

STUDIES IN THE STRUCTURES OF THE MANGANITES
AND RELATED MIXED METAL OXIDES.

A Thesis submitted for the
Diploma of the Imperial College.

J. B. Payne, B.Sc., A.R.C.S., A.R.I.C., M.P.S.

June, 1951.

Imperial College of Science and Technology,
South Kensington.

ABSTRACT

A general survey has been made of the formation and structures of the mixed oxides of manganese with other metals of the type $\begin{pmatrix} R_1^{II} \\ R_2 \end{pmatrix} Mn_2O_4$, the "manganites". Some of the rhenium analogues have also been examined.

A brief introduction to the literature and description of the approach to the study are followed by an account of the experimental techniques used. These comprise the preparation of the mixed oxides, their analysis, and examination by the X-ray powder diffraction method.

Published work on zinc manganite has been checked and extended, and the effect of small amounts of sodium ion on the structure of zinc manganite investigated.

The preparation of manganites of the following has been attempted: the alkali metals and copper; the alkaline earth metals; cadmium; and finally, the iron-cobalt-nickel group.

Potassium and beryllium did not form mixed oxides with manganese. Magnesium and cadmium formed manganites with the tetragonal hausmannite type structure, while the manganites of copper, iron, cobalt, and nickel had cubic unit cells of the spinel type. Calcium and strontium formed mixed oxides of lower symmetry.

The solubility of the constituent oxides in the manganites of magnesium, iron, cobalt, and nickel has been tested.

The results are summarised and the relationship of the structures to hausmannite is discussed.

A note on previous work on the rhenium analogues is followed by a description of attempts to prepare rhenium dioxide and some of the rhenites, including those of zinc, magnesium, calcium, and iron.

CONTENTS.

	<u>Page</u>
Introduction	1
PART I. THE MANGANITES	5-137
Section 1. General Experimental Techniques.	5- 22
1. Preparation of Mixed Oxides	5
2. Analyses	9
3. X-Ray Powder Diffraction Technique	11
4. The Interpretation of the Powder Diffraction Photograph	16
Section 2. Zinc Manganite.	23- 55
Zinc Manganite with Excess Zinc Oxide and manganous manganic Oxide	37
The Effect of Sodium Ions on the Zinc Manganite lattice.	44
Attempted Preparations of Zinc Manganite 2.3 and 4.2 Spinel	54
Section 3. A. Manganites of the Alkali Metals, Lithium Sodium, and Potassium	56
B. Potassium Manganate	61
Section 4. Copper Manganite	67-76
Section 5. Manganites of the Alkaline Earth Metals	77-103
Beryllium	78
Magnesium	79
Magnesium Manganite with Excess Manganous Manganic Oxide and Magnesium Oxide	92
Calcium	95
Strontium	99
Barium	101
Section 6. Cadmium Manganite	104-107

Section 7.	Mixed Oxides of Manganese with Iron, Cobalt and Nickel	108-128
	Iron	111
	Cobalt	118
	Nickel	123
Section 8.	Summary of Results and Discussion	129-137
	Table of Results	129
	Discussion	130
PART II.	ATTEMPTED PREPARATION OF THE RHEUNITES.	138-146
	1. Attempted Preparation of Rhenium Dioxide	139
	2. Attempts at Direct Synthesis	142
	Acknowledgements	147

INTRODUCTION

1

The mixed oxides of iron with other metals, the "ferrites" of the type MFe_2O_4 , have been extensively examined, but the manganese analogues, the "manganites", have attracted less general attention. Many reputed compounds of the oxides of manganese with those of the other metals are recorded in the older literature, both as hydrated and as anhydrous forms. Probably the first of these described is the so-called "calcium manganite", formed in the old Weldon process for the manufacture of chlorine by the oxidation of hydrochloric acid with pyrolusite. The pages of Mellor and Abegg contain many examples of such "compounds"; Abegg's "Handbuch", for example, contains no less than five examples of mixed oxides of calcium and manganese. These older preparations were assigned formulae based on chemical analysis only, and thus the constituent oxides may have been present in only fortuitous stoichiometric ratio. Not until the advent of the method of X-ray crystal diffraction could the existence of a single mixed-oxide phase be established in such cases.

Subsequent to the discovery in 1912, by Laue, Friedrich and Knipping, and W. L. Bragg, of the use of X-rays for the identification of solid phases and the determination

of their structure, a certain amount of work using this tool has been done on zinc manganite and the manganites of iron, cobalt, and nickel. This previous work on each manganite is described more fully in the introduction to the section on the particular manganite; just a brief outline is given here.

Zinc manganite, $2\text{ZnMn}_2\text{O}_4$, has received some attention owing to its occurrence as the mineral heterolite and as a reaction product in the discharged Leclanché dry cell. C. Frondel and E. F. Heinrich (Amer. Mineral., 1942, 27, 48-56) found the mineral to have a tetragonal cell isostructural with manganous manganic oxide; their lattice constants differed a little from those determined by B. Mason (Amer. Mineral., 1947, 32, 426-441), who prepared the pure mixed oxide from the metal carbonates.

Verwey and van Bruggen (Z. Krist., 1935, 92, 136-138) assigned the Hausmannite (Mn_3O_4) structure to iron manganite, but V. Montoro (Gazz. chim. Ital., 1938, 68, 728-733) found this manganite to be a spinel. Frevel's list of spinels (Ind. Eng. Chem., Anal. Ed., 1942, 14, 690) gives lattice constants for cobalt and nickel manganites.

Magnesium, cadmium, and copper manganites are mentioned

in Dana's "System of Mineralogy" (Vol.I, 7th.Ed., 1944). No references are given for the first two, which are said to be analogues of zinc manganite, while a morphological reference suggests that copper manganite may be monoclinic.

These few sources, together with one or two parallel studies described later, comprised all the published structural work on the manganites. Thus there was scope for a general survey of the formation of manganites by metals throughout the Periodic System, and a study of the crystal symmetry of each manganite, if formed.

The work described in this Thesis has been restricted mainly to the mixed oxides of manganese of the type $(R_I^{II}) (R_2^{II}) Mn_2O_4$. Mixed oxides of the type $R^{II} MnO_2$ have not been examined as they have already been investigated in some detail by previous workers. Some little attention has been given to potassium manganate, but not to other examples in this series.

Likely bivalent metal oxides were first selected for the study of mixed oxide formation, and the field then extended to cover other possibilities.

Zinc manganite was first examined, and then the formation, and structure when formed, of the following possible manganites were investigated:-

Group I A. Lithium, Sodium, Potassium.

B. Copper.

Group II A. Beryllium, Magnesium, Calcium, Strontium,
Barium.

B. Cadmium.

Group VIII. Iron, Cobalt, Nickel.

The work was extended later to the examination of possible rhenium analogues, the "rhenites", as Messrs. Johnson, Matthey had kindly made available supplies of pure rhenium metal powder.

No work has been done hitherto on such mixed oxides and, furthermore, the structure of the lower rhenium oxide, ReO_2 , has not been elucidated.

PART I. THE MANCANICES.

Section 1. GENERAL EXPERIMENTAL TECHNIQUES.

1. Preparation of Mixed Oxides.

(a) Sources.

Where possible, reagents of Analar purity have been used. If these were not available, in most cases Hopkins and Williams' "pure" grade of reagent was used. In each case the one used is specified.

The manganese reactant used was either the basic carbonate or the sesquioxide.

The basic carbonate was prepared by precipitation from a solution of manganous sulphate (Analar) at the boiling point with a 10% excess of sodium carbonate (Analar) solution. The flesh pink product was filtered off and washed with distilled water until free from alkali (neutral to litmus) and sulphate ion (no precipitate with barium chloride solution). Very thorough washing was found to be necessary to remove all traces of alkali; one of the results of incomplete washing will be met with in the section on zinc manganite. The basic carbonate was dried in an electric oven at 170°C . for 36 hours and the dried material analysed for its manganese content by the bismuthate method (q.v.).

Analysis.

Wt. of sample taken.	Vol. 0.1004N. Fe^{II} used.	Manganese.
0.0998 g.	41.76 ml.	46.14
0.1016 g.	42.35 ml.	46.02

The sesquioxide, Mn_2O_3 , was obtained by igniting the nitrate. As pure manganese nitrate could not be readily obtained, it was prepared by the interaction of equivalent amounts of manganese sulphate (Analar) and barium nitrate (Analar) in solution. The precipitated barium sulphate was removed by filtration, and the filtrate evaporated and crystallised. The crystals were removed and ignited, first at a low temperature, then at $800^\circ C.$ for 3 hours, thus forming the sesquioxide (I. S. Morozov and V. G. Kuznetsov, Izvest. Akad. Nauk. S.S.S.R., Otdel, Khim. Nauk., 1949, 343-353). The product was analysed by the bisauthate method.

Analysis.

Wt. of sample taken.	Vol. 0.1095N. Fe^{II} used.	% Manganese.
0.1059 g.	60.08 ml.	68.3%
0.1112 g.	63.33 ml.	68.5%

(Calc. for Mn_2O_3 98.4%)

Whenever basic manganese carbonate and manganese sesquioxide or manganic oxide are referred to later in this Thesis, these particular preparations have been used. The preparations of other reactants for use in the synthesis of specific manganites are described under the manganite concerned.

(b) Preparation of Mixtures.

The reactants were weighed to the nearest milligram and mixed thoroughly in an agate mortar. When both reactants had been reduced to fine powders - if not already in that state - mixing was continued for 10 minutes, or, when the reactants were of different colour or shades of colour, until the product was uniform when observed under a lens of magnification x6.

In most cases a preliminary ignition was followed by crushing the ignited mass and remixing for another 10 minutes. Whenever performed, such remixing is mentioned.

(c) Ignitions.

These were conducted in electric resistance furnaces. Two types were used.

(i) When the maximum temperature required was $1,150^{\circ}\text{C}.$, or $1,200^{\circ}\text{C}.$ for short periods, a Catterson-Smith furnace, with a pair of sillimanite tubes and a special iron alloy winding, was used. This furnace was run directly off the 230 volt a.c. mains, with a variable resistance in series to effect temperature control.

(ii) For higher temperatures, up to $1,500^{\circ}\text{C}.$, a Johnson, Matthey platinum-rhodium wound alumina-tube furnace was used. This furnace was run off a transformer,

or sometimes through a transformer controlled by a Sunvic energy regulator connected to the 230 volt a.c. supply.

With both furnaces, temperatures were measured with a platinum/platinum-rhodium thermocouple. Temperatures stated are correct to $\pm 20^{\circ}\text{C}$.

Apart from preliminary work on zinc manganite and a few other isolated instances in which water was used, samples were quenched by quick withdrawal from the furnace into the atmosphere. With the small amounts used in the ignitions, cooling in this manner was quite rapid, a period of a few seconds being sufficient for a temperature drop from $1,000^{\circ}\text{C}$. to below 500°C .

(d) The use of Compression.

Poor crystallinity in many of the mixed oxides prepared, even after prolonged heating and slow cooling, led to an attempt to increase the degree of crystallinity by compressing the mixed reactants prior to the final ignition, after a preliminary ignition to bring about extensive reaction. On compression, the particles of product and any unreacted constituents are brought close together and the areas of contact of each particle with its neighbours are increased, so facilitating the growth,

during the diffusion taking place at high temperatures, of larger crystals than would form in the uncompressed powder. To effect this compression, a Millen 5 ton Mounting Press was used, with a ram of 15 mm. diameter.

Where both uncompressed and compressed specimens had been prepared, in all cases the better definition of the powder diffraction photograph of the compressed specimen showed that this larger crystal formation had taken place. The degree of improvement varied for each manganite, but some improvement was found in all cases.

2. Analyses.

(a) Determination of Manganese in Manganites by the Bismuthate Method.

This determination followed the lines of the bismuthate method for determining manganese in steels (see, e.g., Kolthoff and Sandell, "Quantitative Inorganic Analysis", Macmillan, pp. 709, 710), with several modifications.

About 0.1 g. of the sample was dissolved in 20 ml. of hot, concentrated nitric acid, to which had been added about 0.5 g. of oxalic acid. The solution was boiled until no more brown fumes were evolved, and diluted with 50 ml. of water, and about 0.5 g. of sodium bismuthate was added. The mixture was boiled for a few minutes,

decolorised with sulphurous acid, and again boiled for not less than 5 minutes to expel excess sulphur dioxide and oxides of nitrogen. The cooled solution was treated with about 2 g. of sodium bismuthate, stirred gently for 5-10 minutes, diluted with 50 ml. of 1:30 nitrous-acid-free nitric acid, and filtered through a No.3 sintered-glass filter to remove excess bismuthate. 50 ml. of decinormal ferrous ammonium sulphate solution were added to the filtrate and the excess ferrous iron titrated immediately with standard decinormal potassium permanganate solution. The ratio of the ferrous ammonium sulphate solution to the permanganate solution was obtained, and the manganese content of the sample was calculated from the volume of the ferrous iron solution used by the permanganic acid.

(b) Determination of Tervalent and Higher-valent States of Manganese in the Manganites by the Bunsen Method.

About 0.4 g. of the sample was heated slowly with 20 ml. of concentrated hydrochloric acid, through which a brisk stream of carbon dioxide was conducted. The chlorine evolved from the oxidation of the hydrochloric acid was carried by the carbon dioxide into excess of moderately concentrated potassium iodide solution contained

in two Peligot tubes, which were cooled by immersion in water. After about half an hour, the hydrochloric acid was boiled for 5 minutes to expel any remaining chlorine present. The iodine liberated by the chlorine from the potassium iodide was titrated with standard decinormal sodium thiosulphate solution, and the higher-valent manganese calculated as Mn^{III} .

3. X-Ray Powder Diffraction Technique.

The theory of the powder diffraction method, first used by Debye and Scherrer (Physik. Zeit., 1916, 17, 277) and independently by Hull (Phys. Rev., 1917, (11), 10, 661), warrants no description here; adequate introductory treatments are to be found in "Chemical Crystallography" by C. W. Bunn (Oxford, 1946) and in "An Introduction to X-ray Metallography" by A. Taylor (Chapman and Hall, 1949).

(a) Equipment and Photography.

The X-ray generating equipment used was the Metropolitan-Vickers "Raymax" unit. The X-ray tube was of the demountable, continuously evacuated type. Two aluminium foil windows, on either side of the tube, allowed two X-ray beams, emitted from the target at a glancing angle,

to be received in a pair of cameras, mounted one on either side of the tube, so that two specimens could be photographed concurrently.

Both 9 and 19 cm. cameras were used; the 9 cm. for evidence of interaction from the absence of constituent oxide lines in the photograph, and the 19 cm. for interpretation of the diffraction pattern and determination of lattice constants. The 19 cm. camera, made by the Unicam Instrument Company, was of the type described by A. J. Bradley, H. Lipsch, and R. J. Patch (J. sci. Instrum., 1941, 18, 145); the 9 cm., by the same firm, incorporated the Van Arkel film arrangement (H. Lipsch and A. J. C. Wilson, J. sci. Instrum., 1941, 18, 144.).

The camera constant for each camera, namely one quarter the angle subtended at the axis of the camera by the major arc between the two high-angle knife edges, had been determined previously by workers in this laboratory, using pure quartz as a reference substance (Lipsch and Wilson, loc. cit.).

Powder diffraction photographs were measured to the nearest 0.05 mm. on a millimetre rule, carrying a cursor with a Vernier scale, made by Hilger and Watts, Ltd.

X-Radiation from an iron target was used, as the more

usual copper radiation would have been absorbed by the manganese ions, the absorbed energy exciting secondary X-rays from the ions, which would have caused considerable intensification of the background on the film, normally present to a small extent from incoherent scattering. The use of iron radiation had another advantage, as the wavelength of the Fe K_{β} radiation is a little shorter than that of the absorption edge of manganese. The β radiation was thus largely absorbed by the manganese ions in the specimen being photographed, so lines on the photograph due to diffracted β radiation were usually absent, and only occasionally a very faint β counterpart of the strongest α line appeared in a well-exposed film.

Specimens to be examined by X-rays were finely powdered in a small agate mortar. The powdered specimen was generally mounted in a thin Lindemann glass capillary tube; where moisture had no effect on the specimen, it was sometimes prepared for mounting by making a paste of the powder with gum tragacanth and water and rolling this paste into a thin cylinder, about 0.3 mm. in diameter, which was allowed to dry.

Exposure times, using unfiltered Fe K radiation, with the equipment running at 42 kilovolts and 10 milliamp., were generally half an hour for the 9 cm. camera and two

hours for the 19 cm., when "Industrex D" X-ray film, made by Kodak, Ltd., was used. Occasionally it was necessary to use Kodak "Crystallex" film, which required at least double, and preferably triple, the exposure time of the former type.

(b) Examination of the Powder Diffraction Photograph.

The comparative intensities of the lines were estimated visually on a decimal scale (1 to 10). For very weak lines an arbitrary figure (0.5) below this scale was used.

Usually the line positions were measured with the measuring device just described. Occasionally visual comparison of a series of diffraction patterns was necessary; such comparisons were made by inspecting the films on a ground-glass screen illuminated uniformly by transmitted light.

The measured line positions were converted to θ values, the parameter occurring in the Bragg relation,

$$\lambda = \frac{2d \cdot \sin \theta}{n}$$

by Bradley and Jay's method (Proc. Roy. Soc., 1932, 44, 563), which eliminates errors due to film shrinkage, providing the shrinkage be uniform. Values for $\sin^2 \theta$ were obtained from tables, and values for d/n first

calculated from the Bragg relation, but later obtained from the tables of S. Beatty (Research Report R-94602-10-E, Westinghouse Research Labs., E. Penna., U.S.A.). It may be noted here that conventionally the ratio d/n is always known as "d"; when "n" is 2, 3 etc., "d" then represents distances of $1/2$, $1/3$ etc. the distance between the planes of atoms. These values thus belong to imaginary planes responsible for the second-, third-, etc., order reflexions from the atomic planes.

When $\alpha_1 \alpha_2$ doublets were resolved, ^{both} lines of the doublet were measured, the α_1 distance doubled and added to the α_2 distance and one third of this sum taken as the weighted mean position to conform with the unresolved lines.

The presence of lines due to Fe K_β radiation was checked by multiplying the $\sin^2 \theta$ values of the strongest lines present by $\frac{\lambda^2_{FeK_\beta}}{\lambda^2_{FeK_\alpha}}$, and seeing if the resulting $\sin^2 \theta$ values for the β counterparts of these strongest lines corresponded with those of any of the weaker lines present.

In the tables of diffraction data for mixed oxides in this Thesis, the $\sin^2 \theta$ values are followed by the indices (hkl) of the plane whose reflexion has produced the line,

and these indices are then followed by calculated $\sin^2\theta$ values. These values were calculated from the $\sin^2\theta$ increment, or two increments for dimetric structures, corresponding with the stated lattice constant or constants of the mixed oxide. These increments are simply the values of $\sin^2\theta$ for the 100 and 001 reflexions (see section on interpretation of diffraction photographs).

All "d" values and lattice constants given herein are in Siegbahn Angstroms, or $k\lambda$ units. For conversion to absolute Angstroms, these values must be multiplied by the factor 1.00203.

4. The Interpretation of the Powder Diffraction Photograph.

(a) Indexing the Diffraction Pattern.

When the substance photographed has cubic, tetragonal, or hexagonal symmetry, this may be deduced from the powder diffraction pattern without much difficulty, and the dimensions of the unit cell then determined. If the symmetry is orthorhombic, however, interpretation of the diffraction pattern is much more difficult. At best it is a long and tedious process of trial-and-error and more often than not, if no approximate values for the cell constants are known beforehand, the task proves hopeless. The patterns of monoclinic and triclinic crystals are

generally virtually impossible to elucidate and recourse must be had to single-crystal photographs. Isolated instances are known, though, where such structures have been deduced from the powder diffraction pattern, but in such cases goniometric measurements were also available.

Graphical methods exist for indexing cubic, tetragonal, and hexagonal powder photographs. This process of indexing comprises a provisional assignment of symmetry to the diffraction pattern, followed by the determination of the indices of the crystal planes responsible for the lines present. If all the lines can thus be indexed, the provisionally assigned symmetry is confirmed conclusively. Charts for indexing such photographs have been devised by Hull and Davey (Phys. Rev., 1921, (11), 17, 549) and by T. Bjurstrom (Z. Physik., 1931, 69, 346).

In early attempts to index diffraction patterns, a modified Bjurstrom chart, described by G. W. Bunn ("Chemical Crystallography", Oxford, 1946, pp. 379-381), suitable for indexing tetragonal crystal patterns was constructed. Unfortunately, most of the lines of lower indices were absent from the tetragonal patterns investigated, and without these lines use of the chart is difficult, and ambiguous results were obtained.

