0 = 8\cdot381\pm0\cdot002$ Å and space group $Fm3m$. The oxygens are slightly distorted from a close-packed arrangement, and there occurs an ordered arrangement of the metal ions and of vacancies among the octahedral interstices.

Introduction

In the course of studying the reaction products from combining magnesium and manganese oxides in different proportions, we have observed that a new cubic phase is formed when the ratio of magnesium to manganese exceeds 6. The composition of this phase has been found to correspond to the formula Mg_6MnO_8 and its structure has been determined to be of a simple new type wherein there occurs an ordering of the respective metal ions *as well as of vacancies* among the octahedral interstices of close-packed oxygen ions. Another example of this structure type has been found independently by Christ, Clark & Fahey (1953) for a mineral of formula Cu_6PbO_8. A preliminary note on both these compounds appears elsewhere (Kasper & Christ, 1953).

Preparation and analysis

An intimate mixture of magnesium oxide and manganese carbonate in a molar ratio of 8:1 was fired at 1100° C. for 5 hr. in an oxygen atmosphere. Although the mixed oxide phase described in this paper corresponds to a molar ratio of magnesium oxide to manganese dioxide of 6:1, the excess magnesium oxide was found to be necessary in order that all of the manganese be oxidized to the tetravalent state. The X-ray diffraction pattern showed the presence of the excess magnesium oxide in addition to the new mixed oxide phase. It was found that this excess of magnesium oxide could be removed by boiling the powdered mixture in a 10% ammonium chloride solution for about 15 min. The X-ray diffraction pattern of this treated material no longer contained the lines of magnesium oxide.

A chemical analysis of the mixed oxide phase gave the following results:

	Found (%)	Calculated for Mg_6MnO_8 (%)
Mg	42·9	44·3
Mn (total)	16·9	16·7
Mn (as +4)	16·8	16·7

In view of the difficulties involved in determining magnesium in the presence of large quantities of manganese, the agreement is good.

Measurement of intensities

Preliminary investigations were done by means of Debye–Scherrer photographs. When the new phase was found, however, the attempts to determine the details of structure indicated the desirability of quantitative intensity measurements. That was accomplished readily by using powder in the form of a thick slab and a Geiger counter for the detection of the

diffracted X-rays. For the conditions of reflection from the surface of a thick slab the absorption correction is conveniently constant $(1/\mu)$ for all reflections (*Internationale Tabellen*, vol. 2, p. 562).

The dimensions of the slab were 7·5 cm.×1 cm.× 0·45 cm. (thickness). Actually, the powder was packed in a hole of the above dimensions in a flat aluminum block. The block was mounted in the specimen holder of a General Electric XRD-3 unit and the condition that incident angle was equal to reflection angle was maintained. The diffracted intensity was recorded on a logarithmic chart with slow travel of counter (0·2° per min.). The chart readings were converted to a linear plot by means of a calibrated scale, and areas under peaks were measured with a planimeter. A test of this procedure for MgO indicated that intensities with an accuracy better than 10% could be obtained.

The structure determination

All reflections could be indexed for a cubic cell with $a_0 = 8\cdot381\pm0\cdot002$ Å. Systematic absences occur for h, k, l not all odd or not all even, indicating a face-centering. In addition, among the even-index reflections none was observed for which h, k, l were not all $4n$ or all $4n+2$. These absences are not required by any space group, and they furnished the clue to the solution of the structure.

The a_0 of the cell is very close to double that for MgO (4·203 Å) and it would appear, then, that there are 32 oxygens in the unit cell in a close-packed arrangement, but that the doubling of the cell would result from a special kind of ordering of the metal ions in the octahedral interstices. A random distribution of the metal ions would, of course, not give any intensity for reflections with odd indices. Since there are only 4Mn^{++}, they are indicated to be at the origin and face-centers in any ordered model. Two models then suggest themselves: (a) the 24 Mg^{++} are distributed randomly among the 28 remaining sites, or (b) the Mg^{++} are in the 24-fold positions:

$$(0, 0, 0; \ 0, \tfrac{1}{2}, \tfrac{1}{2}; \ \tfrac{1}{2}, 0, \tfrac{1}{2}; \ \tfrac{1}{2}, \tfrac{1}{2}, 0) +$$
$$0, \tfrac{1}{4}, \tfrac{1}{4}; \ \tfrac{1}{4}, 0, \tfrac{1}{4}; \ \tfrac{1}{4}, \tfrac{1}{4}, 0;$$
$$0, \tfrac{1}{4}, \tfrac{3}{4}; \ \tfrac{3}{4}, 0, \tfrac{1}{4}; \ \tfrac{1}{4}, \tfrac{3}{4}, 0,$$

leaving the ordered face-centered arrangement of 4 holes. Model (a) would give detectable intensities for the reflections not observed, namely h, k, l even but not all $4n$ or $4n+2$. No such reflections could be observed, even on highly-exposed photographs. On the other hand, a reasonably satisfactory agreement of observed and calculated intensities was obtained for model (b). The absences mentioned above result in this case from the fortuitous circumstance that the corresponding structure factors contain the term $(f_{\text{Mn}}-2f_{\text{Mg}})$ and, with f_{Mn} so very nearly $2f_{\text{Mg}}$, they all are extremely small.

While the parameterless model (b) seemed reasonably satisfactory, it did yield some significant inversions in the intensity comparison. Consideration of the distances Mg–O and Mn–O, as well as space-group requirements, indicated the reasonableness of a distortion of oxygens from the ideal close-packed arrangement.

The appropriate description for the structure is:

4 Mg_6MnO_8 per unit cell.

Space group: $Fm3m$–O_h^5.