Subsequently a systematic trial-and-error method, based on Hesse's method (Acta Cryst. 1948, 1, 200), was employed. This method makes use of the fact that certain multiples of the $\sin^2 \theta$ values for the 100 and 001 lines in dimetric diffraction patterns will, when added together, give the $\sin^2 \theta$ values for all the rest of the lines present in the pattern. For cubic symmetry, this reduces to certain multiples of one $\sin^2 \theta$ value, that of the 100 line.

In any orthogonal crystal,

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} = \frac{4\sin^2 \theta}{\lambda^2}$$

where d is the interplanar distance, h , k and l are integers, the indices of the plane, and a , b and c are the three crystal parameters. This reduces, for cubic crystals, to

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{4\sin^2 \theta}{\lambda^2}$$

for tetragonal crystals, to

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} = \frac{4\sin^2 \theta}{\lambda^2}$$

and for hexagonal crystals, to

$$\frac{1}{d^2} = \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} = \frac{4\sin^2 \theta}{\lambda^2}$$

For cubic crystals the indexing is very simple. As $\sin^2 \theta = K(h^2 + k^2 + l^2)$, all that is necessary is to find the highest common factor of all the $\sin^2 \theta$ values; this is the value for the 100 line, and all the other lines can be indexed by multiplying this value by all values of $(h^2 + k^2 + l^2)$.

Indexing dimetric crystals is less straightforward. The $hk0$ lines are first sought out; these will be multiples of the 100 $\sin^2 \theta$ value in the series $(h^2 + k^2)$ for tetragonal, and $(h^2 + hk + k^2)$ for hexagonal crystals. Frequently more than one possible series is obtained; all but the true series are then eliminated in the second step. Successive $hk0$ $\sin^2 \theta$ values are next subtracted from the $\sin^2 \theta$ values of the first few lines in the pattern, and the remainders examined for a $\sin^2 \theta$ value which will account for them all when multiplied by the values of l^2 . Having thus obtained the $\sin^2 \theta$ values for the 100 and 001 lines, all possible combinations are tried and coincidences with observed values to within ± 0.0005 for well-resolved, and ± 0.0010 for diffuse patterns are taken as the indices of the line in question. The $\sin^2 \theta$ values for 100 and 001 are then adjusted to get the best agreement between observed and calculated values: this

operation is dealt with more fully in the next section. The possibility of fortuitous agreement between observed and calculated $\sin^2 \theta$ values, leading to uncertainty as to the correct indices for the line under consideration is, of course, always present. Sometimes such coincidences can be eliminated when the coinciding indices are those of a plane whose reflexion should be absent on the grounds of symmetry, but in other cases such ambiguity must remain until a pattern of higher resolution can be examined, or a single-crystal photograph obtained.

(b) Evaluation of Lattice Constants.

The values of a for cubic, and a and c for tetragonal crystals were calculated from the $\sin^2 \theta$ increments, i.e. the $\sin^2 \theta$ values for 100 and 001, using the relations

$$a = \frac{\lambda}{2} \sqrt{\frac{1}{\sin^2 \theta_{(100)}}} \quad \text{and} \quad c = \frac{\lambda}{2} \sqrt{\frac{1}{\sin^2 \theta_{(001)}}}$$

which follow from the equations given in the last section.

Owing to the error introduced by absorption and eccentricity of the specimen (Bradley and Jay, Proc. Phys. Soc., 1932, 44, 563) which is a function of the angle θ , the mean value of each increment is not the most accurate. This error, which is almost a linear function of $\sin^2 \theta$ in cubic crystals, diminishes with increase in

in θ and becomes zero in the limit $\sin^2 \theta = 1$ (i.e. when $\theta = 90^\circ$). Thus the greater the angle of the line measured, the more accurate is the $\sin^2 \theta$ increment obtained from the line. Furthermore, the high angle lines are more sensitive to changes in the lattice constants, as small variations in $\sin \theta$ represent large variations in θ when θ approaches 90° .

For cubic crystals, the best figure for the lattice constant can be readily obtained by plotting the $\sin^2 \theta$ values of the high angle lines against the values of a calculated for each line. Extrapolation to $\sin^2 \theta = 1$ then gives the value for a with absorption and eccentricity errors eliminated. The lattice constants for tetragonal and hexagonal crystals cannot easily be obtained by extrapolation. The method used to reduce these errors to a minimum was to adjust the two $\sin^2 \theta$ increments so that the difference between calculated and observed $\sin^2 \theta$ values decreased with increase in θ , becoming very small or zero at the highest line. The lattice constants were then calculated from these adjusted increments.

The limits of accuracy of the lattice constants recorded in the powder diffraction data tables in this Thesis vary from ± 0.001 to ± 0.003 Å. These limits were

found by observing that changing the lattice constants by these amounts resulted in less agreement between calculated and observed $\sin^2 \theta$ values than was obtained with the value stated. Lattice constants of diffuse films with few or no high angle lines are given only to two decimal places, as the third place is of no significance for such films.

Section 2. ZINC MARGARITE.

Literature.

Naturally occurring zinc manganite, the mineral heterolite, is described by J. D. Dana in his "System of Mineralogy" (Vol. I, 7th. Ed., 1944). Several references of historical interest are given and crystal data are quoted from a paper by C. Frondel and E. W. Heinrich (Amer. Mineral., 1942, 27, 48-56). From single-crystal Weissenberg photographs these workers found the crystal to have a body-centred tetragonal structure, of the hausmannite (Mn_3O_4) type, with space group 14/amd. Measurements of powder diffraction photographs of the mineral gave lattice constants $a = 5.74 \text{ \AA}$, $c = 9.15 \text{ \AA}$, with a c/a ratio of 1.594, as compared with 1.5952 from morphological measurements. A table of indices and d values for the powder diffraction photograph was given.

In 1946, L. S. Copeland and P. S. Griffith (J. Electrochem. Soc. 1946, Preprint No. 89 - 22) following the work of H. F. McMurdie (Ibid., 1944, Preprint No. 86 - 15) and of H. F. McMurdie, D. S. Craig & G. W. Vinal (Ibid, 1946, Preprint No. 90 - 31) on the reaction in the Leclanché dry cell, concluded that heterolite was formed during discharge. By precipitating mixed zinc and manganese solutions with aqueous ammonia in the presence of hydrogen peroxide or potassium permanganate as an oxidising agent,

Copeland and Griffith obtained zinc manganite the diffraction photograph of which agreed closely with that of the hetaerolite from the discharged cells. Heating the precipitated product in nitrogen at 500°C . served only to sharpen the lines of the diffraction pattern and to produce slight shifts in their positions. The average manganese valency was found to be always within 5% of the tervalent state, as required by the formula $\text{ZnO.Mn}_2\text{O}_3$.

The most recent paper on zinc manganite is one by B. Mason (Amer. Mineral., 1947, 32, 426-41). He used the powder diffraction method to investigate the phase relationships of the system $\text{Fe}_3\text{O}_4 - \text{Mn}_3\text{O}_4 - \text{ZnMn}_2\text{O}_4 - \text{ZnFe}_2\text{O}_4$. The zinc manganite was obtained by igniting together the carbonates of manganese and zinc. He described the unit cell of zinc manganite as face-centred tetragonal, of volume about twice that given by Prondel and Heinrich, whose work is not referred to by him. The lattice constants were $a = 8.076 \text{ \AA}$, $c = 9.225 \text{ \AA}$. On dividing the a dimension by $\sqrt{2}$, the a and c dimensions become approximately the same as those given for hetaerolite. Impurities in the mineral could account for the small difference in the two pairs of constants. Presumably Mason used the larger unit cell to bring out the structural

relation to the spinel unit of Fe_3O_4 in his system.

Complete mutual miscibility of zinc manganite and manganous manganite was found.

Manganese in the bivalent state was shown by R. Rigamonti (Gazz. Chim. Ital., 1946, 76, 474-84) to form a mixed oxide with zinc, ZnO, MnO , with a hexagonal cell, $a = 3.281 \text{ \AA}$, $c = 5.256 \text{ \AA}$.

Abegg, in his "Handbuch der anorganischen Chemie" (Vol. IV, p. 838), mentioned a compound of zinc oxide with manganese dioxide, prepared by Risler, of formula $\text{ZnO}, 5\text{MnO}_2$, but no structural work has been done on mixed oxides with manganese in the quadrivalent state.

Experimental Work and Results.

As the structure of zinc manganite had already been satisfactorily established, examination of this manganite was the first undertaken, so that experience could be gained in the technique of X-ray powder diffraction photography, and the accuracy of the 19 cm. camera used to check the recorded diffraction data and to determine more precise lattice constants. Furthermore, it had been suggested that the effect of varying the heat treatment of the specimens of zinc manganite might repay study; also a

pure sample, of measured lattice constants, was needed for conductivity measurements, as this mixed oxide has been reported in a private communication to exhibit anomalous semi-conductivity in possessing a negative temperature coefficient.

Dana (loc. cit.) described the artificial preparation of hetaerolite, due to Gorgeu (Bull. Soc. chim., 1873, 2nd series, 10, 653), by the fusion of the mixed sulphates of zinc, manganese, and sodium.

This method was tried by fusing in a porcelain crucible the three mixed sulphates in the atom ratio, respectively, of 3:3:1. A small brown residue remained after extraction with dilute acetic acid, which was found to consist of manganese dioxide and zinc oxide only, when the d values from the powder diffraction photograph were compared with those given by Hanawalt, Rinn and Prevel (Ind. Eng. Chem., Anal. Ed., 1938, 10, 476.).

The method adopted for the preparation of zinc manganite was that described by B. Mason (loc.cit.).

Manganous sulphate (Analar) was dried at 100°C. for 12 hours to form the monohydrate, which is stable at this temperature. This monohydrate was dissolved in water, together with zinc sulphate heptahydrate (Hopkin. &

Williams' "Pure"), in the amounts required to give a zinc to manganese atom ratio of 1 to 2. The solution was heated and the metals precipitated together as their basic carbonates by the addition of a 10% excess of an aqueous solution of sodium carbonate to the boiling solution. The precipitate was filtered off, washed free from carbonate and sulphate, and dried at 170°C . for 36 hours.

The dried basic carbonates were then ignited in air in an alumina boat at $1,000^{\circ}\text{C}$. for 48 hours to convert them to the oxides and bring about the formation of zinc manganite. The product was cooled slowly during a period of 3 hours.

The zinc manganite so formed was reignited in fireclay. A portion was heated at 700°C ., and other portions at higher temperatures, at 100° intervals, to $1,300^{\circ}\text{C}$. Each portion was held at its particular temperature for 2 hours and then quenched in cold water. Six quenched specimens were thus obtained. The fireclay boats containing the $1,200^{\circ}\text{C}$. and the $1,300^{\circ}\text{C}$. specimens were found on examination to have been extensively attacked by the oxides, so these quenches were repeated from alumina boats, together with the $1,100^{\circ}\text{C}$. sample, because of the possibility of slight unnoticed attack at this temperature.

This range of quenched specimens was analysed for manganese and tervalent manganese, Mn^{III} , by the methods described in the section of general technique. Zinc and manganese were determined together as pyrophosphate and the amount of zinc present found by difference.

Determination of Zinc in Zinc Manganite.

About 0.2 g. of the sample was dissolved in 20 ml. of concentrated hydrochloric acid, and the solution boiled to remove free chlorine. When the solution had become colourless, it was cooled and almost neutralised with ammonia solution. 20 ml. of 2N. ammonium acetate solution were added and then, slowly, 20 ml. of freshly prepared 10% diammonium hydrogen phosphate solution. The mixture was diluted to 300 ml. with cold water, and made neutral to phenol red with ammonia solution. Precipitation of the metal ammonium phosphates was completed by heating on a steam bath for 2 hours and allowing to stand overnight. The zinc and manganese ammonium phosphates were collected on a weighed Gooch crucible and ignited, slowly at first, and finally over a Teclu burner, until constant in weight. The total pyrophosphate weight, less that due to the manganese pyrophosphate, of manganese content already determined, gave the figure for the zinc content.

Analyses.Manganese.

Sample:	Wt. taken.	Vol. Fe^{II} used.	Normality	Manganese.
Slow cooled	0.1011 g.	38.80 ml.	0.1023	43.1%
quenched 700° C.	0.0996 "	35.08 "	0.1095	42.4%
from 800°	0.1016 "	36.10 "	"	42.8%
900°	0.1022 "	36.81 "	"	43.3%
1,000°	0.1022 "	39.83 "	0.1023	43.8%
1,100°	0.1037 "	38.35 "	0.1095	44.5%
1,200°	0.1019 "	37.36 "	"	44.1%
1,300°	0.1020 "	39.53 "	"	46.6%

Manganese as Mn^{III} .

Sample:	Wt. taken	Vol. Thio. used.	Normality.	Manganese as Mn^{III} .
Slow cooled	0.4036 g.	39.52 ml.	0.1030	55.4%
quenched 700° C.	0.3964 "	39.82 "	0.0979	54.0%
from 800°	0.3981 "	37.66 "	0.1030	53.5%
900°	0.4007 "	37.42 "	"	52.8%
1,000°	0.4016 "	36.94 "	"	52.1%
1,100°	0.3970 "	36.16 "	0.1031	51.6%
1,200°	0.4021 "	35.44 "	"	49.9%
1,300°	0.3945 "	31.70 "	"	45.5%

Zinc.

Sample:	Wt. taken	Wt. of Zinc Pyrophosphate.	Zinc.
slow cooled	0.1984 g.	0.1193 g.	25.8%
quenched 700° C.	0.1997 "	0.1168 "	25.1%
from 800°	0.2029 "	0.1206 "	25.5%
900°	0.2026 "	0.1216 "	25.8%
1,000°	0.2007 "	0.1223 "	26.2%
1,100°	0.1972 "	0.1166 "	25.4%
1,300°	0.1983 "	0.1187 "	25.7%

Powder diffraction photographs were taken of these seven specimens, the 19 cm. camera being used for the 1,000° C. specimen and the 9 cm. camera for the rest. "Crystallex" film was used, with an exposure of 3 hours for the 19 cm. camera, and 40 mins. for the 9 cm.

The manganese and zinc contents of these specimens show a slight increase with increase in temperature of quenching, but insufficient to indicate a significant change in the state of oxidation of the manganese. The sudden increase in the manganese content from the 1,200° C. to the 1,300° C. quenched sample was found to be due to the loss, by volatilisation, of some of the zinc oxide at this temperature, as an appreciable deposit of zinc oxide was observed in the ends of the furnace tube after the ignition.

The decrease in the figure for tervalent manganese with

increase in temperature, however, is pronounced and was at first thought to be evidence of structural change in pure zinc manganite, especially as there were changes in the diffraction photographs over the range. It was found subsequently, though, that there was present in these samples of zinc manganite a small amount of alkali. This alkali must have been adsorbed during the preparation of the mixed carbonates, and the precipitate insufficiently washed. 2% of soluble alkali, calculated as sodium carbonate, was found to be present. This contamination was discovered when a fresh set of zinc manganite samples containing an excess of zinc and quenched from a range of temperatures, did not show any change in the Mn^{III} content over the series.

The diffraction patterns of the 700°, 800° and 900° C. quenched specimens were identical; above this, the number of lines decreased, some of the pairs of lines in the lower temperature series coalescing into single lines.

This interesting structural change with temperature was thus ascribed to the presence of the alkali contamination, so an investigation of this effect, to be described later in this section, has been carried out.

Most of the lines on the 19 cm. powder diffraction

photograph of the $1,000^{\circ}\text{C}$. quenched sample were indexed using the body-centred tetragonal cell described by Frendel and Heinrich (loc. cit.), but these results are not recorded here as they do not represent those for pure zinc manganite and are superseded by results following addition of controlled amounts of alkali to zinc manganite (q.v.).

The progressive change in the figure for the Mn^{III} content in samples quenched from a range of temperatures was shown to be absent in pure zinc manganite. Zinc oxide (Analar) and pure manganese sesquioxide, the preparation of which has been described in the section on general methods, were mixed in the atom ratio, zinc to manganese, of 1:2, to give stoichiometric zinc manganite. The product was fired in air at $1,000^{\circ}\text{C}$. for 48 hours, and then one portion heated at 800°C . for 2 hours and air quenched and the other at $1,200^{\circ}\text{C}$. for the same period, followed by quenching.

The two samples were analysed as before.

Analyses.

	Manganese.			
Sample:	Wt. taken.	Vol. Fe^{II} used.	Normality.	Manganese.
quenched 800°C .	0.1005 g.	37.74 ml.	0.1095	45.2%
from $1,200^{\circ}$	0.1022 "	38.97 "	"	45.9%

Manganese as Mn^{III}

Sample:	Wt. taken	Vol. Thio. used	Manganese Normality as Mn ^{III}	
quenched 800°C.	0.4150 g.	33.52 ml.	0.1031	45.8%
from 1,200°C	0.4010 "	32.22 "	"	45.5%

Zinc.

Sample:	Wt. taken	Wt. of Zinc Pyrophosphata	Zinc
quenched 800°C	0.1958 g.	0.1280 g.	28.1%
from 1,200°C	0.2014 "	0.1273	27.1%

It is seen that the manganese and Mn^{III} results are similar, as required by the formula $\text{ZnMn}_2^{\text{III}}\text{O}_4$, and that there is no change in the Mn^{III} value when the quenching temperature is raised.

These figures give a mean atom ratio, Zn : Mn : O, of 1:2.01:4.06, which agrees well with the formula $\text{ZnMn}_2^{\text{III}}\text{O}_4$.

The 19 cm. diffraction photographs of these two samples were identical. All the lines were indexed on the hausmannite tetragonal cell, with $a = 5.70$ and $c = 9.22$ kX units.

The powder diffraction photographs of these samples of zinc manganite prepared from the constituent oxides were diffuse, with no resolution of $\alpha_1 \alpha_2$ doublets at the high angle end of the film, so neither of these photographs could be used for the evaluation of accurate

lattice constants. Furthermore, although good-quality patterns were obtained from the quenched series prepared from the basic carbonates, contamination with alkali precluded their use for this purpose. Hence it was necessary to prepare a fresh specimen from the basic carbonates for the determination of precise constants.

The constituent basic carbonates were prepared separately this time, carefully washed until free from all traces of alkali, dried at $170^{\circ}\text{C}.$, and analysed for the metal present. The dried basic carbonates were then mixed in the theoretical proportion and ignited in air at $900^{\circ}\text{C}.$ for 48 hours. The zinc manganite so prepared was photographed.

The diffraction pattern obtained was of excellent quality, showing clear resolution of the last 8 high angle lines into $\alpha_1\alpha_2$ doublets.

ZINC MANGANITE, ZnMn_2O_4 .							
<u>Powder Diffraction Data.</u>						<u>Fron del and Heinrich.</u>	
Inten- sity.	θ	$\sin^2\theta$ observed	hkl.	$\sin^2\theta$ calc.	d.	Inten- sity	d.
0.5	11.43	0.0393	101'	0.0397	4.903	1	4.871
4	18.550	0.1012	112'	0.1013	3.055	7	3.045
2	19.782	0.1145	200'	0.1147	2.856	4	2.855
8	20.914	0.1274	103'	0.1275	2.708	9	2.698
10	23.128	0.1543	211'	0.1543	2.461	10	2.460
0.5	23.475	0.1587	202	0.1586	2.427	-	-
1	24.782	0.1757	004'	0.1757	2.306	3	2.300

Inten- sity.	θ	$\sin^2 \theta$ observed	hkl.	$\sin^2 \theta$ calc.	d.	Inten- sity	d.
2	28.618	0.2294	220'	0.2293	2.018	3	2.017
2	32.606	0.2904	204'	0.2904	1.794	3	1.792
4	33.407	0.3032	105'	0.3032	1.756	5	1.752
3	35.099	0.3306	312'	0.3306	1.681	4	1.683
2	36.670	0.3566	303'	0.3568	1.619	3	1.616
6	38.271	0.3835	321'	0.3836	1.560	5	1.560
9	39.509	0.4048	224'	0.4050	1.5195	8	1.518
1	42.275	0.4525	116	0.4527	1.437	-	-
4	42.622	0.4588	400'	0.4586	1.428	4	1.430
0.5	45.529	0.5092	206'	0.5100	1.355	1	1.350
2	46.851	0.5323	305'	0.5325	1.325	3	1.323
1	48.436	0.5598	332	0.5599	1.292	-	-
			(107'	0.5668		2	1.277)
1	49.218	0.5733	420	0.5733	1.277	-	-
5	49.957	0.5861	413'	0.5860	1.263	3	1.263
0.5	51.792	0.6176	422	0.6172	1.230	-	-
0.5	52.796	0.6344	404'	0.6343	1.214	1	1.212
7	55.634	0.6814	127'	0.6814	1.171	5	1.169
1	56.947	0.7026	008'	0.7028	1.153	4	1.151
$\alpha_1 \alpha_2$ 4	59.906	0.7486	424	0.7490	1.117	-	-
" 6	60.784	0.7618	415'	0.7618	1.108	4	1.107
" 3	62.690	0.7896	512	0.7892	1.088	-	-
			(335'	0.7905		3	1.089)
" 8	64.567	0.8156	503	0.8154	1.070	-	-
" 4	66.593	0.8422	521'	0.8422	1.053	2	1.053
" 7	72.616	0.9108	336	0.9113	1.013	-	-
			327	0.9107		-	-
" 8	73.282	0.9173	440	0.9172	1.009	-	-
" 10	84.650	0.9909	505	0.9911	0.9709	-	-

Lattice Constants.

Tetragonal cell, $a = 5.710 \pm 0.001$, $c = 9.225 \pm 0.001$
kX units.

Published Lattice Constants.

B. Mason:- $a = 8.076 (= \sqrt{2} \times 5.711)$, $c = 9.225$ A.
Frondel and Heinrich:- $a = 5.74$, $c = 9.15$
(for betaerolite) kX units.

Lines indexed by Frondel and Heinrich are marked by a short dash, thus:- hkl'.

Lines in brackets have been indexed incorrectly by these workers.

Altogether, 33 lines have been indexed, nine more than those given by Frondel and Heinrich. The agreement between calculated and observed $\sin^2 \theta$ values is good and limits the error in the evaluation of the lattice constants to ± 0.001 KX unit.

Lines indexed by Frondel and Heinrich are marked as indicated, and their values for intensity and d are recorded alongside for comparison.

The indices of two of their lines, 107 and 335, enclosed in brackets in the table, are incorrect. It can be seen that the calculated $\sin^2 \theta$ value for 107 greatly diverges from the observed value, whilst that for the substituted indices, 420, agrees closely. The observed and calculated $\sin^2 \theta$ values, ascribed to the 335 reflexion, are fairly close to each other, but a reflexion from this set of planes is impossible on symmetry grounds as the structure is body-centred, and the sum $h + k + l$ for body-centred unit cells must always be even. This is so as planes carrying indices with odd sums are interleaved a half

wavelength away by the planes of body-centred ions; hence the diffracted X-ray beams from these interleaving planes are exactly 180° out of phase with those from the first set of planes, and so cancel each other out.

Apart from this inadmissibility of a 335 reflexion on theoretical grounds, observational evidence excluded these indices and supported 512, the ones used instead, in patterns from manganese-excess specimens, described later in this section. In these patterns the calculated $\sin^2\theta$ value for 335 diverged progressively from the observed figure with increase in manganese excess, whilst the two values for 512 were consistently similar.

Zinc Manganite with Excess Zinc Oxide and Manganous Manganic Oxide.

In order to determine the extent of solubility, if present, of zinc oxide, and to confirm the solubility of manganous manganic oxide in zinc manganite, a series of mixtures containing excess zinc and excess manganese were prepared. These were quenched from intervals in a temperature range to see if any structural changes or partial miscibility occurred in the range used.



These mixtures were prepared by mixing the calculated

quantities of the basic carbonates, prepared as before, and igniting the product in air at $1,000^{\circ}\text{C}$. for 48 hours, followed by slow cooling for 3 hours. The zinc manganite containing excess zinc so prepared was remixed and then samples were heated for 2 hours at, and quenched from, 700° , 900° , $1,000^{\circ}$ and $1,200^{\circ}\text{C}$. This series contained 26 atom-% excess of zinc.

The four samples were analysed for manganese, tervalent manganese, and zinc with the following results:-

Analyses.

Manganese.

Sample:	Wt. taken	Vol. Fe^{II} used Normality	Manganese.
quenched 700°C .	0.1003 g.	34.93 ml 0.1095	41.9%
from 900°	0.1003 "	34.77 " "	41.7%
$1,000^{\circ}$	0.1001 "	34.60 " "	41.6%
$1,200^{\circ}$	0.0998 "	34.41 " "	41.5%

Manganese as Mn^{III} .

Sample:	Wt. taken	Vol. Thio. used Normality	Manganese as Mn^{III} .
quenched 700°C .	0.3991 g.	30.40 ml. 0.1031	43.1%
from 900°	0.4002 "	30.52 " "	43.2%
$1,000^{\circ}$	0.3993 "	30.46 " "	43.2%
$1,200^{\circ}$	0.4002 "	30.05 " "	42.5%

Zinc.

Sample:	Wt. taken.	Wt. of Zinc Pyrophosphate.	Zinc.
Quenched 700° C.	0.2035 g.	0.1461 g.	30.8%
from 900°	0.2021 "	0.1480 "	31.4%
1,000°	0.1988 "	0.1464 "	31.7%
1,200°	0.2002 "	0.1451 "	31.1%

Mean composition:- Manganese 41.7%
Manganese as Mn^{III} 43.0%
Zinc 31.4%

Atom ratio, Mn : Zn : O
2 : 1.26 : 4.42

No significant variation in the state of oxidation of the manganese is present in this quenching range.

The four powder diffraction photographs of this series showed the presence of two phases, zinc manganite and zinc oxide; the stronger lines only of the latter were observed. No change in the lattice constants of the zinc manganite phase was evident, so it may be concluded that zinc oxide is not measurably soluble in zinc manganite, otherwise the presence of excess zinc ions in the lattice would very probably have brought about a change in the constants. Further confirmation of this fact was obtained by preparing and examining a 50 atom-% zinc excess specimen; only the lines of pure zinc manganite and zinc oxide were recorded on the diffraction photograph of this preparation.

Manganese-rich Zinc Manganite, $\text{ZnMn}_2\text{O}_4 + \text{Mn}_3\text{O}_4$.

Zinc manganite containing 13 atom-% excess of manganese was prepared in the same manner as the zinc-excess preparation. Samples were quenched from 700° , 900° , $1,000^\circ$ and $1,200^\circ\text{C}$.

These samples were analysed.

Analyses.

Sample:	Manganese.		Vol. Fe^{II}	
	Wt. taken.	used	Normality	Manganese
quenched 700°C .	0.1002 g.	39.45 ml.	0.1095	47.4
from 900°	0.1009 "	39.81 "	"	47.5
$1,000^\circ$	0.1020 "	40.17 "	"	47.4
$1,200^\circ$	0.0993 "	39.22 "	"	47.5

Sample:	Manganese as Mn^{III}		Vol. Thio.	
	Wt. taken.	used	Normality as Mn^{III}	Manganese
quenched 700°C .	0.3997 g.	32.88 ml.	0.1031	46.6
from 900°	0.4013 "	32.74 "	"	46.2
$1,000^\circ$	0.4003 "	35.22 "	0.0960	46.4
$1,200^\circ$	0.4000 "	35.42 "	"	46.7

Zinc.

Sample:	Wt. taken.	Wt. of Zinc Pyrophosphate.	Zinc.
quenched 700°C .	0.2018 g.	0.1173 g.	25.0
from 900°	0.2006 "	0.1145 "	24.6
$1,000^\circ$	0.2037 "	0.1172 "	24.7
$1,200^\circ$	0.2011 "	0.1189 "	25.4

Mean composition:- Manganese 47.4%
 Manganese as Mn^{III} 46.5%
 Zinc 25.0%

Atom ratio, Mn : Zn : O
 2.26: 1 :4.50

As with the zinc excess series, no valency change in the manganese is shown.

The four diffraction photographs showed only those lines due to zinc manganite, hence solid solution had taken place.

Lattice Constants.

	a.	c in kX units
Sample quenched from 700°C.	5.71	9.25
900°C	5.72	9.26
1,000°C	5.71	9.24
1,200°C	5.72	9.23
Mean constants	5.71 ₅	9.24 ₅

There is little change in these constants from those for pure zinc manganite, $a = 5.716$, $c = 9.225$ kX units, but this is to be expected as the cell of hausmannite is but little larger, a becoming 5.75 and c 9.42 kX units.

A 22% excess manganese series was then prepared in the same manner as the previous series.

Analyses.

Manganese.				
Sample:	Wt. taken.	Vol. Fe^{II} used.	Normality.	Manganese.
quenched 700° C.	0.0990 g.	39.79 ml.	0.1095	48.4
from 900°	0.1001 "	40.49 "	"	48.7
1,000°	0.0987 "	39.96 "	"	48.7
1,200°	0.0984 "	40.05 "	"	49.0

Manganese as Mn^{III} .				
Sample:	Wt. taken.	Vol. Thio. used.	Normality.	Manganese as Mn^{III} .
quenched 700° C.	0.4000 g.	35.68 ml.	0.0960	47.0
from 900°	0.3999 "	35.74 "	"	47.1
1,000°	0.3992 "	35.48 "	"	46.9
1,200°	0.3992 "	35.70 "	"	47.2

Zinc.			
Sample:	Wt. taken.	Wt. of Zinc Pyrophosphate.	Zinc.
quenched 700°	0.2011 g.	0.1133 g.	24.3
from 900°	0.2013 "	0.1108 "	23.6
1,000°	0.1992 "	0.1090 "	23.5
1,200°	0.2001 "	0.1108 "	23.8

Mean composition:— Manganese 48.6
Manganese as Mn^{III} 47.1
Zinc 23.7

Atom ratio, $\text{Mn} : \text{Zn} : \text{O}$

2.44: 1 : 4.76

Again the manganese valency is constant.

In both the 13 and 22 manganese excess analyses the oxygen content exceeds (by about 3%) that required by $\text{ZnMn}_2\text{O}_4 + \text{Mn}_3\text{O}_4$. As this result is obtained by difference, any small losses in the manganese and zinc determinations would be magnified in this difference; moreover, any impurities - moisture, carbon dioxide, etc. - in the original samples would show as oxygen by this method of estimation. These facts would account for the high results.

As before, no lines other than those due to zinc manganite were present on the four diffraction photographs. The mean cell constants were the same as those of the 13% excess series, so this further addition of manganous manganic oxide to the solid solution had no measurable effects on the constants.

Lattice Constants.

	a	c in KX units.
Sample quenched from 700°C.	5.71	9.25
900°C	5.72	9.26
1,000°C	5.71	9.25
1,200°C	5.72	9.22
Mean constants	5.71 ₅	9.24 ₅

This miscibility of manganous manganic oxide in zinc manganite confirms B. Mason's finding (loc. cit.) that the system $\text{ZnMn}_2\text{O}_4 - \text{Mn}_3\text{O}_4$ was completely miscible.

The Effect of Sodium Ions on the Zinc Manganite Lattice.

(1) Zinc Manganite with added Sodium Carbonate.

The presence of lines other than those of zinc manganite in the diffraction photographs of samples of alkali contaminated zinc manganite quenched from $900^{\circ}\text{C}.$, or from lower temperatures, led to the examination of the effect of the addition of known amounts of sodium carbonate to pure zinc manganite, followed by ignition and quenching of the product.

(a) 2% Added Sodium Carbonate.

2% of sodium carbonate (Anlar) by weight was added to a sample of pure zinc manganite. After thorough mixing, the mixture was ignited at $1,000^{\circ}\text{C}.$ in air for 48 hours. Part of the product was removed and cooled rapidly, while the rest was heated for 24 hours at $900^{\circ}\text{C}.$ and then rapidly cooled.

9 cm. powder diffraction photographs of the two quenched samples contained only lines of zinc manganite, and the two patterns were identical.

As less than 1% of sodium ions were present in the zinc manganite, detectable differences in the two quenches were hardly to be expected, but this concentration was tried as 2% of soluble alkali, calculated as sodium carbonate,

had been found in the impure zinc manganite that showed these extra lines.

(b) 10% Added Sodium Carbonate.

The sodium carbonate was this time added to the zinc manganite as an aqueous solution. The mixture was dried, remixed, and ignited at $1,000^{\circ}\text{C}$. for 48 hours. A further remixing was followed by another ignition at $1,000^{\circ}\text{C}$. for 48 hours. Part of the sample was then rapidly cooled and the remainder rapidly cooled from 900°C ., after 40 hours at this temperature.

The two 9 cm. diffraction photographs showed marked differences, about a dozen extra lines being present in that of the low temperature specimen. 19 cm. photographs were disappointingly diffuse, so the two samples were compressed, reheated, and quenched as before. The new 19 cm. diffraction photographs were of much better quality.

All the lines in both patterns were accounted for. 17 lines in the $1,000^{\circ}\text{C}$. picture conformed with a distorted zinc manganite cell, having a increased from 5.71 to 5.74 and c decreased from 9.23 to 9.06 kX units; the four remaining weak lines were those of sodium oxide. Two lines of sodium oxide were present in the 900°C . pattern; 27 lines belonged to the main phase of ~~zinc~~

zinc manganite, with $a = 5.71$ and $c = 9.22$ kX units, while the other 13, 6 of which were strong lines, could be related to a similar tetragonal cell, with $a = 5.77$ and $c = 8.90$ kX units. Although only 13 lines defined this tetragonal cell, the agreement between observed and calculated $\sin^2 \theta$ values was too close to be explained by coincidence.

These two diffraction photographs were closely similar to the corresponding ones obtained from the alkali-contaminated zinc manganite previously mentioned.

An approximate check of the sodium content of the sample was made by precipitating the manganese and zinc as carbonates with ammonium carbonate and weighing the sodium left as sodium chloride. 4.3% of sodium, equivalent to 9.9% of sodium carbonate, was found to be present.

The tabulated diffraction data for these two patterns are given in the following pages.

ZINC MANGANITE with 10% added Sodium Carbonate,
quenched from 1,000° C.

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed	hkl.	$\sin^2 \theta$ calc.	d.	
3	10.03				5.55	Na ₂ O
2	18.75	0.1033	112	0.1023	3.00	
0.5	19.77	0.1144	200	0.1136	2.856	
0.5	20.32				2.783	Na ₂ O
1	21.32	0.1322	103	0.1309	2.657	
10	23.13	0.1543	211	0.1533	2.460	
1	28.55	0.2284	220	0.2272	2.021	
1	31.36				1.856	Na ₂ O
0.5	32.99	0.2964	204	0.2958	1.775	
0.5	34.02	0.3130	105	0.3131	1.727	
2	35.09	0.3304	312	0.3296	1.681	
2	36.85	0.3596	303	0.3581	1.612	
4	38.15	0.3815	321	0.3806	1.562	
10	39.86	0.4108	224	0.3995	1.507	
1	42.46	0.4558	400	0.4544	1.458	
3	49.95	0.5861	413	0.5853	1.261	
0.5	52.90	0.6360	404	0.6367	1.212	
0.5	60.01	0.7502	424	0.7502	1.116	
3	61.22	0.7682	415	0.7676	1.102	
1	64.33	0.8123	503	0.8125	1.072	
2	72.19				1.015	Na ₂ O

Lattice Constants. Tetragonal cell, $a = 5.74$,
 $c = 9.06$ kl units.

ZINC MANGANITE with 10% added Sodium Carbonate,
quenched from 900° C.

Powder Diffraction Data.

Intens- ity.	θ	$\sin^2 \theta$ observed	ZnMn_2O_4 hkl.	Phase. $\sin^2 \theta$ calc.	Second phase. hkl. $\sin^2 \theta$ calc.	d.
3	9.88					5.63 H_2O
5	18.61	0.1018	112	0.1013		3.03 H_2O
2	18.80	0.1039			112 0.1033	3.00
0.5	19.48	0.1112			200 0.1122	2.896
1	19.82	0.1149	200	0.1147		2.849
6	20.96	0.1280	103	0.1277		2.701
2	21.51	0.1344			103 0.1343	2.635
7	22.97	0.1522			211 0.1521	2.476
10	23.17	0.1547	211	0.1544		2.455
1	23.54	0.1595			202 0.1594	2.419
1	24.97	0.1783	004	0.1760		2.288
1	28.31	0.2249			220 0.2244	2.038
1	28.67	0.2300	220	0.2294		2.014
1	31.22					1.864 H_2O
1	32.68	0.2916	204	0.2907		1.789
3	33.49	0.3044	105	0.3037		1.752
2	34.94	0.3280			312 0.3277	1.688
2	35.11	0.3308	312	0.3307		1.680
3	36.77	0.3583	303	0.3570		1.614
4	37.86	0.3767			321 0.3765	1.574
5	38.31	0.3842	321	0.3837		1.558
8	39.58	0.4060	224	0.4054		1.517
7	40.03	0.4136			224 0.4132	1.502
1	42.02	0.4480			400 0.4488	1.443
3	42.66	0.4593	400	0.4587		1.428
1	46.98	0.5344	305	0.5330		1.321
1	48.50	0.5609	332	0.5601		1.289
4	49.95	0.5859	413	0.5864		1.259
2	52.92	0.6364	404	0.6347		1.211
4	55.74	0.6830	127	0.6824		1.169
2	57.06	0.7044	008	0.7040		1.151
3	59.99	0.7499	424	0.7495		1.116
4	60.83	0.7625	415	0.7624		1.107
1.	61.48	0.7721			415 0.7719	1.100
2	62.66	0.7891	512	0.7894		1.088
1	63.93	0.8069			503 0.8075	1.076

6	64.60	0.8160	503	0.8158		1.069
1	66.59	0.8422	521	0.8424		1.052
1	71.36	0.8979			400 0.8976	1.020
5	72.66	0.9129	327	0.9117		1.012
5	73.13	0.9172	440	0.9174		1.010
5	84.41	0.9915	505	0.9918		0.9706

Lattice Constants.

Zinc manganite, $a = 5.71$,	Second phase, $a = 5.77$,
$c = 9.22$ kX units	$c = 8.90$ kX units

(c) 20% Added Sodium Carbonate.

The effect of doubling the amount of sodium carbonate added was then investigated. The mode of preparation was that used for the previous product. A preliminary ignition at $1,100^{\circ}\text{C}$. for 16 hours was followed by remixing and compressing and reheating at $1,070^{\circ}\text{C}$. for 20 hours, when a portion of the charge was removed and allowed to cool. A second portion was removed after heating at $1,000^{\circ}\text{C}$. for 20 hours and the third and last portion after further heating at 910°C . for 50 hours.

All three diffraction photographs were identical.

The 910°C . pattern, which contained 34 lines, was measured. 14 of these lines were related to a tetragonal cell, with

$a = 5.79$ and $c = 8.83$ kX units; 11 lines were those of zinc oxide; 3 strong lines belonged to sodium oxide; the remaining 6 lines, which were faint, were unexplained.

(2) Zinc Manganite with part of the Zinc replaced by Sodium.

The presence of an appreciable amount of zinc oxide in the 20% added sodium carbonate specimen, presumably displaced from the mixed oxide by the alkali, led to the attempt to replace zinc ions in the zinc manganite lattice by pairs of sodium ions. Accordingly, mixtures of zinc and sodium carbonates with basic manganese carbonate were prepared, in the following four ratios:-

Na : Zn : Mn. Stoichiometric Composition:



These mixtures were ignited in air at $1,100^\circ\text{C}$. for 15 hours, removed, remixed, compressed, and reheated at $1,100^\circ\text{C}$. for 20 hours.

The 19 cm. diffraction photographs were all of low quality, the quality deteriorating as the sodium content

increased. All showed lines of sodium oxide, these lines predominating in the last two specimens. Apart from one or two faint lines the presence of which could not be accounted for, the remainder of the lines complied with a tetragonal cell similar to that for zinc manganite. A progressive trend in cell constants was evident with increase in sodium content, thus:-

Na : Zn : Mn	Tetragonal phase, cell constants in kX units.		
	a.	c.	Vol. kX ³
1 : 2 : 5	5.71	9.19	300
1 : 1 : 3	5.72	9.15	299
2 : 1 : 4	5.73	9.09	299
4 : 1 : 6	5.7 ₅	9.0 ₃	298

The constants of the 4:1:6 sample are less accurate than the others as only four low-angle lines of the tetragonal phase were present.

Neither lines of zinc oxide nor lines of manganese oxides were present. The absence of lines of manganous manganic oxide in the 4:1:6 sample suggests that all the excess manganese is in solution in the small amount of impure zinc manganite in the system. In spite of this the c dimension, of 9.0₃ kX units, is much less than that for pure zinc manganite, 9.23 kX units, instead of being greater through the influence of the excess manganous

manganic oxide, the a dimension of which is 9.42 kX units.

Conclusion.

These results admit of a tentative explanation in the light of a possible ternary system composed of the manganites of sodium, zinc, and manganese.

In the 10% added sodium carbonate sample, quenched from 900°C., two cognate solid solutions may be present, which differ slightly in composition. The phase with lattice constants 5.71 and 9.22 kX units would comprise, on this scheme, zinc manganite with a small amount of sodium manganite in the lattice, insufficient to affect measurably the cell size, and the phase with similar lattice constants, 5.77 and 8.90 kX units, would be richer in sodium. At 1,000°C. and above, the solid solubility region is larger, and a single phase is obtained of intermediate lattice constants 5.74 and 9.06 kX units. In the three cases, only very little sodium is incorporated in the structures, as excess sodium oxide was present in both samples.

Increasing the amount of sodium carbonate added to 20% resulted in part displacement of zinc oxide from the zinc manganite lattice, the predominant phase remaining consisting of zinc manganous manganite containing more sodium than

the previous specimens, the lattice constants being further changed to 5.79 and 8.83 kX units.