$(0, 0, 0; \ 0, \tfrac{1}{2}, \tfrac{1}{2}; \ \tfrac{1}{2}, 0, \tfrac{1}{2}; \ \tfrac{1}{2}, \tfrac{1}{2}, 0) +$

4 Mn at (a) 0, 0, 0

24 Mg at (d) $0, \tfrac{1}{4}, \tfrac{1}{4}; \ \tfrac{1}{4}, 0, \tfrac{1}{4}; \ \tfrac{1}{4}, \tfrac{1}{4}, 0;$
$\qquad\qquad 0, \tfrac{1}{4}, \tfrac{3}{4}; \ \tfrac{3}{4}, 0, \tfrac{1}{4}; \ \tfrac{1}{4}, \tfrac{3}{4}, 0$

8 O_I at (c) $\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}; \ \tfrac{3}{4}, \tfrac{3}{4}, \tfrac{3}{4}$

24 O_{II} at (e) $X, 0, 0; \ 0, X, 0; \ 0, 0, X;$
$\qquad\qquad \bar{X}, 0, 0; \ 0, \bar{X}, 0; \ 0, 0, \bar{X}$

4 vacancies at (b) $\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}$.

Table 1. *Comparison of observed and calculated intensities*

(Cu $K\alpha$ radiation)

hkl	I_o	I_c		hkl	I_o	I_c		hkl	I_o	I_c
111	209	209		622	29	29		840	70	72
200	0	1		444	55	47		911 ⎫	10	11
220	0	1		711 ⎫	13	13		753 ⎰		
311	50	57		551 ⎰				842	0	0
222	38	45		640	0	0		664	0	0
400	346	338		642	0	0		931	11	10
331	15	12		731 ⎫	9	9		844	74	76
420	0	0		553 ⎰				933 ⎫		
422	0	0		800	24	22		771 ⎬	12	8
333 ⎫	32	28		733	0	1		755 ⎰		
511 ⎰				820 ⎫	0	0		10,0,0 ⎫	0	0
440	181	172		644 ⎰				860 ⎰		
531	26	25		822 ⎫	0	0		951 ⎫	21	25
600	0	0		660 ⎰				773 ⎰		
620	0	0		751 ⎫	8	9		10,2,2 ⎫	32	32
533	4	6		555 ⎰				666 ⎰		
				662	15	16		953	27	38

$R = 0\cdot063; \quad I_c \sim \exp\left[-2B\,(\sin\theta/\lambda)^2\right]\left\{\dfrac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right\}pF^2; \quad B = 0\cdot30 \text{ Å}^2.$

Intensities were calculated for a variation of X from 0·200 to 0·250 and it was found that best agreement with observed intensities was obtained for $X = 0·230$ ±0·003. In particular, for the reflections most sensitive to the oxygen parameter (principally those with odd indices) there were no longer the significant discrepancies present in the ideal model with $X = \frac{1}{4}$. In addition, there was an indication of a small temperature effect on the intensities. A value of $2B = 0·6$ $Å^2$ was determined and the correction $\exp[-2B(\sin\theta/\lambda)^2]$ was applied to the calculated values.

The comparison of the intensities (Table 1) is very satisfactory, as can be judged from the very low value (0·063) of the reliability index.

Discussion of structure

The structure is illustrated by means of parallel planes at different Z-levels in Fig. 1. The octahedra of oxygen ions surrounding Mn^{4+} are regular, but those
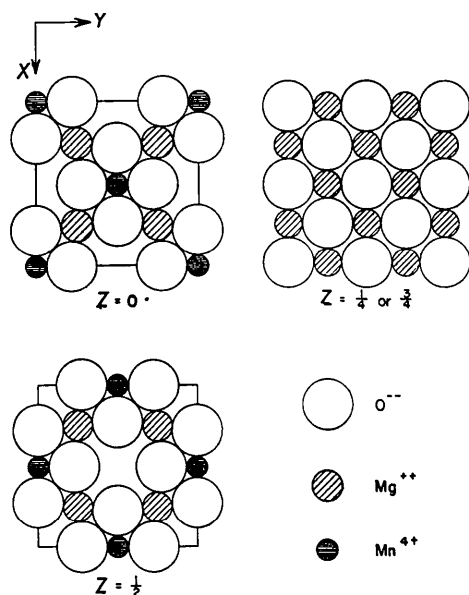

Fig. 1. The ordered arrangement of ions and vacancies in Mg_6MnO_8.

around Mg^{++} are slightly distorted. The interatomic distances for $X = 0·230$ are:

6 Mn–O	1·928 Å
2 Mg–O	2·095 Å
4 Mg–O	2·102 Å

These distances compare very well with those expected from ionic radii. Thus, the Mg–O distance in MgO is 2·102 Å, and Mn–O (from sum of radii) is 1·90 Å. On the other hand, for the idealized model with $X = \frac{1}{4}$, and both sets of distances equal to 2·095 Å, the Mn–O distance would be abnormally long.

A more interesting feature of the structure, perhaps, is the ordering of the holes. Bertaut (1953), in calculating electrostatic energies for defect structures, has shown that the energy of stabilization for ordering holes is quite high and has concluded that in general ionic substances with vacancies would be ordered. This structure confirms Bertaut's general conclusion. In this connection, it is convenient to regard the structure as of the MgO type with a defect, in which one-quarter of the Mg^{++} are replaced by the pair Mn^{4+} and a hole.

It is somewhat surprising that more cases of this structure type are not known. A logical extension of the well-established principles of the crystal chemistry of simple ionic compounds would lead one to expect such a structure provided the following simple requirements are met: (1) the coordination number for oxygen is 6 for both ions; (2) the respective valencies of the two ions are 2 and 4; (3) the proportions of the ions are 6 to 1 in favor of the divalent ion.

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