This evidence of greater solubility of sodium manganite in zinc manganite containing excess manganese is supported in the series where zinc is replaced by sodium. Here, as less zinc and more sodium is included in the preparations, the remaining zinc manganite, getting progressively richer in manganese, shows a progressive change in lattice constants, the effect of the increase in sodium manganite in the structure more than offsetting the increase in cell volume that would otherwise be brought about by the increasing manganous manganite content.

Attempted Preparation of Zinc Manganite

2.3 and 4.2 Spinel.

2.3 Spinel.

H. F. McKurdie and H. Golovato (J. Res. Nat. Bur. Sc., 1948, 41, No. 6, 589-600) found manganous manganic oxide to possess a cubic spinel structure above $1,170^{\circ}\text{C}$. in the high temperature X-ray camera, so an attempt was made to 'freeze' the high temperature form, both in manganous manganic oxide and, if present, in zinc manganite by heating specimens to $1,400^{\circ}\text{C}$. for 8 hours and then rapidly quenching them.

In both cases, however, only the tetragonal phase resulted, so the phase change in manganous manganic oxide and zinc manganite, if present, is too rapid to be "frozen" by air-quenching.

Further investigation would require a high temperature X-ray camera study of zinc manganite.

4.2 Spinel.

Basic zinc and manganese carbonates were mixed in the proportion required to give a mixed oxide of composition $\text{Mn}^{\text{IV}}\text{Zn}_2\text{O}_4$ the hypothetical manganese zincate 4.2 spinel. Part of the mixture was ignited in air, the rest in oxygen to facilitate the oxidation of the manganese to

the quadrivalent state. Preliminary ignition at $1,000^{\circ}\text{C.}$ for 48 hours was followed by 2 hours at $1,200^{\circ}\text{C.}$, after which a portion of the charge was air-quenched, and then 2 hours at 800°C. , when the remainder was air-quenched.

Only the lines of zinc oxide and zinc manganite were present in the four 9 cm. diffraction photographs; thus 4.2 spinel formation did not take place under the conditions used.

Section 3.

MANGANATES OF THE ALKALI METALS

AND

POTASSIUM MANGANATE.

Section 3A. Manganites of the Alkali Metals.

Literature.

No work has been done on the structure of alkali metal manganites of the type $R\text{MnO}_2$. Mixed oxides, consisting chiefly of MnO_2 , with small amounts of alkali metal ion and the corresponding equivalent amounts of manganous ion, have received some attention. A recent paper by A. McL. Matheson and A. J. Wadsley (Amer. Mineral., 1950, 35, 99-101) refers to an example of this type of mixed oxide, cryptomelane. This mineral may be formulated R_8O_{16} , where R. is mainly Mn^{IV} , replaced to some extent by Mn^{II} . They found the structure to be monoclinic, and the best formula for this example to be $\text{KRMn}_7\text{O}_{16}$.

Experimental Work and Results.

To prevent the formation of manganates during ignitions of alkali-manganese oxide mixtures, these ignitions were conducted in nitrogen. Nevertheless, it was found that some lower mixed oxide formation took place in the cases of sodium and lithium, when the carbonates of these metals were heated in air with basic manganous carbonate. Reference to this observation is made later.

Hopkin and Williams' lithium carbonate, of unspecified purity, and Analar sodium and potassium carbonates were

used, after drying at 140°C . for one hour. Manganese sesquioxide was mixed with these three dried carbonates in amounts sufficient to give an alkali metal to manganese atom ratio of 1:1. The three mixtures were ignited in nitrogen at $1,150^{\circ}\text{C}$. for 12 hours, removed, remixed, compressed, and ignited in nitrogen at $1,150^{\circ}\text{C}$. for a further 24 hours. The charges were then allowed to cool slowly in nitrogen during 24 hours.

9 cm. powder diffraction photographs of the three specimens showed the absence of mixed oxide formation in the sodium and potassium mixtures, as only lines of alkali metal oxide and manganous oxide were present in the patterns. The lithium-manganese specimen, however, gave a pattern dissimilar from those of the constituent oxides, showing that mixed oxide formation had taken place in this instance.

This absence of mixed oxide formation with sodium and potassium, of the type $\text{R}_2\text{O}, \text{Mn}_2\text{O}_3$, under these conditions does not, of course, prove the non-existence of such mixed oxides. It may be that the oxygen dissociation pressure of such a mixed oxide is sufficiently high for oxygen loss during the nitrogen ignition to be fast enough to leave only manganous oxide and the alkali metal oxide.

Analysis of the lithium-manganese mixed oxide.

Manganese.

Wt. taken.	Vol. 0.0981N.Fe ^{II} used.	Manganese.
0.0917 g.	50.60 ml.	59.5%

Manganese as Mn^{III}.

Wt. taken	Vol. 0.0930N.Thio.used.	Manganese as Mn ^{III} .
0.4066 g.	44.16 ml.	55.5%

Atom ratio, Li : Mn : O

1 : 1 : 1.90

These results give the approximate formula $\text{LiMn}^{\text{III}}\text{O}_2$.

The 19 cm. diffraction photograph of this mixed oxide was of poor quality, only 15 lines being measurable. The pattern was totally dissimilar from those of structures of the hausmannite type; no dimetric structure could account for the lines present. An exhaustive examination of the pattern for the purpose of indexing was not made, owing to the few lines present and the poor definition of the film.

The intensities and d values for the pattern are included here.

LITHIUM MANGANITE, LiMnO_2 .

Powder Diffraction Data.

Intensity.	d.	Intensity.	d.
4	5.73	2	1.399
3	3.55	2	1.300
3	3.43	2	1.214
1	2.862	1	1.204
10	2.275	2	1.194
7	2.001	1	1.141
4	1.505	3	0.9910
1	1.433		

As noted earlier in this section, the same heat treatment in air of mixtures for lithium and sodium manganites had resulted in some lower mixed oxide formation, and only with potassium had appreciable amounts of the manganate been formed.

These mixtures were analysed, and 19 cm. diffraction photographs were taken.

Analyses.

Manganese.

Sample.	Wt. taken.	Vol. 0.0981N. Fe^{II} used.	Manganese.
Li-Mn	0.0887 g.	46.64 ml.	56.7%
Na-Mn	0.1048 g.	48.27 ml.	49.6%

Manganese as Mn^{III} .

Sample.	Wt. taken.	Vol. 0.0930N. TiO_2 used.	Manganese as Mn^{III} .
Li-Mn	0.3958 g.	69.46 ml.	89.7%
Na-Mn	0.3904 g.	46.10 ml.	60.3%

Atom ratios, R : Mn : O

Lithium ... 1 : 1 : 2.19

Sodium 1 : 1 : 2.04

Although the atom ratios correspond approximately with the manganite formula MnO_2 , the high Bunsen results indicate the presence of considerable amounts of manganese in higher valent states. Treatment of the two specimens with water and dilute acid gave no coloration indicative of manganate or permanganate, however. It thus seems probable that the manganese was present as Mn^{III} and Mn^{IV} only, and that possibly mixtures of mixed oxides had been obtained.

The diffraction photograph of the lithium mixture showed the absence of lines of lithium oxide and the oxides of manganese, but several intense lines showed a large amount of sodium oxide to be present in the sodium sample. As both patterns were diffuse and the number of phases present uncertain, no attempt was made at further interpretation.

It may be noted here that the pattern obtained from the sodium sample bore no resemblance to patterns obtained in the examination of the effect of added sodium ion on the zinc manganite structure.

Section 3B. Potassium Manganate.

Although potassium manganate is not a mixed oxide in the generally accepted sense, i.e. not a close-packed oxygen lattice with the cations of the two metals distributed regularly among the interstices, it was thought that this oxysalt might well repay some attention as no previous work had been done on its structure.

As the manganate is reported to be isomorphous with the orthorhombic sulphate and chromate, it seemed probable that the manganate, too, would be orthorhombic, with cell constants of the same order as those of the sulphate and chromate. By drawing a parallel with the published diffraction data for potassium sulphate, it was hoped that the difficulties of indexing such a structure would thereby be considerably lessened.

Experimental Work and Results.

20 g. of potassium permanganate (Analar) and 60 g. of potassium hydroxide (Analar) were dissolved in 100 ml. of water and the solution was boiled until half its volume had evaporated. The dark green solution left was diluted with 50 ml. of water and cooled on ice. The potassium manganate that crystallised was collected on a sintered glass filter, washed with dry ether, dried, and transferred

to a sealed container as the product was hygroscopic.

The potassium manganate was determined thus:-

About 0.5 g. of the sample was dissolved, together with 3 g. of potassium bisulphate, in 50 ml. of water. The manganese dioxide precipitated was removed by filtration. The filtrate and washings were made up to 100 ml. and this solution was then used to titrate 10 ml. of standard decinormal sodium oxalate solution. The amount of manganate present was calculated from the equation:-



Analysis.

Wt. taken.	Vol. reqd. for 10 ml. 0.0987N. sodium oxalate.	Potassium manganate.
0.5026 g.	12.62 ml.	92.0%

Unfortunately, difficulty was experienced in getting a diffraction photograph of this preparation suitable for interpretation. Owing to the hygroscopicity of the specimen, powdering was first carried out on a warm porous tile, with a nickel spatula, the powdered specimen being then photographed in a sealed Lindemann capillary. The diffraction photograph produced contained barely discernible lines, the strongest of which corresponded with the strongest line of manganese dioxide. Next, some of the sample was crushed rapidly in a cold agate mortar

and the mass, already moist, was rammed into a Lindemann capillary. Only a few faint streaky lines, useless for interpretation, were obtained in the diffraction photograph.

A fresh approach to the problem was tried by preparing the manganate by a dry method which was found by H. I. Schlesinger et al. (H. I. Schlesinger, R. D. Mullinix, and S. Popeff, Ind. Eng. Chem., 1919, 11, 317; H. I. Schlesinger, V. T. Jackson and E. E. Cordery, *ibid.*, 1923, 15, 53) to give a high yield.

Pure manganese dioxide was prepared by the ignition, at a low temperature, of some of the pure manganese nitrate the preparation of which was described in the section on general methods. Two moles of this dioxide were mixed with a solution of one mole of potassium hydroxide (Analar) and the product dried. The crushed mixture was ignited at 270°C . in oxygen. Every few hours the charge was removed and remixed to facilitate oxygen absorption. After 10 days ignition, the manganate content had reached a maximum.

Analysis.

Wt. Taken.	Vol. reqd. for 10 ml. 0.0909N sodium oxalate.	Potassium manganate.
0.4334 g.	17.07 ml.	72.5

Although the powder diffraction photograph was rather

diffuse it was found possible to measure 30 lines. No lines of potassium hydroxide were present, and only one faint line could be ascribed to manganese dioxide. On comparing the d values of these lines with those given by F. P. Goeder (Proc. Nat. Acad. Sci., 1928, 14, 766-771) for potassium sulphate, no obvious relation was observed. Attempts to fit his indices to apparently similar lines in the manganate photograph met with little success. A rough qualitative fit for about a dozen lines could be obtained, but the calculated $\sin^2 \theta$ values showed pronounced deviation from the observed figures.

Since Goeder's powder diffraction photograph was taken using molybdenum radiation and a small camera, and as the work was done in 1928, a 19 cm. photograph was taken of potassium sulphate (Analar), using iron radiation, in order to check his results with a pattern of much greater dispersion. The film was of fair quality, over 60 lines being measured. Goeder's indices, whatever adjustment was made to the lattice constants he gave, could not be made to fit the lines, however. Four strong lines out of the first 20 were completely at variance with the possibilities.

In seeking a means to escape this impasse, diffraction photographs were taken of ammonium sulphate and potassium

chromate, both these crystals having orthorhombic constants similar to those for potassium sulphate. No progress in indexing was made with these pictures, either; indeed, the pattern of ammonium sulphate bore not the slightest qualitative resemblance to either the potassium sulphate or chromate pattern. The chromate and sulphate patterns were qualitatively similar, however.

No further investigation has been carried out along this line, owing to the exigencies of time and the increasing digression from the main topic of this research.

It may be stated as a general conclusion that the diffraction photograph of a 72.5% pure sample of potassium manganate showed a qualitative resemblance to the potassium sulphate pattern, and that the manganate may have orthorhombic symmetry, with cell constants not too different from those of potassium sulphate. It appears possible that the structure of ammonium sulphate and potassium sulphate may require some revision.

Diffraction data for the sample of potassium manganate are recorded below.

POTASSIUM MANGANATE, K_2MnO_4

Powder Diffraction Data

Intensity	d.	Intensity	d.	Intensity	d.
1	4.59	1	2.272	0.5(7MnO ₂)	1.614
1	4.46	1	2.249	2	1.482
0.5	4.23	1	2.136	4	1.464
0.5	4.00	2	2.118	1	1.450
0.5	3.88	2	1.922	0.5	1.400
0.5	3.82	0.5	1.814	2	1.382
8	3.05	0.5	1.715	0.5	1.282
10	2.957	1	1.697	0.5	1.179
4	2.921	1	1.668	2	1.069
2	2.467	0.5	1.651	1	1.052

Section 4.

COPPER MANGANITE.

Literature.

Mention has already been made in the Introduction of Dana's reference to crednerite, copper manganite, CuMn_2O_4 . Crystal measurements indicated probable monoclinic symmetry.

No other structural work on this manganite is recorded in the literature.

Experimental Work and Results.

Copper oxide (Analar) and manganese sesquioxide were ignited together in the atom ratio Cu:Mn of 1:2. The ignition was conducted at 800°C ., as the decomposition $4\text{CuO} = 2\text{Cu}_2\text{O} + \text{O}_2$ takes place above 800°C ., and in oxygen to encourage the reverse reaction, in the event of slight decomposition. After 24 hours at this temperature, the charge was allowed to cool for two hours while still in oxygen.

The 9 cm. diffraction photograph showed some lines of manganese sesquioxide, but none of cupric oxide, so partial mixed oxide formation had taken place.

The product was analysed for manganese, tervalent manganese, and copper.

Determination of Copper.

About 0.3 g. of the sample was dissolved in 10 ml. of boiling nitric acid containing about 0.5 g. of oxalic acid. The solution was diluted to 40 ml. with water, boiled, and nearly neutralised with aqueous ammonia solution. About 3 g. of potassium iodide were added to the cooled solution, and the iodine liberated was titrated with standard, decinormal sodium thiosulphate solution.

Analyses.

Manganese.		
Wt. taken.	Vol. 0.0961N. Fe^{II} used.	Manganese.
0.1047 g.	45.56 ml.	46.9%

Manganese as Kn^{III}		
Wt. taken.	Vol. 0.0930N. Thio. used.	Manganese as Kn^{III} .
0.4086 g.	40.10 ml.	50.1%

Copper.		
Wt. taken.	Vol. 0.0930N. Thio. used.	Copper.
0.2679 g.	11.45 ml.	25.3%

Atom ratio, Cu : Mn : O

1.00:2.15:4.36

These results approximate to the formula $\text{Cu}^{\text{II}} \text{Mn}_2^{\text{III}} \text{O}_4$.

The 19 cm. powder diffraction photograph was of poor quality, so the specimen was compressed and the heat

treatment in oxygen repeated.

The 19 cm. photograph of this compressed specimen was of fair quality. 10 lines of manganese sesquioxide were present, representing about 20% of the sample; the other 17 lines were all indexed as a spinel with a cell edge of 8.31 kX units.

The presence of excess manganese as the sesquioxide in this preparation led to two further lines of investigation.

First, an exactly stoichiometric mixture was prepared by adjusting the composition of the previous preparation and re-igniting the adjusted mixture. After heating at 800°C. in oxygen for 12 hours, the temperature was raised and kept at 1,000°C. for three hours (a trial run had shown that the spinel phase persisted at this temperature in oxygen, if the temperature increase was slow), reduced to 900°C. and maintained at this figure for 12 hours, and then reduced to 800°C. and held for a further 24 hours.

Secondly the copper oxide content of the sample was increased considerably to ascertain the possibility of the formation of a mixed oxide of the type $\text{Cu}_{\frac{1}{2}}^{\text{I}}\text{Mn}_{\frac{3}{2}}^{\text{III}}\text{O}_4$, which may have been present in the original preparation,

although this was unlikely, as a spinel could hardly be formulated with this composition, and the presence of cuprous copper would have resulted in a low result for Mn^{III} in the Bunsen determination.

Continuing with the first line of study, the stoichiometric sample was analysed and a 19 cm. diffraction photograph was taken.

Analyses.

Manganese.		
Wt. taken.	Vol. 0.0981N. Fe^{II} used.	Manganese.
0.1024 g.	43.53 ml.	45.8%
Manganese as Mn^{III} .		
Wt. taken.	Vol. 0.0930N. Thio used.	Manganese as Mn^{III} .
0.4020 g.	36.04 ml.	45.8%
Copper.		
Wt. taken.	Vol. 0.0930N. Thio used.	Copper.
0.4365 g.	19.68	26.6%

Atom ratio, Cu : Mn : O

1.00:2.00:4.12

These results confirm the formula $\text{Cu}^{\text{II}} \text{Mn}_2^{\text{III}} \text{O}_4$.

The lines on the 19 cm. diffraction photograph were very diffuse, and no high-angle lines were measurable.

The nine lines that could be measured were those of a spinel, with $a = 8.29$ kX units. Copper manganite only was present, therefore, showing mixed oxide formation to be complete. The powder diffraction data for this photograph are given at the end of this section.

Excess of copper oxide was included in the mixture prepared in the course of the other line of investigation. The mixture was ignited at 800°C . in oxygen for 48 hours. After 24 hours, the charge was removed, remixed, and compressed before the firing was continued. The product was analysed and a 19 cm. diffraction photograph was taken.

Analyses.

Manganese.		
Wt. taken.	Vol. 0.0981N. Fe^{II} used.	Manganese.
0.1046 g.	37.22 ml.	38.3%
Manganese as Mn^{III} .		
Wt. taken.	Vol. 0.0930N. Thio used.	Manganese as Mn^{III} .
0.3873 g.	32.90 ml.	43.4%
Copper.		
Wt. taken.	Vol. 0.0930N. Thio used.	Copper.
0.2994 g.	17.12 ml.	33.8%

Atom ratio, Cu : Mn : O

1.53:2.00:4.99

These results show most of the manganese to be present in the tervalent state, and the absence of a low Bunsen result points to the absence of cuprous copper. Thus a mixture of cupric oxide and copper manganite was probably present; such a mixture would contain approximately the amount of oxygen found.

The 19 cm. diffraction pattern consisted exclusively of well-defined spinel lines. 13 such lines were present. The cell constant obtained was 8.303 ± 0.003 kX units.

The absence of lines of copper oxide, implying solid solution of copper oxide in copper manganite, suggested the possible alternative of the presence of a "4.2" spinel. Copper : manganese in the ratio present could be formulated thus, and the rather high Bunsen result lent support to this possibility. Consequently, a further preparation, containing still more copper oxide, approaching the ratio Cu:Mn of 2:1, was made. The same heat treatment was used for this preparation as that used for the last.

Analyses.

Manganese.		
Wt. taken	Vol. 0.0981N. Fe^{II} used.	Manganese.
0.1097 g.	25.00 ml.	24.6%

Manganese as Mn^{III} .		
Wt. taken.	Vol. 0.0930N. Thio. used.	Manganese as Mn^{III} .
0.4154 g.	23.40 ml.	28.8%

Copper.		
Wt. taken.	Vol. 0.0930N. Thio used.	Copper.
0.1969 g.	16.81 ml.	50.5%

Atom ratio, Cu : Mn : O
1.78:1.00:3.48

These results agree with those theoretically required for a mixture of CuO and $\text{Cu}^{\text{II}} \text{Mn}_2^{\text{III}} \text{O}_4$. 4.2 spinel formation had not, therefore, taken place.

The 19 cm. diffraction photograph, of excellent quality, contained 16 lines. All but one, a very faint line, the d value of which corresponded with that of the strongest copper oxide line, were lines of a spinel, with $a = 8.304 \pm 0.001$ Å units.

It thus appears that almost all the copper oxide was present in solid solution in the copper manganite spinel. Coupled with this unusual phenomenon, the incorporation

of bivalent metal ions into a spinel lattice, is the curious near-constancy of the cell size over this range of compositions. A parallel state of affairs is present in copper ferrite. Here, mixtures containing Cu:Fe ratios of between 75:50 and 35:130 all give X-ray diffraction photographs of practically identical ferrite patterns (E. J. W. Verwey, A. N. van Arkel, and M. G. van Bruggen, *Rec. trav. Chim.*, 1936, 55, 346-347). When these workers subjected samples to prolonged heating at moderate temperatures, they found that another unidentified phase appeared; this phenomenon was not observed in this study of copper oxide-rich copper manganite, even though the ignitions were prolonged.

It is remotely possible that the copper oxide present in excess may not be in solid solution, but as a separate phase in an amorphous state, the presence of the mixed oxide inhibiting its crystal growth. At the ignition temperatures used, not far below the melting point of copper oxide (which is about $1,200^{\circ}\text{C.}$), this is inherently unlikely, however.

Further investigation, to determine the limits in the range of compositions of this constant-cell-volume spinel, and to elucidate the arrangement of the Cu^{II} ions

in the spinel lattice, seems to be desirable.

At one stage in the work on copper manganite, when it was thought possible that a mixed oxide of the type $\text{Cu}_2^{\text{I}}\text{Mn}_2\text{O}_4$ had been formed, the desirability of the reduction of cupric copper to the cuprous state led to the performance of an ignition of a mixture in air at $1,060^\circ\text{C}.$, for 30 hours. Copper oxide and basic manganous carbonate were used, in the proportion Cu:Mn of 1:1.

The analysis of this preparation gave a very low Bunsen result, showing that a considerable amount of cuprous copper was present. The diffraction pattern was totally dissimilar from those of copper manganite spinel.

No lines of manganese oxides, or of cupric and cuprous oxides were present.

It is possible that several phases were present, comprising the three oxides Mn_3O_4 , CuO , and Cu_2O in one or more solid solutions. No further work has been done on this aspect, owing to the difficulty of determining the phases present.

X-ray diffraction data for copper manganite and for copper manganite containing a large excess of copper oxide are given overleaf.

COPPER MANGANITE, CuMn_2O_4 .

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed	hkl.	$\sin^2 \theta$ calc.	d.
3	19.26	0.1089	220	0.1087	2.929
10	22.76	0.1496	311	0.1495	2.497
1	27.83	0.2179	400	0.2174	2.070
2	34.84	0.3263	422	0.3262	1.691
4	37.34	0.3678	333	0.3669	1.591
6	41.23	0.4343	440	0.4349	1.465
1	49.87	0.5846	533	0.5844	1.263
0.5	60.67	0.7600	642	0.7610	1.108
2	63.63	0.8028	553	0.8018	1.078

Lattice Constant.

Spinel unit cell, $a = 8.29$ kx units.

COPPER MANGANITE with Excess Copper Oxide.Cu : Mn :: 1.78 : 1.00Powder Diffraction Data

Intensity	θ	$\sin^2 \theta$ observed	hkl.	$\sin^2 \theta$ calc.	a.
3	19.26	0.1088	220	0.1084	2.929
10	22.75	0.1495	311	0.1491	2.498
0.5	23.77	0.1625	222	0.1626	2.397
0.5	24.68				2.314 (CuO)
2	27.79	0.2173	400	0.2168	2.672
3	34.80	0.3256	422	0.3252	1.693
8	37.24	0.3662	333	0.3659	1.596
10	41.21	0.4340	440	0.4336	1.467
1	47.40	0.5418	620	0.5420	1.312
3	49.76	0.5828	533	0.5827	1.265
1	50.60	0.5971	622	0.5962	1.250
0.5	53.76	0.6504	444	0.6504	1.198
$\alpha_1 \alpha_2^3$	60.587	0.7589	642	0.7588	1.110
$\alpha_1 \alpha_2^8$	63.406	0.7996	553	0.7995	1.081
$\alpha_1 \alpha_2^4$	68.633	0.8673	800	0.8673	1.037
$\alpha_1 \alpha_2^5$	81.027	0.9757	660	0.9757	0.9780

Lattice Constant.

spinel unit cell, $a = 8.304 \pm 0.001$ kX units.

Section 5. MANGANEITES OF THE ALKALINE EARTH METALS.

Literature.

There are no records of structural studies on manganites of metals in this Group of the Periodic Table. This is surprising, as the possibility of replacing the bivalent manganese in manganous manganic oxide by a bivalent alkaline earth metal, particularly the lighter ones of small ionic radius, seems very promising.

The magnesium analogue of zinc manganite is mentioned in Dana's "System of Mineralogy" (p.715), but no reference to work on this mixed oxide is given. L. Navias (J. Amer. Ceram. Soc., 1936, 19, 1-7) concluded that beryllium and magnesium manganites had been formed, by observations of the degree of discoloration in fired cakes of the mixed constituent oxides. A calcium manganite, probably $3\text{CaO}, \text{Mn}_2\text{O}_3$, is recorded by V. F. Zhuravlev (Tsement, 1938, 15, No.7, 43-5). Numerous references are made in the older literature to manganese mixed oxides in this Group. Abegg (Handbuch der anorg. Chem., IV, 837, 838), for instance, lists several representatives for each metal (excepting beryllium), all of the type $\text{ROx}(\text{MnO}_2)$ and characterized by analysis only.

Experimental Work and Results.

With no previous structural work to guide the

investigation, direct attempts were made to synthesise all five possible manganites by igniting together the constituents in their most convenient forms.

Beryllium.

Beryllium oxide (Hopkin and Williams' "pure") and basic manganese carbonate were mixed in the proportion necessary to give a product containing beryllium and manganese in the atom ratio of 1:2. The mixture was ignited in air at $1,000^{\circ}\text{C}$. for 12 hours, and then at 900°C . for a further 12 hours. The product was removed from the furnace and allowed to cool in air.

A diffraction photograph, taken in the 9 cm. camera, showed a pattern of lines identical with the pattern given by manganous manganic oxide, together with 4 extra lines, the d values of which corresponded with those for the strongest lines of beryllium oxide given in Hanawalt, Rinn, and Frevel's table (Ind. Eng. Chem., Anal. Ed., 1938, 10, 476). Thus no mixed oxide formation had taken place.

Since the temperature of ignition might have been too low to bring about solid solution, another attempt at the formation of a mixed oxide was made. This time the

reactants were heated to $1,300^{\circ}\text{C}$. and maintained at this temperature for 8 hours. The air-cooled product, which had been sintered by this heat treatment, was photographed in the 19 cm. camera, so that small changes in line positions could be detected. Again, however, the pattern corresponded with that of pure manganous manganic oxide, with the 4 extra lines of beryllium oxide.

This absence of mixed oxide formation is curious, inasmuch as mixed oxides are formed by the next four alkaline earth metals, of ionic radii far greater than that of beryllium. This proves to be yet another instance of the differences often shown by the first member of a Group in the Periodic Table to properties common to other members of the Group.

Magnesium.

Gorgeu's method of preparation, mentioned under zinc manganite, was tried first. The two sulphates were mixed with sodium sulphate in the ratio 3:3:1 and fused in a porcelain crucible. The melt was extracted with water and the residue washed with very dilute acetic acid. As with the zinc product, this residue proved on X-ray examination to be largely manganese dioxide; a few faint

lines which might have been due to a little magnesium manganite were also present.

Magnesium oxide (Analar) and basic manganese carbonate were ignited together for the next attempt at preparation. These compounds, in the atom ratio Mg:Mn of 1:2, were heated at $1,150^{\circ}\text{C.}$ in air for 4 hours, at $1,000^{\circ}\text{C.}$ for 12 hours and finally at 900°C. for another 12 hours. The product was rapidly air-cooled.

A 9 cm. powder diffraction photograph of the specimen showed pronounced differences in the positions of most of the lines present when compared with a 9 cm. photograph of pure manganous manganic oxide; hence some mixed oxide formation had taken place.

The definition of this 9 cm. diffraction photograph was poor, so it was decided that further heat treatment of the sample to improve crystallinity was desirable, before taking a 19 cm. photograph.

The original sample was again heated to $1,150^{\circ}\text{C.}$ and maintained at this temperature for 12 hours. The temperature was then reduced by 50° steps, being held constant at each step for 12 hours. After 12 hours at 850°C. , the specimen was cooled rapidly in air.

The 19 cm. photograph of this slow-cooled specimen was

still diffuse, however, with no resolution of the high angle lines into $\alpha_1\alpha_2$ doublets. 31 lines were measured, 22 of which conformed with a hausmannite type unit cell, showing good agreement between observed and calculated $\sin^2\theta$ values. The cell constants were $a = 5.71$ and $c = 9.29$ kÅ units. Each of the remaining 9 lines formed a pair of equal intensity with one of the lines already indexed. When the unindexed line was given the same indices as the indexed line of the pair, it was found that close agreement of calculated with observed $\sin^2\theta$ values resulted for all these 9 lines, the tetragonal cell required by these lines having lattice constants $a = 5.79$ and $c = 8.83$ kÅ units.

There were thus two phases present in this sample, of which the first one mentioned, judging from line intensities, predominated slightly. These two phases are similar in lattice dimensions to the two phases present in the sample of zinc manganite containing 10% added sodium carbonate and quenched from 900°C . Thus:-

	First phase.		Second phase.	
	a.	c.kÅ units	a.	c.kÅ units.
Specimen under discussion...	5.71	9.29	5.79	8.83
Zinc manganite with 10% alkali.....	5.71	9.22	5.77	8.90

The powder diffraction data for this photograph are

included here to show the correspondence between calculated and observed $\sin^2 \theta$ values resulting from the two phase interpretation.

Intensity.	θ	$\sin^2 \theta$ observed	First phase.		Second phase		d.
			hkl.	$\sin \theta$ calc.	hkl.	$\sin \theta$ calc.	
10	11.48	0.0396	101	0.0395			4.85
2	13.56	0.1013	112	0.1006			3.04
2	18.81	0.1040			112	0.1037	3.00
1	19.47	0.1111			200	0.1115	2.897
1	19.83	0.1150	200	0.1147			2.850
5	20.83	0.1264	103	0.1261			2.716
1	21.56	0.1350			103	0.1358	2.628
9	22.90	0.1514			211	0.1514	2.483
9	23.15	0.1545	211	0.1542			2.457
3	24.64	0.1738	004	0.1733			2.317
4	28.19	0.2231			220	0.2230	2.045
4	28.66	0.2299	220	0.2293			2.015
2	33.22	0.3001	105	0.2994			1.763
1	35.03	0.3295	312	0.3300			1.683
2	36.74	0.3579	303	0.3555			1.619
2	37.72	0.3743			321	0.3744	1.579
2	38.29	0.3839	321	0.3835			1.558
8	39.40	0.4030	224	0.4026			1.522
5	40.08	0.4147			224	0.4148	1.500
2	41.95	0.4469	116	0.4472			1.445
4	42.63	0.4587	400	0.4587			1.426
0.5	46.68	0.5293	305	0.5288			1.328
2	49.80	0.5835	413	0.5829			1.264
2	52.67	0.6322	404	0.6320			1.215
2	52.98	0.6374			404	0.6378	1.210
0.5	55.17	0.6737	127	0.6740			1.177
0.5	56.42	0.6941	008	0.6931			1.160
1	60.53	0.7580	415	0.7581			1.112
0.5	61.59	0.7738			415	0.7737	1.098
0.5	64.35	0.8126	503	0.8142			1.072
0.5	73.43	0.9187	440	0.9174			1.008

A higher temperature of ignition and the effect of quenching were next tried. Two samples of the mixed

oxide and carbonate were ignited at $1,330^{\circ}\text{C}$. for 6 hours. One was then quenched in water, while the other was allowed to cool slowly over a period of three hours.

These two specimens were analysed for magnesium, manganese and manganese as Mn^{III} .

Determination of magnesium by "oxine".

About 0.3 g. of the sample was dissolved in 4 ml. of concentrated hydrochloric acid and the solution boiled until free from chlorine. 10 ml. of 20% ammonium chloride solution were added, and then 6N. aqueous ammonia solution until the solution was alkaline to phenol red, when a further 2 ml. of ammonia solution were added. Prolonged saturation with hydrogen sulphide, followed by the removal of the precipitated manganese sulphide by filtration, was carried out. The operation was repeated until all the manganese had been removed. The solution was acidified with hydrochloric acid, the hydrogen sulphide boiled off, and the precipitated sulphur removed by filtration. The manganese-free solution was heated to 70°C . and oxine solution (5% 8-hydroxyquinoline in 25% acetic acid) in about 20% excess was added dropwise. The liquid was made alkaline to phenol red with ammonia solution and the mixture was then digested for half an hour on a steam bath.

The precipitate was collected on a weighed Jens No.4 sintered glass filter crucible, washed with 1% aqueous ammonia solution until free from chloride, and dried at 100°C. to constant weight.

Analyses.

Manganese.

Sample:	Wt. taken.	Vol. 0.1004N. Fe^{II} used.	Manganese.
Slow cooled	0.1031 g.	50.18 ml.	53.7%
Quenched from 1,330°C.	0.0985 g.	49.78 ml.	55.8%

Manganese as Mn^{III} .

Sample:	Wt. taken.	Vol. 0.0960N. Thio. used.	Manganese as Mn^{III} .
Slow cooled	0.3671 g.	37.26 ml.	53.5%
Quenched from 1,330°C.	0.3317 g.	29.42 ml.	44.7%

Magnesium.

Sample:	Wt. taken.	Wt. of oxine complex.	Magnesium.
Slow cooled	0.2586 g.	0.4673 g.	12.6%
Quenched from 1,330°C.	0.1229 g.	0.2280 g.	12.9%

Atom ratio, Mg : Mn : O

Slow cooled 1.07: 2 : 4.29

Quenched from 1,330°C. 1.04: 2 : 3.85

The slow cooled sample thus may be formulated

$\text{MgMn}_2^{\text{III}}\text{O}_4$, but the 1,330°C. quenched sample is deficient in oxygen and Mn^{III} , so reaction was probably incomplete.

The powder diffraction photographs of these samples supported the analytical conclusions. The slow cooled specimen gave a pattern containing 17 lines belonging to the hausmannite type phase, with $a = 5.70$ and $c = 9.26$ kX units, this phase comprising about 90% of the mixture; 8 weak unrecognised lines were also present. The "quenched" pattern contained lines of the two tetragonal phases again; 12 lines corresponded with a unit cell of dimensions $a = 5.73$ and $c = 9.29$ kX units; 8 lines with a cell of $a = 5.70$ and $c = 9.03$ kX units; 3 of the remaining 4 lines were those of magnesium oxide, and the last was unaccounted for.

The presence of incomplete reaction in the quenched specimen and lines unaccounted for in the slow cooled one led to the preparation of various samples, followed by analysis and X-ray examination. Temperatures of ignition and quenching were varied and later compression of the samples was employed. The conditions and results are recorded under the four headings that follow.

(1) Series of air-quenched samples.

The reactants were ignited at $1,400^{\circ}\text{C}$. in air for one hour and the first portion then quenched. The temperature was reduced to $1,100^{\circ}\text{C}$., held for 6 hours,

and the second portion quenched. A third portion was slow cooled from 1,100°C. to 600°C. during 50 hours. The last, fourth portion was quenched after 40 hours at 800°C.

Analyses.

Manganese.			
Sample:	Wt. taken.	Vol. 0.1004N. Fe^{II} used.	Manganese.
slow cooled	0.1011 g.	50.72 ml.	55.3%
quenched 800°C.	0.1069 g.	53.77 ml.	55.5%
from 1,100°C.	0.1063 g.	53.31 ml.	55.3%
1,400°C.	0.1036 g.	51.77 ml.	55.1%

Manganese as Mn^{III} .			
Sample:	Wt. taken.	Vol. 0.0960N. Thio used.	Manganese as Mn^{III} .
slow cooled	0.2975 g.	30.90 ml.	54.8%
quenched 800°C.	0.2858 g.	29.56 ml.	54.6%
from 1,100°C.	0.3009 g.	30.86 ml.	54.1%
1,400°C.	0.2917 g.	29.68 ml.	53.7%

Magnesium.			
Sample:	Wt. taken.	Wt. of Oxine complex.	Magnesium.
quenched from 1,100°C.	0.2005 g.	0.3466 g.	12.1%

These figures show that there is no significant variation in composition with temperature.

Mean composition:- Manganese 55.3%
Manganese as Mn^{III} 54.3%

Atom ratio, Mg : Mn : O

1 : 2.02 : 4.08

Lattice constants.

slow cooled		a.	c. kX units
quenched from	800° C.	5.70	9.28
"	" 1,100°	5.71	9.29
"	" 1,400°	5.74	9.11
		5.73	9.25

The films were diffuse, and several weak lines were not accounted for.

(11) Further heating to eliminate unindexed lines.

The preparation was ignited in air, first at 1,400° C. for 2 hours and then at 1,200° C. for 24 hours. Two air-quenched samples, one from 1,400° C. and the other from 1,100° C., were prepared, and a third sample slow cooled over 4 days.

Analyses.

Manganese.			
Sample:	Wt. taken.	Vol. 0.1004N. Fe ^{II} used.	Manganese.
slow cooled	0.0990 g.	50.35 ml.	55.9%
quenched 1,100° C.	0.1011 g.	51.25 ml.	55.9%
from 1,400°	0.1013 g.	51.69 ml.	56.3%

Manganese as Mn^{III} .

Sample:	Wt. taken	Vol. 0.0958N. Thio used.	Manganese as Mn^{III} .
Slow cooled	0.4003 g.	40.66 ml.	53.4%
Quenched 1,100°C.	0.3924 g.	39.74 ml.	53.3%
from 1,400°C	0.3950 g.	39.32 ml.	52.4%

Again there is no significant variation in composition with temperature.

Lattice Constants.	a.	c. kX units.
Slow cooled	5.71	9.30
quenched from 1,100°C.	5.73	9.17
" " 1,400°C	5.73	9.18

All the films showed poor definition. All the lines in the three photographs were indexed on the hausmannite type cell.

(iii) Samples compressed to improve crystallinity.

The mixed reactants were ignited in air at 1,100°C. for 12 hours, compressed, and then heat treated in the manner described under heading (ii). One sample was air-quenched from 1,350°C. and the other slow cooled.

Lattice constants.	a.	c. KX units.
Slow cooled	5.710 ± 0.003	9.298 ± 0.003
Quenched from 1,350°C.	5.767 ± 0.003	9.044 ± 0.003

All the lines present were indexed, and the definition

was better than that obtained hitherto. Powder diffraction data for the slow cooled sample are presented at the end of this section.

(iv) High temperature quenched sample.

Another air-quenched sample, from $1,500^{\circ}\text{C}.$, was prepared, to see if the lattice constant change, observed in successive previous high temperature quenches, proceeded further.

The lattice constants obtained were $a = 5.73$, $c = 9.35$ KX units.

Concluding and summarizing this section on magnesium manganite, the earlier preparations were incompletely reacted, a temperature of about $1,400^{\circ}\text{C}.$ being required for this purpose. The appearance of two tetragonal phases in the earlier quenched samples, and the possibly fortuitous resemblance to the two phases in the alkali containing zinc manganite preparation, cannot readily be explained, particularly as the effect was not reproducible in later preparations. Again, the unit cell size changes in the high temperature quenches, not present in the last high temperature quench, admit of no obvious explanation, as there is no regularity evidenced in these changes. It is possible that impurities present in the furnace tube were

the cause of these changes, as the last ignition was performed in a different furnace to the rest.

The identity of magnesium manganite, $\text{MgMn}_2^{\text{III}}\text{O}_4$, has been satisfactorily established, and the symmetry and lattice constants determined, notwithstanding these inconsistencies.

The powder diffraction data for magnesium manganite are given on the next page.

MAGNESIUM MANGANITE, MgMn_2O_4 .

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed	hkl.	$\sin^2 \theta$ calc.	d.
5	11.52	0.0398	101	0.0395	4.84
2	18.55	0.1012	112	0.1006	3.04
1	19.86	0.1154	200	0.1146	2.844
7	20.87	0.1269	103	0.1260	2.712
9	23.18	0.1549	211	0.1541	2.454
3	24.66	0.1741	004	0.1730	2.317
6	28.68	0.2300	220	0.2293	2.014
0.5	32.52	0.2890	204	0.2876	1.797
3	33.24	0.3004	105	0.2989	1.763
1	35.17	0.3317	312	0.3298	1.678
1	36.65	0.3563	303	0.3552	1.618
5	38.32	0.3844	321	0.3834	1.556
10	39.42	0.4032	224	0.4022	1.522
5	42.68	0.4596	400	0.4586	1.425
0.5	46.71	0.5298	305	0.5282	1.327
2	49.92	0.5854	413	0.5845	1.262
0.5	51.77	0.6171	422	0.6164	1.230
3	52.67	0.6322	404	0.6316	1.215
2	55.20	0.6743	127	0.6730	1.177
1	56.33	0.6925	008	0.6918	1.161
3	60.49	0.7573	415	0.7575	1.110
3	64.44	0.8139	503	0.8138	1.071
1	66.57	0.8420	521	0.8420	1.053
3	71.72	0.9016	327	0.9023	1.017
4	73.32	0.9176	440	0.9173	1.008

Lattice Constants.

Body-centred tetragonal cell, space group $14/\text{amd}$,

$$a = 5.710 \pm 0.003$$

$$c = 9.298 \pm 0.003 \text{ kX units.}$$

Magnesium Manganite with excess Manganese.

A series of four samples, ignited and heat treated in the same way as the first stoichiometric series, but containing 30 atom% excess manganese, was prepared.

Analyses.

Manganese.

Sample:	Wt. taken.	Vol. 0.1004N. Fe^{II} used.	Manganese
Slow cooled	0.1006 g.	53.12 ml.	58.2%
quenched 800°C.	0.1060 g.	55.78 ml.	58.0%
from 1,100°C.	0.1030 g.	54.07 ml.	57.9%
1,400°C.	0.1024 g.	53.78 ml.	57.9%

Manganese as Mn^{III} .

Sample:	Wt. taken.	Vol. 0.0960N. Thio. used.	Manganese as Mn^{III} .
Slow cooled	0.2908 g.	29.92 ml.	54.3%
quenched 800°C.	0.2984 g.	30.76 ml.	54.4%
from 1,100°C.	0.2926 g.	30.04 ml.	54.2%
1,400°C.	0.2908 g.	29.62 ml.	53.7%

Magnesium.

Sample:	Wt. taken.	Wt. of Oxine Complex.	Magnesium.
quenched from 1,100°C.	0.1336 g.	0.2685 g.	9.94%

Mean composition:— Manganese 58.0%

Manganese as Mn^{III} 54.15%

Atom ratio, Mg : Mn : O
1 : 2.59 : 4.91

The results of these analyses agree with the theoretical requirement for $\text{MgMn}_2^{\text{III}}\text{O}_4 + 30 \text{ atom Mn}_3\text{O}_4$. The temperature of quenching had no effect on the product.

All the powder diffraction photographs were identical; that of the slow cooled sample was measured. All but a few faint lines conformed with the magnesium manganite structure; these faint lines were not those of manganous manganic oxide. The lattice constants were $a = 5.70$ and $c = 9.29$ kX units.

From these results, it seemed that solid solution had taken place to a large extent, if not completely, so confirmation of this was sought, and greater solubility investigated, by preparing samples containing 60 and 100 atom% excess of manganese. Mixtures for these were ignited as before; two quenches of the 60% sample, from 900°C . and $1,400^\circ\text{C}$., were taken, but only one, from $1,200^\circ\text{C}$., of the 100% sample.

The powder diffraction photographs, of which those of the 900° and $1,400^\circ\text{C}$. quenches were identical, showed only lines of the magnesium manganite structure, thus solution was complete in both cases.

Lattice constants.

	a.	c. kX units.
60 atom Mn excess (1,400°C. quench)	5.72	9.32
100 " " " (1,200°C. ")	5.72	9.32

A slight upward trend is evident in the c dimension, compared with the 30% excess value, which is to be expected with increasing manganese content, as the constants for manganous manganic oxide are $a = 5.75$ and $c = 9.42$ kX units.

The foregoing indicates that, within the limit stated, manganous manganic oxide is miscible with magnesium manganite, and that the excess manganese is present as Mn_3O_4 .

Magnesium manganite with excess Magnesium.

Although further replacement of manganese by magnesium in the magnesium manganite lattice was inherently unlikely, as such substitutional solid solution would require some of the remaining manganese ions to become quadrivalent to maintain electrical neutrality, the possibility of the existence of such a solid solution was suggested by an investigation by H. v. Wartenberg and E. Prophet (Z. anorg. Chem., 1932, 208, 376), who pointed out that the system Mn_3O_4 -MgO showed a continuous gradation of solidification

point over the whole composition range, with no eutectic formation.

This possibility was put to the test by preparing a sample containing a 25 atom% excess of magnesium in the usual manner. Ignition at $1,400^{\circ}\text{C}$. for 14 hours, with a break after 2 hours for remixing and pressing, was followed by slow cooling during 42 hours.

The 19 cm. diffraction photograph contained only the lines of magnesium manganite and several extra lines whose d values corresponded with those of the strongest lines of magnesium oxide. Consequently, no solid solution of magnesium oxide in magnesium manganite had been brought about by the heat treatment used.

Calcium.

Before attempting the preparation of the manganite by the usual method of ignition of the oxide with basic manganese carbonate, a synthesis described by Rousseau (Compt. Rend., 1893, 116, 1061) was tried. 15 g. of calcium chloride and 3 g. of calcium carbonate were ignited with 2 g. of manganous chloride in porcelain at a dull red heat over a Bunsen burner for two hours. The cold mass was extracted with water and dried over

phosphorus pentoxide. The powder diffraction photograph was very diffuse, the only strong lines measurable with any accuracy being those of manganous manganic oxide. Analysis confirmed this observation, as the trivalent manganese comprised two thirds of the total amount of manganese present. Therefore no appreciable mixed oxide formation had taken place.

The usual method was then tried. Calcium oxide (Hopkin and Williams', a sample prepared from marble) and basic manganese carbonate, in the ratio Ca:Mn of 1:2, were mixed and ignited in air. After 4 hours at $1,150^{\circ}\text{C}.$, the temperature was reduced, first to $1,000^{\circ}\text{C}.$ and maintained for 12 hours, then to $900^{\circ}\text{C}.$ and the heating continued for a farther 12 hours. The product was rapidly air-cooled.

The absence of lines of calcium oxide and manganese oxides in the 9 cm. powder diffraction photograph showed that mixed oxide formation had occurred.

The specimen was re-ignited at $1,300^{\circ}\text{C}.$ for 4 hours and then allowed to cool slowly; the diffraction photograph of this re-ignited preparation was identical with the first pattern, showing that no further interaction had been brought about by the higher temperature used. The mixed oxide formation had therefore reached its limit at

the lower ignition temperature used first.

The sample was analysed for manganese and manganese as Mn^{III} .

Manganese.

Wt. taken.	Vol. 0.0981N. Fe^{II} used.	Manganese.
0.0982 g.	47.39 ml.	52.0%

Manganese as Mn^{III} .

Wt. taken.	Vol. 0.0960N. Thio used.	Manganese as Mn^{III} .
0.3710 g.	37.26 ml.	53.0%

Atom ratio, Ca : Mn : O
1 : 2 : 3.9

These results point to the formula $\text{CaMn}_2^{\text{III}}\text{O}_4$.

The 19 cm. powder diffraction photograph was more complex than those of the manganites hitherto studied. 49 lines were measured, and the pattern bore no qualitative resemblance to those of the previous manganites.

To obtain a diffraction photograph of improved quality, a compressed sample that had been again subjected to the heat treatment just described was photographed; much better definition was evident in this photograph.

The diffraction pattern could not be indexed with a hausmannite type cell, as was to be expected from its

qualitative dissimilarity from patterns of this structure. Furthermore, indexing on the basis of any dimetric cell has not been accomplished. It seems likely that the structure of calcium manganite is orthorhombic or one of lower symmetry still.

The values of intensity and d for the reflexions in the photograph are given below.

CALCIUM MANGANITE, CaMn_2O_4 .

Powder diffraction data.

Intensity	d.	Intensity	d.	Intensity	d.
1	2.989	2	1.551	3	1.144
2	2.855	6	1.489	3	1.118
7	2.695	9	1.473	10	1.076
2	2.545	0.5	1.430	3	1.066
1	2.485	0.5	1.417	3	1.048
4	2.277	3	1.357	1	1.031
10	2.218	2	1.349	4	1.024
2	2.165	1	1.327	4	1.019
6	2.060	0.5	1.313	2	1.009
1	1.876	0.5	1.298	10	0.9924
1	1.805	0.5	1.282	3	0.9798
1	1.656	0.5	1.267	4	0.9750
5	1.620	1	1.234		
2	1.605	2	1.180		
2	1.587	1	1.162		
5	1.569	1	1.152		

Strontium.

Strontium carbonate (Hopkin and Williams' "pure") was mixed with basic manganese carbonate in the atom ratio Sr:Mn of 1:2. The mixture was ignited in air at $1,300^{\circ}\text{C}$. for 8 hours and then air-cooled rapidly. Part of the product had fused, whilst the rest was sintered; the sintered portion was taken for subsequent examination. A high ignition temperature was used to minimise the formation of strontium peroxide, which is produced in quantity from the monoxide below red heat.

The 9 cm. diffraction photograph showed by the absence of recognisable lines the formation of a mixed oxide.

The sample was analysed for manganese and manganese as Mn^{III} .

Analysis.

Manganese.		
Wt. taken.	Vol. 0.0981N. Fe^{II} used.	Manganese.
0.0989 g.	36.88 ml.	40.2%

Manganese as Mn^{III} .		
Wt. taken.	Vol. 0.0960N. Thio. used.	Manganese as Mn^{III} .
0.3720 g.	33.00 ml.	46.8%

Atom ratio, Sr : Mn : O

1 : 2 : 4.7

The high oxygen content and the parallel increase in the valency of the manganese indicate the presence of a

mixed oxide containing about equal amounts of Mn^{III} and Mn^{IV} . Strontium peroxide proved to be absent, as a cold, dilute sulphuric acid extract of the sample failed to decolorise dilute potassium permanganate solution.

The 19 cm. diffraction photograph showed poor resolution so the sample was compressed and the previous ignition repeated. The photograph of this sample was of better quality, so it was taken for measurement. 47 lines were measured. The pattern bore a slight resemblance to that of calcium manganite, but insufficient to warrant the tentative conclusion that the two substances were isostructural.

In common with the previous manganite, the structure was not of the hausmannite type. The assignment of a dimetric structure to index the pattern has not been possible, and it is believed that lower symmetry is present.

The powder diffraction data for this mixed oxide are given on the next page.

STRONTIUM-MANGANESE MIXED OXIDE.Powder Diffraction Data.

Intensity	d.	Intensity	d.	Intensity	d.
2	3.26	5	1.852	6	1.268
2	3.00	1	1.830	2	1.253
3	2.931	0.5	1.739	0.5	1.217
1	2.856	0.5	1.695	3	1.198
10	2.707	2	1.653	1	1.165
2	2.535	1	1.629	2	1.152
1	2.456	6	1.566	2	1.139
1	2.412	4	1.531	1	1.131
0.5	2.317	1	1.515	2	1.096
0.5	2.282	2	1.480	1	1.060
1	2.265	0.5	1.466	3	1.051
1	2.219	0.5	1.450	2	1.045
2	2.125	3	1.436	9	1.027
9	2.082	0.5	1.407	3	1.018
1	2.046	0.5	1.397	5	0.9983
2	1.883	8	1.352		

Barium.

Amalar barium carbonate and basic manganese carbonate mixed in the ratio Ba: Mn of 1:2 and were heated in air at $1,200^{\circ}\text{C}$. for one hour and $1,000^{\circ}\text{C}$. for 12 hours. The product was remixed, compressed, and re-ignited at $1,300^{\circ}\text{C}$. for 12 hours and then slow-cooled to 800°C . over 4 days. This slow cooling was necessary to encourage crystallisation as a previous quenched sample gave no diffraction lines when examined by X-rays.

The specimen was analysed and a 9 cm. powder diffraction photograph was taken.

Analysis.

Manganese.

Wt. taken.	Vol. 0.0981N. Fe^{II} used.	Manganese.
0.1031 g.	32.46 ml.	33.9%

Manganese as Mn^{III} .

Wt. taken.	Vol. 0.0930N. Thio. used.	Manganese as Mn^{III} .
0.3966 g.	37.10 ml.	47.8%

Atom ratio, Ba : Mn : O
1 : 2 : 4.8

It is seen that the analytical results are analogous to those for the strontium mixed oxide, only the trends are now more pronounced. Much of the manganese, approaching half the total, must be present as Mn^{IV} to satisfy both the Bunsen and the total oxygen results. Barium peroxide was shown to be absent by the failure to decolorise permanganate of a cold, dilute sulphuric acid extract from the sample.

The 9 cm. photograph showed mixed oxide formation to have taken place, so a 19 cm. photograph was next taken. Double the usual 2 hours exposure time was necessary and even then the pattern was very faint against a heavy background.

The pattern showed a distinct resemblance to the one obtained from the strontium mixed oxide. As with the two previous manganites, the pattern could not be indexed as one of a dimetric structure.

Intensities and d values for the pattern follow.

BARIUM-MANGANESE MIXED OXIDE.

Powder Diffraction Data.

Intensity	d.	Intensity	d.	Intensity	d.
1	4.37	2	1.801	1	1.297
3	4.25	3	1.754	2	1.210
5	3.69	3	1.701	2	1.195
1	2.873	1	1.661	1	1.189
1	2.572	2	1.634	2	1.185
1	2.459	1	1.613	1	1.179
2	2.196	1	1.587	4	1.070
10	2.135	1	1.558	3	1.037
1	2.016	1	1.536	2	1.030
6	1.851	1	1.421	3	0.9864
1	1.824	3	1.413		

Section 6. CADMIUM MANGANITE.

Literature.

Apart from a remark in Dana ("System of Mineralogy", Vol.I, 7th. Ed., 1944, p.715), accompanied by no reference, that the cadmium analogue of zinc manganite exists, no work on this mixed oxide appears to have been published.

Experimental Work and Results.

Preparation of the mixed oxide was attempted by igniting the carbonate with manganic oxide.

Cadmium carbonate (Hopkin and Williams' "pure") was mixed with manganic oxide in the atom ratio Cd:Mn of 1:2. The mixed reactants were ignited in air at $900^{\circ}\text{C}.$ for 24 hours; the temperature was then raised to $1,000^{\circ}\text{C}.$, and the ignition continued for a further 8 hours, after which the product was cooled rapidly in air. It was necessary to limit the ignition temperature to $1,000^{\circ}\text{C}.$, as above this temperature cadmium oxide volatilises and decomposes. Because of this temperature limitation, manganic oxide was used instead of the carbonate.

The 9 cm. powder diffraction photograph of the sample showed the absence of lines of cadmium oxide and the oxides of manganese; thus mixed oxide formation had taken place. The 19 cm. photograph, for which it was found necessary to use an exposure of four hours instead of the usual two,

was diffuse, with no measurable high-angle lines. Early attempts to index this picture were unsuccessful.

The mixed oxide was next compressed and subjected to the same heat treatment used in the first instance.

The manganese content, and manganese as Mn^{III} were determined.

Analyses.

Manganese.

Wt. taken.	Vol. 0.0981N. Fe^{II} used.	Manganese.
0.1066 g.	38.37 ml.	38.8%

Manganese as Mn^{III} .

Wt. taken.	Vol. 0.0930N. Thio. used.	Manganese as Mn^{III} .
0.4055 g.	30.58 ml.	38.5%

These results agree well with the manganese required by the formula $\text{CdMn}_2^{\text{III}}\text{O}_4$, namely 38.4%.

The 19 cm. powder diffraction photograph obtained from this compressed specimen was of much better quality than the previous one. Indexing was accomplished, the hausmannite type of structure being revealed. 27 of the 31 lines present were thus indexed, giving constants of $a = 5.808 \pm 0.003$ and $c = 9.765 \pm 0.003$ kx units for the unit cell. 3 of the 4 faint remaining lines belonged to

manganic oxide, hence about 5% had remained unreacted, but the last faint line, a very low angle one, could not be identified.

The tabulated powder diffraction data for cadmium manganite are given below.

CADMIUM MANGANITE, CdMn_2O_4 .

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed	hkl.	$\sin^2 \theta$ calc.	d.	Extra lines.
1	7.19	0.0157			7.72	?
2	8.50	0.0218			6.54	Mn_2O_3
6	17.96	0.0951	112	0.0946	3.13	
0.5	19.47	0.1111	200	0.1108	2.897	
3	19.93	0.1162	103	0.1159	2.834	
10	22.65	0.1483	211	0.1483	2.508	
1	28.47	0.2272	213	0.2267	2.026	
0.5	30.65	0.2599	301	0.2591	1.895	
2	31.16	0.2678	204	0.2676	1.867	
3	31.43	0.2720	105	0.2727	1.852	
3	34.25	0.3168	312	0.3162	1.716	
1	35.55	0.3380	303	0.3375	1.664	
4	37.52	0.3709	321	0.3699	1.596	
10	38.02	0.3792	224	0.3784	1.569	
1	39.74	0.4087	116	0.4082	1.510	
5	41.78	0.4440	400	0.4432	1.464	
0.5	44.72	0.4952	305	0.4943	1.373	
4	48.38	0.5589	413	0.5591	1.292	
2	51.87	0.6188	127	0.6187	1.229	
3	52.51	0.6296	316	0.6298	1.218	
2	57.50	0.7113	424	0.7108	1.146	
5	57.83	0.7164	415	0.7159	1.141	
0.5	59.40	0.7408			1.123	Mn_2O_3
1	60.65	0.7598	512	0.7594	1.108	
2	62.11	0.7811	503	0.7807	1.093	
1	64.41	0.8134	521	0.8131	1.071	
2	66.40	0.8397	327	0.8403	1.054	
1	67.35	0.8517	336	0.8514	1.047	
3	74.90	0.9321	129	0.9323	1.001	
4	75.57	0.9377	505	0.9375	0.9982	
2	82.30	0.9820			0.9754	Mn_2O_3

Lattice Constants.

Hausmannite type cell, $a = 5.808 \pm 0.003$

$c = 9.765 \pm 0.003$ kX units.

Section 7. MIXED OXIDES OF MANGANESE

WITH

IRON, COBALT, AND NICKEL.

Literature.

Only the mixed oxides of iron with manganese have been studied at all thoroughly. B. J. V. Verwey and H. G. van Bruggen (Z. Krist., 1935, 92, 135-138) investigated the structure of solid solutions of ferric oxide and manganous manganic oxide. A continuous range of solid solution was found, the tetragonal hausmannite structure of manganous manganic oxide persisting, as the iron content increased, with decreasing c/a ratio until, at the atom ratio of Mn:Fe of 3:2, the ratio became unity and the face-centred cube of the spinel structure replaced the hausmannite cell. The spinel structure was present in all mixtures richer in iron than 40%.

V. Montoro (Gazz. chim. Ital., 1938, 68, 728-733) heated mixtures of ferrous ferric oxide and manganous manganic oxide to $1,200^{\circ}\text{C}$. under unspecified conditions. He found that the structure change occurred at a composition different from that found by Verwey and van Bruggen. Both mixtures of iron and manganese oxides in the atom ratio 2:1 and 1:2 had spinel cube unit cells, whilst mixtures richer in manganese than 66.7% had a hausmannite structure with a small c/a ratio.

Although Montoro started off with ferrous ferric oxide

in his preparation, this would have been oxidized to ferric oxide in air on heating, so his products were the same as those of the first two workers. Indeed, Montoro remarked that, on slow cooling the mixed oxides, some ferric oxide was formed.

A recent paper on the high temperature X-ray study of the Fe_3O_4 - Mn_3O_4 system has been published by H. F. McMurdie, B. M. Sullivan, and F. A. Mauer (J. Res. Nat. Bur. Stand., 1950, 45, 35-41). The findings of Verwey and van Bruggen, including the spinel structure limit of 60% manganese, were confirmed at room temperatures. In the temperature range 380° - 1170°C ., the mixtures of oxides with compositions above 60% manganese were found to be partly miscible. On heating a sample with a tetragonal structure - i.e. a sample containing more than 60% manganese - a temperature was reached when a cubic phase of the spinel type started to form. This cubic phase was in equilibrium with the tetragonal phase over a range of temperatures, the amount of cubic phase increasing with increase in temperature. Eventually a temperature was reached when the spinel phase only was present, which persisted up to the melting point of the mixed oxide.

A cobalt manganite, of composition $(\text{Mn}, \text{Co})\text{O} \cdot (\text{Mn}, \text{Co})_2\text{O}_3$,

was prepared by S. Holgersson and A. Karlsson (Z. anorg. Chem., 1929, 183, 384-394) by igniting the mixed nitrates at 800° - 850° C. This mixed oxide had a spinel structure, with $a = 8.108$ A.

Prevel, in his list of spinels (Ind. Eng. Chem., Anal. Ed., 1942, 14, 690), gives the value for the cell edge of the cobalt manganite formulated above as 8.27 A.

Nickel manganite, NiMn_2O_4 , is given a constant of 8.38 A. in this list of spinels; no references are made to the sources of these values.

Experimental Work and Results.

As a standard for comparison with results from cobalt and nickel mixed oxides, and to check the composition of the spinel to hausmannite transition, a representative set of iron and manganese mixed oxides was prepared first.

For each of the three metals, a series of three compositions was taken, with ratios metal:manganese of 2:1, 1:2, and 1:4; these covered the transition point in the iron-manganese series, spinel $\rightarrow$ hausmannite structure, and also gave manganese-rich specimens to ascertain the solubility of manganous manganic oxide in the manganite in question.

Iron.

Ferrous ferric oxide was mixed with manganous manganic oxide to give three products with the iron and the manganese in the ratios just given. The ferrous ferric oxide was prepared by heating to redness iron (carbonyl) and ferric oxide in the correct proportion in nitrogen; the ferric oxide used was prepared by dissolving iron (carbonyl) in nitric acid (Analar), evaporating, and igniting the ferric nitrate left. The manganous manganic oxide was formed by igniting basic manganese carbonate in air at $1,100^{\circ}\text{C}$.

These mixed oxides were ignited in air for one hour at $1,200^{\circ}\text{C}$., and then rapidly air-cooled.

The three samples were analysed for manganese and manganese as Mn^{III} .

Analyses.

Manganese.

Sample:	Wt. taken.	Vol. 0.1004N. Fe^{II} used.	Manganese.
Fe:Mn :: 2:1	0.1129 g.	23.22 ml.	22.7%
" 1:2	0.0994 g.	41.93 ml.	46.5%
" 1:4	0.0999 g.	50.33 ml.	55.6%

Manganese as Mn ^{III}			
Sample:	Wt. taken.	Vol. 0.0958N. Thio used.	Manganese as Mn ^{III} .
Fe:Mn :: 2:1	0.3905 g.	2.40 ml.	3.2%
1:2	0.4029 g.	18.80 ml.	24.6%
1:4	0.3967 g.	24.96 ml.	33.1%

The formula MnFe_2O_4 requires.....23.8% manganese

" " FeMn_2O_4 " 46.5% "

" " $\text{FeMn}_2\text{O}_4 + 2/3\text{Mn}_3\text{O}_4$ requires 56.7% "

The results of the manganese analyses show good agreement with the theoretical requirements for the formulae given. The small Mn^{III} content in the 2:1 specimen, which should all be Mn^{II}, may be accounted for by the presence of a little manganous manganic oxide, as some uncombined ferric oxide was observed from the diffraction photograph to be present. The 1:2 sample requires all the manganese to be present as Mn^{III}. However, the chlorine liberated by the Mn^{III} in the determination would first oxidise all the Fe^{II} to Fe^{III}, before any passed into the potassium iodide solution. If this preliminary iron oxidation be allowed for, the percentage of Mn^{III} becomes 48.0, which is then similar to the figure for total manganese. In the 1:4 sample also allowing for this initial iron oxidation, the percentage becomes

46.8, compared with the $46.2 \text{ Mn}^{\text{III}}$ required by the total manganese determination, less the Mn^{II} present in the excess manganous manganic oxide.

Powder diffraction photographs of these three samples were very diffuse. It was possible to index most of the lines of the 2:1 and 1:2 pictures on a spinel cell, and the 1:4 on a hausmannite unit. Several lines were unaccounted for, so reaction appeared to be incomplete. These specimens were thus compressed, reheated in air at $1,200^{\circ}\text{C}$. for two hours, and 19 cm. diffraction photographs taken. All the lines of the 1:2 and 1:4 samples were accounted for this time; the 1:2 sample had a spinel unit, with $a = 8.511 \pm 0.002 \text{ kX units}$, while the 1:4 had the hausmannite type tetragonal cell, with $a = 5.836 \pm 0.003$ and $c = 9.102 \pm 0.003 \text{ kX units}$. 9 faint lines in the pattern of the 2:1 specimen belonged to ferric oxide, although the rest of the pattern was that of a spinel, so the sample was reheated at $1,450^{\circ}\text{C}$. in air for two hours. This time all the lines were those of a spinel, with $a = 8.433 \pm 0.003 \text{ kX units}$.

Both the 2:1 and 1:2 specimens were strongly ferromagnetic, but not the 1:4 mixed oxide.

The preceding results for the iron-manganese mixed oxides may be summarised briefly thus:-

Composition. Fe : Mn	Formula.	Unit cell type.	Lattice constants.	
			a	c kX units
2 : 1	$\text{Mn}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$	Spinel	8.433 ± 0.003	-
1 : 2	$\text{Fe}^{\text{II}}\text{Mn}_2^{\text{III}}\text{O}_4$	spinel	8.511 ± 0.002	-
1 " 4	" + $2/3\text{Mn}_3\text{O}_4$	Haus- mannite	5.836 ± 0.003	9.102 ± 0.003

Montoro's finding (loc.cit.) is thus corroborated, in that the 1:2 iron to manganese ratio mixture is a spinel, whilst the other workers mentioned, who found the spinel to hausmannite change to take place when the manganese content had reached 60%, seem to be in error over this point. It may be, though, in view of the findings of McMurdie, Sullivan, and Mauer (loc.cit.) that the 1:2 mixed oxide had a spinel structure at high temperatures, and that this structure has been "frozen" by the rapid cooling of the sample after ignition.

Montoro's lattice constants for the three compositions were:-

Fe:Mn ::	2:1	8.472
"	1:2	8.490
"	1:4	a = 5.856, c = 9.067.

Powder diffraction data for the three mixed oxides are recorded on the next three pages.

MANGANESE FERRITE, MnFe_2O_4 , Air Cooled from $1,450^\circ\text{C}$.

<u>Powder Diffraction Data.</u>					
Intensity.	θ	$\sin^2\theta$ observed.	hkl.	$\sin^2\theta$ calc.	d.
2	11.49	0.0396	111	0.0394	4.85
4	13.96	0.1055	220	0.1051	2.975
10	22.40	0.1452	311	0.1445	2.535
0.5	23.47	0.1586	222	0.1577	2.426
4	27.35	0.2111	400	0.2102	2.103
1	34.24	0.3166	422	0.3154	1.717
6	36.62	0.3558	333	0.3548	1.618
8	40.48	0.4214	440	0.4205	1.488
0.5	46.59	0.5278	620	0.5256	1.329
2	48.78	0.5658	533	0.5550	1.284
0.5	49.59	0.5798	622	0.5782	1.263
1	52.62	0.6314	444	0.6307	1.216
2	59.13	0.7368	642	0.7358	1.126
5	61.73	0.7756	553	0.7753	1.097
2	66.51	0.8412	800	0.8410	1.053

Lattice Constant.

spinel unit cell, $a = 8.433 \pm 0.003$ kX units.

IRON MANGANITE, FeMn_2O_4 .

Powder Diffraction Data.

Intensity.	θ	$\sin^2\theta$ observed.	hkl.	$\sin^2\theta$ calc.	d.
2	11.36	0.0388	111	0.0387	4.90
4	18.78	0.1036	200	0.1032	3.00
10	22.17	0.1423	311	0.1419	2.560
1	23.20	0.1552	222	0.1548	2.452
5	27.07	0.2070	400	0.2064	2.124
2	33.83	0.3100	422	0.3096	1.735
7	36.21	0.3490	333	0.3483	1.635
9	40.00	0.4132	440	0.4129	1.503
0.5	42.23	0.4517	531	0.4516	1.437
0.5	45.95	0.5166	620	0.5161	1.344
4	48.16	0.5551	533	0.5548	1.296
1	48.91	0.5681	622	0.5677	1.281
2	51.89	0.6192	444	0.6193	1.228
1	58.23	0.7228	642	0.7225	1.137
$\alpha_1 \alpha_2^7$	60.77	0.7616	553	0.7612	1.107
1	65.32	0.8257	800	0.8257	1.063
0.5	74.57	0.9291	660	0.9289	1.003
$\alpha_1 \alpha_2^8$	79.64	0.9677	555	0.9677	0.9820
1	82.11	0.9811	662	0.9806	0.9757

Lattice Constant.

Spinel unit cell, $a = 8.511 \pm 0.002$ Å units.

IRON MANGANITE CONTAINING EXCESS MANGANESE

Fe : Mn : 1 : 4

Powder Diffraction Data.

Inten- sity.	θ	$\sin^2 \theta$	hkl.	$\sin^2 \theta$ calc.	d.
2	11.32	0.0383	101	0.0387	4.92
3	18.43	0.0999	112	0.1000	3.05
1	19.28	0.1091	200	0.1098	2.926
4	21.07	0.1292	103	0.1290	2.688
10	22.67	0.1485	211	0.1485	2.506
1	23.18	0.1549	202	0.1549	2.454
1	25.14	0.1804	004	0.1805	2.274
3	27.94	0.2196	220	0.2195	2.062
1	33.74	0.3089	105	0.3094	1.738
1	34.44	0.3198	312	0.3195	1.709
1	36.19	0.3487	303	0.3485	1.636
3	37.35	0.3680	321	0.3680	1.592
9	39.24	0.4003	224	0.4000	1.527
2	41.49	0.4390	400	0.4390	1.458
2	48.93	0.5684	413	0.5680	1.281
0.5	50.42	0.5941	422	0.5932	1.253
2	51.91	0.6195	404	0.6195	1.228
2	59.91	0.7487	415	0.7485	1.117
1	62.58	0.7880	503	0.7875	1.088
2	69.61	0.8786	440	0.8781	1.031
3	79.47	0.9680	505	0.9680	0.9826

Intense Constants

Reckonante type unit cell, $a = 5.836 \pm 0.003$

$c = 9.102 \pm 0.003$ KX units.

Cobalt.

The cobalt oxide available for the preparations (Hopkin and Williams' "para"), which consisted mainly of Co_3O_4 , was first analysed.

Determination of Cobalt in Cobalt Oxide.

About 0.5 g. of the sample was weighed in a silica boat, ignited in air at 750°C . for 48 hours, cooled and reweighed as Co_3O_4 .

Wt. of sample taken.	Wt. of ignited sample.	% Cobalt.
0.4441 g.	0.4149 g.	68.6%

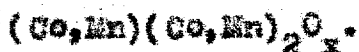
The cobalt oxide was mixed with basic manganese carbonate in the proportions necessary to give products containing cobalt and manganese in the three specified ratios. These mixtures were ignited in air at $1,200^\circ\text{C}$. for one hour and then at $1,100^\circ\text{C}$. for 15 hours. The ignited mixtures were next compressed and reheated at $1,150^\circ\text{C}$. for a further 16 hours, when the charges were removed from the furnace and air-cooled.

Owing to the fact that manganese cannot be determined by the bismuthate method in the presence of cobalt, the oxygen contents of the mixed oxides were found by determining the weight loss on ignition. An early attempt to analyse the mixed oxides by precipitating the cobalt

with α -nitroso- β -naphthol, converting to the sulphate and weighing, proved unsuccessful.

Sample.	Wt. of mixture before ignition.	Wt. after ignition.	Wt. of Co-Mn present	Wt. of oxygen.
2 : 1	4.3803 g.	3.6007 g.	2.599 g.	1.002 g.
1 : 2	3.6748 g.	2.6968 g.	1.913 g.	0.784 g.
1 : 4	6.4497 g.	4.6256 g.	3.191 g.	1.435 g.

The tervalent manganese could not be determined by the Hansen method, as tervalent cobalt also oxidises hydrochloric acid; all the mixed oxides had thus to be formulated



The oxygen contents of the three mixed oxides correspond with the respective formulae: $(\text{Mn}, \text{Co})(\text{Co}, \text{Mn})_2\text{O}_4$.



The 19 cm. diffraction photograph of the 2:1 cobalt to manganese mixed oxide contained only the lines of a spinel. The lattice constant was 8.265 ± 0.003 kÅ units (Prevel (loc.cit.) gives 8.27 as the constant). The pattern of the 1:2 specimen showed this mixed oxide to possess a hausmannite type structure. All the lines were indexed, resulting in a unit cell with constants $a = 5.72$ and $c = 9.24$ kÅ units. The manganese-excess mixed oxide picture was more sharply defined than the other two. A similar sized hausmannite unit cell was present, with the c dimension somewhat larger. The lattice constants were

$a = 5.726 \pm 0.003$ and $c = 9.324 \pm 0.003$ kX units.

Diffraction data for the three mixed oxides follow.

COBALT-MANGANESE MIXED OXIDE, $(\text{Mn}, \text{Co})(\text{Co}, \text{Mn})_2\text{O}_4$.

Co : Mn :: 2 : 1

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed.	hkl.	$\sin^2 \theta$ calc.	d.
1	11.72	0.0412	111	0.0410	4.75
4	19.36	0.1099	220	0.1094	2.914
10	22.87	0.1510	311	0.1505	2.486
1	23.96	0.1648	222	0.1642	2.378
3	27.95	0.2197	400	0.2189	2.062
2	35.03	0.3295	422	0.3283	1.683
7	37.49	0.3703	333	0.3694	1.587
8	41.48	0.4387	440	0.4378	1.458
1	47.76	0.5482	620	0.5472	1.305
3	50.15	0.5893	533	0.5882	1.258
1	50.96	0.6033	622	0.6019	1.243
3	61.08	0.7663	642	0.7561	1.104
7	63.95	0.8073	553	0.8071	1.075
3	69.31	0.8752	800	0.8755	1.033

Lattice Constant.

Spinel unit cell, $a = 8.265 \pm 0.003$ kX units.

COBALT-MANGANESE MIXED OXIDE, (Co,Mn)(Mn,Co)₂O₄.

Co : Mn :: 1 : 2

Powder Diffraction Data.

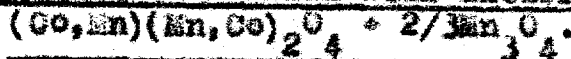
Intensity.	θ	$\sin^2 \theta$ observed.	hkl.	$\sin^2 \theta$ calc.	d.
1	11.53	0.0399	101	0.0396	4.83
3	13.60	0.1017	112	0.1010	3.03
2	19.83	0.1150	200	0.1144	2.848
5	20.95	0.1279	103	0.1272	2.702
10	23.18	0.1549	211	0.1540	2.455
1	24.83	0.1763	004	0.1752	2.301
3	28.64	0.2300	220	0.2289	2.015
1	32.63	0.2908	204	0.2896	1.792
2	33.42	0.3033	105	0.3024	1.754
3	35.14	0.3314	312	0.3299	1.678
1	36.72	0.3575	303	0.3560	1.615
6	38.27	0.3835	321	0.3829	1.561
9	39.53	0.4050	224	0.4041	1.518
5	42.65	0.4590	400	0.4578	1.426
2	49.94	0.5858	413	0.5849	1.262
1	52.84	0.6352	404	0.6330	1.212
1	55.51	0.6793	127	0.6796	1.172
1	60.68	0.7603	415	0.7601	1.108
3	64.44	0.8138	503	0.8138	1.071

Lattice Constants.

Heusmannite type unit cell, $a = 5.72$

$c = 9.24$ kx units.

COBALT-MANGANESE MIXED OXIDE WITH EXCESS MANGANESE,



Co : Mn :: 1 : 4.

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed.	hkl.	$\sin^2 \theta$ calc.	d.
1	11.47	0.0395	101	0.0393	4.86
3	13.49	0.1005	112	0.1000	3.05
2	19.79	0.1146	200	0.1140	2.854
8	20.78	0.1258	103	0.1253	2.723
10	23.10	0.1539	211	0.1533	2.462
2	24.56	0.1728	004	0.1720	2.324
4	28.56	0.2285	220	0.2280	2.020
1	32.38	0.2858	204	0.2850	1.804
4	33.09	0.2980	105	0.2973	1.769
2	35.00	0.3290	312	0.3280	1.684
1	36.52	0.3541	303	0.3533	1.623
7	38.18	0.3820	321	0.3813	1.563
10	39.28	0.4009	224	0.4000	1.524
0.5	41.83	0.4448	116	0.4440	1.449
5	42.52	0.4567	400	0.4560	1.429
1.	46.48	0.5257	305	0.5253	1.332
0.5	48.27	0.5569	332	0.5560	1.294
0.5	49.04	0.5701	420	0.5700	1.279
4	49.71	0.5819	413	0.5813	1.266
0.5	51.54	0.6132	422	0.6130	1.234
2	52.45	0.6286	404	0.6280	1.219
3	54.98	0.6706	127	0.6693	1.180
2	56.07	0.6884	008	0.6880	1.165
1	59.48	0.7422	424	0.7420	1.122
4	60.23	0.7535	415	0.7533	1.113
1	62.29	0.7839	512	0.7845	1.091
6	64.09	0.8091	503	0.8098	1.074
2	66.22	0.8374	521	0.8378	1.064
5	71.31	0.8973	327	0.8973	1.020
$\propto 1^{\circ} 2^{\circ}$	72.80	0.9126	440	0.9120	1.011
$\propto 1^{\circ} 2^{\circ}$	82.23	0.9817	505	0.9818	0.9750

Lattice Constants.

Hausmannite type unit cell, $a = 5.726 \pm 0.003$

$c = 9.324 \pm 0.003$ kX units.

Nickel.

Mixtures of the three compositions were prepared from nickel oxide and basic manganese carbonate. The nickel oxide was prepared by igniting nickel carbonate (Hopkin and Williams' "pure"), of uncertain composition, at 900°C . for an hour. The nickel content of the product was determined by the dimethylglyoxime method.

Determination of nickel in nickel oxide.

About 0.1 g. of the sample was dissolved in 20 ml. of concentrated hydrochloric acid and 5 ml. of concentrated nitric acid by boiling for 5 minutes, diluting and further boiling until the solution was clear. The solution was made up to 250 ml. and 25 ml. taken for the determination. This volume was diluted to 150 ml., made slightly alkaline with aqueous ammonia, then just acid with hydrochloric acid and heated to 80°C . 20 ml. of 1% alcoholic solution of dimethylglyoxime were added slowly at this temperature. The mixture was again made just alkaline with aqueous ammonia, stirred, and allowed to stand for an hour. The precipitated nickel dimethylglyoxime complex was collected on a No. 4 sintered glass filter crucible and dried at 100°C . to constant weight.

The three mixtures were ignited in air at $1,200^{\circ}\text{C}$. for

an hour, removed, powdered, remixed, and reheated at $1,100^{\circ}\text{C}$. for 12 hours, followed by rapid air cooling.

Very diffuse diffraction photographs were obtained from these samples. The pattern from the nickel-rich specimen, except for one line, was that of nickel oxide. The other two preparations gave patterns of a spinel type, but several lines could not be accounted for. Both showed the stronger nickel oxide lines.

The three samples were then compressed and the heat treatment repeated.

Analyses.

Manganese.			
Sample:	Wt. taken.	Vol. 0.1004N. Fe^{II} used.	Manganese.
Ni:Mn :: 2:1	0.0994 g.	20.66 ml.	22.9%
" 1:2	0.1022 g.	41.74 ml.	45.0%
" 1:4	0.1002 g.	49.45 ml.	54.4%

Manganese as Mn^{III} .			
Sample:	Wt. taken.	Vol. 0.0930N. Thio. used.	Manganese as Mn^{III} .
Ni:Mn :: 2:1	0.2237 g.	8.34 ml.	19.0%
" 1:2	0.2451 g.	18.82 ml.	39.2%
" 1:4	0.2604 g.	23.72 ml.	46.5%

The high figure for the Mn^{III} in the 2:1, and the low value in the 1:2 sample indicated that mixed oxide formation was far from complete in these two samples. Reaction

seemed to be complete in the 1:4 preparation, however, as the theoretical Mn^{III} content for $\text{NiMn}_2^{\text{III}}\text{O}_4 + 2/3\text{MnO}, \text{Mn}_2\text{O}_3$ is 45.0%.

These observations on the analyses were supported by the evidence of the diffraction photographs. The strength of the nickel oxide lines in the photograph of the 2:1 nickel to manganese specimen indicated the presence of more than 50% free nickel oxide in the specimen; all the other lines conformed with a spinel cell, with $a = 8.41$ kX units. In the 1:2 mixture, about half the nickel oxide was still uncombined; again the remainder of the lines were those of a spinel, with $a = 8.422 \pm 0.003$ kX units. Only one faint line of nickel oxide was observed in the photograph of the manganese-rich sample, but even with this excess of manganese, the cubic symmetry of a spinel was maintained, the cell edge now becoming 8.427 ± 0.003 kX units.

An attempt was made to increase the extent of solid solution by heating the three mixtures to $1,450^\circ\text{C}$. for two hours in air, but this resulted only in the formation of mixed oxides of the type NiO, MnO . These mixed oxides have the simple cubic cell of rock salt. Apart from three faint lines of manganous manganic oxide, all the lines present in these three photographs were accounted for by

this simple cubic cell.

The diffraction data for the three photographs of the compressed, partly reacted series follows.

NiO-Mn₃O₄, Partial Mixed Oxide Formation.

Ni : Mn :: 2 : 1.

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed.	hkl.	$\sin^2 \theta$ calc.	d.	Lines of:-
1	19.01	0.1061	220	0.1056	2.986	Spinel.
3	22.48	0.1462	311	0.1452	2.547	"
5	23.71	0.1616			2.403	NiO
10	27.66	0.2154			2.081	"
1	34.36	0.3186	422	0.3168	1.712	Spinel.
2	36.73	0.3577	333	0.3564	1.614	"
2	40.61	0.4237	440	0.4224	1.484	"
9	40.99	0.4302			1.473	NiO
1	48.98	0.5693	533	0.5676	1.280	Spinel.
7	50.22	0.5906			1.257	NiO
5	53.37	0.6438			1.204	"
2	62.02	0.7798	553	0.7788	1.094	Spinel.
6	67.85	0.8578			1.086	NiO
2	83.74	0.9894	555	0.9900	0.9718	Spinel.

Lattice Constant.

Spinel unit cell, $a = 8.41$ kX units.

NiO-Mn₃O₄: Extensive Mixed Oxide Formation.

Ni : Mn :: 1 : 2

Powder Diffraction Data

Intensity.	θ	$\sin^2 \theta$ observed.	hkl.	$\sin^2 \theta$ calc.	d.	Other lines.
2	11.50	0.0397	111	0.0395	4.54	
3	19.00	0.1059	220	0.1054	2.968	
10	22.42	0.1454	311	0.1448	2.534	
2	23.65	0.1609			2.408	NiO
5	27.38	0.2115	400	0.2108	2.101	
5	27.63	0.2150			2.083	NiO
2	34.27	0.3170	422	0.3162	1.715	
8	36.65	0.3564	333	0.3557	1.618	
10	40.51	0.4220	440	0.4216	1.438	
2	40.93	0.4293			1.475	NiO
0.5	42.80	0.4616	531	0.4611	1.422	
1	46.60	0.5280	620	0.5270	1.329	
4	48.84	0.5668	533	0.5665	1.283	
1	49.61	0.5801	622	0.5797	1.268	
2	50.18	0.5898			1.257	NiO
2	52.68	0.6324	444	0.6324	1.215	
2	53.30	0.6428			1.205	NiO
1	55.08	0.6722	551	0.6719	1.179	
2	59.19	0.7377	642	0.7378	1.125	
9	61.84	0.7773	553	0.7773	1.096	
3	66.65	0.8429	800	0.8432	1.052	
1	67.84	0.8527			1.043	NiO
2	76.91	0.9492	660	0.9486	0.9926	
$\alpha_1 \alpha_2$	83.85	0.9885	555	0.9880	0.9716	

Lattice Constant.

spinel unit cell, $a = 8.422 \pm 0.003$ kX units.

NICKEL MANGANITE, NiMn_2O_4 , with Excess MANGANESE.

Ni : Mn :: 1 : 4.

Powder Diffraction Data.

Intensity.	θ	$\sin^2 \theta$ observed.	hkl.	$\sin^2 \theta$ calc.	d.	Other lines.
2	11.53	0.0399	111	0.0395	4.84	
3	19.03	0.1063	220	0.1053	2.964	
10	22.47	0.1460	311	0.1448	2.528	
1	23.52	0.1592			2.421	h10
5	27.41	0.2120	400	0.2106	2.098	
3	34.30	0.3175	422	0.3158	1.714	
8	36.68	0.3568	333	0.3553	1.617	
10	40.54	0.4224	440	0.4212	1.487	
1	42.84	0.4622	531	0.4607	1.421	
1	46.58	0.5276	620	0.5264	1.330	
5	48.85	0.5670	533	0.5659	1.283	
2	49.64	0.5805	622	0.5790	1.267	
3	52.67	0.6322	444	0.6317	1.215	
1	55.07	0.6721	551	0.6712	1.179	
4	59.17	0.7374	642	0.7370	1.125	
9	61.80	0.7767	553	0.7764	1.096	
5	66.62	0.8425	800	0.8422	1.053	
$\alpha_1 \alpha_2^2$	76.74	0.9474	660	0.9475	0.9925	
$\alpha_1 \alpha_2^{10}$	83.32	0.9865	555	0.9870	0.9726	

Lattice Constant.

spinel unit cell, $a = 8.427 \pm 0.003$ kx units.

Section 8. SUMMARY OF RESULTS AND DISCUSSION.

Element.	Ratio R:Mn	Formula.	Symmetry.	Lattice Constants. in kX units.			c/a/2 ratio	Cell volume (a ³ or 2a ² c)	Ionic radius of element (Pauling).
				a.	a/2.	c.			
Lithium	1:1	LiMnO ₂	L				-	-	0.60
Sodium	1:1	in air, some lower mixed oxide formed. in nitrogen, mixed oxide not formed.					-	-	0.95
Potassium	1:1	"	"				-	-	1.33
Copper	1:2	in O ₂ CuMn ₂ O ₄	S	8.29		-	1	570	0.8 ^{II} (Cu ^{II})
	1:1.3	" " " " + CuO	S	8.303		-	1	573	
	1.8:1	" " " " + CuO	S	8.304		-	1	573	
Beryllium	1:2	mixed oxide not formed.							0.31
Magnesium	1:2	MgMn ₂ O ₄	H	5.710	8.074	9.298	1.15	606	0.65
Calcium	1:2	CaMn ₂ O ₄	L				-	-	0.99
Strontium	1:2	(SrMn ₂ O ₄)	L				-	-	1.13
Barium	1:2	?	L				-	-	1.35
Zinc	1:2	ZnMn ₂ O ₄	H	5.710	8.074	9.225	1.14	603	0.74
Cadmium	1:2	CdMn ₂ O ₄	H	5.808	8.213	9.765	1.19	660	0.97
Iron	2:1	MnFe ₂ O ₄	S	8.433		-	1	599	0.60(Fe ^{III}) 0.75(Fe ^{II})
	1:2	FeMn ₂ O ₄	S	8.511		-	1	617	
	1:4	" " " " + Mn ₃ O ₄	H	5.836	8.252	9.102	1.10	620	
Cobalt	2:1	(Mn, Co)(Co, Mn) ₂ O ₄	S	8.265		-	1	565	0.72(Co ^{II})
	1:2	(Co, Mn)(Mn, Co) ₂ O ₄	H	5.72	8.09	9.24	1.14	605	
	1:4	" " " " + Mn ₃ O ₄	H	5.726	8.098	9.324	1.15	611	
Nickel	2:1	partial formation	S	8.41		-	1	-	0.70(Ni ^{II})
	1:2	"	S	8.422		-	1	-	
	1:4	NiMn ₂ O ₄ + Mn ₃ O ₄	S	8.427		-	1	598	
Manganese (bivalent)	1:2	Mn ^{II} Mn ^{III} ₂ O ₄	H	5.75	8.13	9.42	1.16	623	0.80(Mn ^{II}) 0.62(Mn ^{III})

S = spinel structure.
H = hausmannite "
L = lower than dimetric.

* F. Ephraim, "Inorganic Chemistry"
5th Ed., 1948, p.36

It may be seen from the Table of Results that the manganites generally possess one of two structures, the hausmannite or the spinel type.

The hausmannite structure is analogous to the spinel structure of ferrous ferrite (Aminoff, *Z. Krist.*, 1926, 64, 475) and, indeed, hausmannite assumes the spinel structure above $1,170^{\circ}$ (H. P. McMurdie and E. Colovato, *J. Res. Nat. Bur. Stand.*, 1948, 41, No. 6, 589-600). One of the otherwise cubic spinel edges is greater than the other two edges in this structure. The large face-centred tetragonal cell so formed is more simply described by a body-centred tetragonal cell of half the volume, the a dimension of which is $1/\sqrt{2}$ times that of the spinel analogue. Thus the unit cell of hausmannite contains $\text{Mn}_4^{\text{II}} \text{Mn}_8^{\text{III}} \text{O}_{16}$, with the four Mn^{II} ions in the four particular tetrahedral holes and the eight Mn^{III} ions in the eight particular octahedral holes of a close-packed oxygen lattice, originally cubic, which is slightly expanded along the c direction and compressed along the two a directions. This distortion is evidence of an appreciable covalent contribution present in the mainly ionic Mn - O bonds, which would tend to cause distortion from cubic symmetry by the directed nature of such bonding. Verwey

and van Bruggen (Z. Krist., 1935, 92, 136-138) attribute this tetragonal distortion to the non-spherical symmetry of the manganese ions.

Replacement of the Mn^{II} ions by the ions of other metals should change the cell volume by reason of the change in ion size, and also the c/a ratio with the variation in covalent contribution to the bonding. Both these expected changes were present in the manganites investigated.

Considering first the effect of the size of the ion replacing Mn^{II} , the following results are observed.

Replacing ion.	Ionic radius.	Cell volume.
Mn^{II}	0.65	606
Ni^{II}	0.70	<600
Co^{II}	0.72	605
Zn^{II}	0.74	603
Fe^{II}	0.75	617
(Cu^{II})	0.8	573)
Mn^{II} (in Mn_3O_4)	0.80	623
Cd^{II}	0.97	660

The general trend of increased volume with ion size is well shown. Magnesium is anomalous, and it will be seen later that the cell c/a ratio for magnesium manganite also does not conform with the general trend. It may be that there is a more than usual covalent contribution in the Mg - O bonds, as compared with the rest of the

series. In this connexion it is of interest to note that the "tetrahedral" radius for Mg^{II} is 1.40 (Pauling, "The Nature of the Chemical Bond," Cornell, 1945), which comes above that for Zn^{II} , 1.31.

The fact that cobalt manganite has a somewhat larger cell than the radius of the Co^{II} ion would suggest may be accounted for by part replacement of the Co^{II} by Mn^{II} , of radius 0.80, a possibility that has been referred to previously.

Copper manganite is discussed later.

When the ionic radius of the ion of the replacing metal is greater than 0.97, the manganites formed have lower symmetry, so the approximate cubic close-packing of the oxygen ions can no longer be present. The occupation of tetrahedral holes by ions of radius 0.97 is noteworthy, as the limiting size in an oxygen lattice of close-packed spheres of radius 1.40 for ions in tetrahedral holes is only a radius of 0.59. The large cell volume accompanying such occupation is evidence of the considerable distention of the close-packing brought about by these large ions.

Turning now to the relation between ion size and c/a ratio, there is a general upward trend in the ratio with increase in ion size, as shown in the table below.

Replacing ion.	Ionic radius.	c/a ratio.
Mn ^{II}	0.65	1.15
Ni ^{II}	0.70	1.00
Co ^{II}	0.72	1.14
Zn ^{II}	0.74	1.14
Fe ^{II}	0.75	1.00
(Ca ^{II}	0.8	1.00)
Mn ^{II} (in Mn ₃ O ₄)	0.80	1.16
Cd ^{II}	0.97	1.19

The anomalous ratio of magnesium manganite has already been commented on.

No obvious reason presents itself for the spinel symmetry of iron manganite.

Copper manganite is referred to later.

In comparing these results with those for the analogous mixed oxides of the two metals adjacent to manganese in the Periodic Table, the chromites and the ferrites, the main difference evident is the fact that all seven chromites and ferrites are "2.3" spinels (E. J. W. Verwey and E. L. Heilmann, J. chem. Phys., 1947, 15, 174-180). Thus directed bonding is less significant in the structures of these two groups of mixed oxides than in the manganites. The same general trend in cell volume is shown by the chromites - with the same two exceptions to this trend, magnesium and cobalt - and also by the ferrites, though

zinc ferrite does not conform, and the ferrites of magnesium, nickel, and cobalt are all of equal cell volume.

	Cell volume for	chromite.	ferrite.
Magnesium		574	585
Nickel		571	585
Cobalt		576	585
Zinc		571	596
Iron		580	590
(Copper		-	586)
Manganese		611	625
Cadmium		630	655

(calculated from Verwey and Heilmann's table, loc.cit.)

In general, the cell volume is less than that of the corresponding manganite, as would be expected from the distortion of the close-packed oxygen lattice in the manganites, the ions of Mn^{II} , Cr^{II} , and Fe^{II} being similar in radius.

The cell volume of copper ferrite is less than would be anticipated from the ionic radius, 0.8.

The size of the copper manganite unit cell, together with the analogous copper ferrite unit, and the fact that it is a spinel, point to a possibly smaller ionic radius

for Cu^{II} than that given in the literature, if it is assumed that no other factors are causing this cell volume to be smaller than expected. The figure given here was not published by Pauling, and the original reference for this figure is not given by Sphraia. Verwey and Heilmann state that the figure 1.01 for the ionic radius of Cu^{II} , which they say is given in many tables in the literature, is obviously incorrect. In view of this doubtful authenticity of 0.8 as the radius, and in the light of the proviso just made, it is suggested that the ionic radius for Cu^{II} is less than 0.7, when the cell size would then conform with the general trend.

The solubility of manganous manganite in the manganites of zinc, magnesium, iron, cobalt, and nickel, which was found to be complete in the proportions tried, was to be expected from the fact that these manganites were isostructural. The anticipated general trend in the lattice constants with increase in manganese content, towards those of manganous manganite, was also observed. Conversely, the lack of solubility of zinc and magnesium oxides in the corresponding manganites followed the usual rule that dissimilar structures are generally immiscible, with the notable exception of the solubility of copper

oxide in copper manganite.

This survey of the manganites has necessarily been cursory, so that the field could be covered in a reasonable time. A much more exhaustive study of each manganite is needed, and useful future work, comprising the use of the high-temperature X-ray powder diffraction camera and the ignition of reactants under various oxygen pressures and wide ranges of composition, is indicated. Ranges of solubilities of constituent oxides in each manganite, at room and elevated temperatures, could be investigated, and the possibility of structural change with temperature, like that occurring in iron and manganous manganite, explored.

Points of special interest, concerning particular manganites, that require further attention are referred to in the sections on experimental work, but a few comments on the iron group manganites are included here.

The manganites of the three elements iron, cobalt, and nickel form a structurally interesting series in their spinel range of compositions and their change to the hausmannite type of structure. The persistence of the spinel structure in manganese-rich nickel manganite ($\text{Ni:Mn}:1:4$) is extraordinary; apparently the directed $\text{Ni} - \text{O}$ bonds oppose the distorting effect of the $\text{Mn} - \text{O}$

bonds. Further work on this series, particularly on the nickel-manganese mixed oxides, along the lines previously suggested, to find the composition of the spinel-heusmannite transition point, and its shift with temperature, would be of special interest.

Conclusion.

The results obtained in this survey have filled several gaps in the data on the structure of the manganites, and have thus brought the knowledge of this series to a level comparable with that for the analogous chromites and ferrites.

The possibilities for future study have been delineated, and several interesting and suggestive phenomena have been observed for particular manganites.

These concluding remarks lead naturally to a consideration of the possibilities of analogous mixed oxides of rhenium, element 75 in this Group of the Periodic Table. The second part of this Thesis records some preliminary investigations in this field.

PART II. ATTEMPTED PREPARATION OF THE RHENITES.

Introduction.

Rhenium, the last metal in Group VIIA of the Periodic Table, shows marked differences in chemical properties to manganese, particularly in the stability of its oxides. Inquiry into the possible formation of mixed oxides analogous to the manganites is, therefore, of particular interest.

Only mixed oxides with alkali metals are mentioned in the literature. I. and W. Noddack (Z. anorg. Chem., 1933, 215, 134) described a sodium rhenite, Na_2ReO_3 , prepared by fusing rhenium dioxide with sodium hydroxide in the absence of air, which was left as an insoluble brown residue on extraction with water. Various hyperrhenates were said by the same workers (ibid., 1933, 215, 136) to be formed when rhenium dioxide was heated with an alkali perrhenate and excess alkali for long periods at 700°C . No structural work has been done in this field, however.

The oxides themselves merit a few words here in view of their importance as source materials for possible mixed oxides. The only stable lower oxide is the dioxide. Re_2O_3 is unstable (W. Geilmann and F. W. Wrigge, Z. anorg. Chem., 1933, 214, 239), while Re_3O_4 is unknown. A series of diffraction photographs of rhenium with oxygen-content increasing up to ReO_2 , showed a continuous transition

from the rhenium to the rhenium dioxide pattern (I. and W. Noddack, Z. anorg. Chem., 1929, 181, 32). The structure of rhenium dioxide has not been determined; W. Biltz and G. A. Lehrer (Z. anorg. Chem., 1933, 214, 227) decided that it did not possess tetragonal symmetry, but went no further.

Preparation of substantially pure rhenium dioxide was thus the initial step to be taken in this work. Firstly, to provide a supply of the rhenium constituent for the preparation of mixed oxides and secondly, to obtain a powder diffraction pattern of rhenium dioxide, both for structure determination, if possible, and as a standard for comparison with patterns of suspected mixed oxides. After this, attempted preparations of mixed oxides were to follow the lines analogous to those described under the manganites.

Experimental Work and Results.

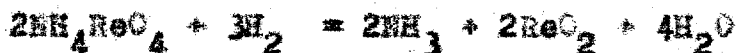
1. Attempted Preparation of Rhenium Dioxide.

Biltz and Lehrer (loc. cit.) recommended the reduction of rhenium heptoxide with rhenium at 600° to 650°C. ,



as the best method for the preparation of rhenium dioxide.

However, as the heptoxide is exceedingly hygroscopic and sublimates readily at 300°C., the inconvenience in manipulation entailed by this method led to the trial of the direct reduction of ammonium perrhenate to the dioxide with hydrogen at low temperatures (I. and V. Noddack, *ibid.*, 1929, 181, 24), thus,



Ammonium perrhenate was prepared from rhenium metal by dissolving the metal in 1:1 nitric acid, neutralising the solution with aqueous ammonia solution and crystallising.

A small, dried sample of the ammonium perrhenate was heated in a stream of dry hydrogen at 150°C., the temperature given in the literature, for six hours. No ammonia was evolved during this period.

The temperature was then raised to 220°C., and the heating continued as long as any ammonia was evolved. This was checked by determining the titre of a known volume of standard acid through which the exit gases bubbled. After 26 hours, no more ammonia was evolved.

Determination of Rhenium Dioxide in the Product.

This was attempted by oxidising the rhenium dioxide with ferric sulphate on gentle warming, and titrating the ferrous iron formed with permanganate (W. Geilmann and

F. W. Griggs, Z. anorg. Chem., 1935, 222, 56-64). An impossibly high result was obtained, and it was found, on trying a control determination, using the pure metal, that reduction still took place, the extent depending on the duration of the determination and the temperature used.

Abandoning this method, recourse was had to the nitron perrhenate precipitation method (W. Geilmann and A. Veigt, Z. anorg. Chem., 1930, 193, 311); this is a method inherently of low accuracy as the $\text{Re}:\text{ReO}_2$ ratio is small. About 0.1 g. of the sample was dissolved in 5 ml. of 100 volume hydrogen peroxide solution and 10 ml. of water with gentle warming. Excess hydrogen peroxide was decomposed by boiling the solution, one ml. of 2N. sulphuric acid was added and then 5 ml. of a 5% solution of nitron (diphenyl-endo-anilo-hydro-triazole) in aqueous 10% acetic acid were added when the solution had cooled to 80°C . The mixture was allowed to cool, first in air, and then in melting ice for two hours, with frequent stirring. The precipitated nitron perrhenate was collected on a No. 4 sintered glass filter crucible, washed with 20 ml. of 0.3% aqueous nitron acetate solution and finally with 2 ml. of ice-cold, saturated aqueous nitron perrhenate solution. The precipitate was dried to constant weight

at 130°C .

Only 17% of rhenium dioxide was found to be present in this sample.

The reduction was next tried using moist hydrogen, in the hope that the complete reduction to the metal would be thereby retarded. More accurate temperature control was effected by using a Pyrex tube wound with Nichrome wire to heat the ammonium perrhenate, instead of the usual furnace. After 50 hours heating in the range $195\text{--}200^{\circ}\text{C}$., reduction was complete as no more ammonia was evolved. A pair of determinations of the rhenium dioxide present still gave only a mean of 20%.

At this stage, attempts to prepare rhenium dioxide by reduction were abandoned in favour of a direct synthesis, which was also used in attempts to prepare the rhenites.

2. Direct Synthesis of Rhenium Dioxide and Attempted Preparation of the Rhenites.

This method of direct synthesis comprised heating rhenium in vacuo at 800°C . with the theoretical amount of an oxygen source only, to give the dioxide, or with sufficient of the oxide of the other metal, to give



The rhenium alone, or mixed with the oxide of the other metal, was placed in a silica tube 50 mm. long and 3 mm. in internal diameter, sealed at one end. This capsule was inserted into a similar larger tube, sealed at one end, 100 mm. long and 6 mm. in internal diameter, containing the reagent used as an oxygen source. The tubes were evacuated, and then the outer tube was sealed.

Barium peroxide was the first oxygen source used, but this reagent proved unsatisfactory, as the barium oxide formed on decomposition reacted with the silica of the tube at 800°C. , causing collapse after 12 hours heating. Subsequently potassium chlorate was used; this liberates all its oxygen above 450°C. , and had the advantage that if any of the potassium chloride left became admixed with the rhenium preparation, the simple cubic potassium chloride diffraction pattern could readily be recognised and allowed for in the pattern of the mixed oxide.

Using this technique, preparations of the dioxide and the mixed oxides with zinc, magnesium, calcium, and iron were attempted.

Dried potassium chlorate (Analar) was used. The oxides were those used in the corresponding manganite preparations. In all cases the sealed tube, inclined in the furnace

tube with the open end of the inner tube upward, was heated slowly to 300°C . so that evolution of oxygen from the potassium chlorate was not too violent. The tube was maintained at 300°C . for 12 hours, and then allowed to cool slowly to room temperature during six hours. The outer tube was broken open and the preparation - which had sintered in all cases - was removed from the inner tube.

No sign of positive pressure in the tube was evidenced on breaking, so all the oxygen had been absorbed by the rhenium. It was originally intended to determine the weight increase of the preparation after ignition and so obtain a more accurate figure for the oxygen content of the product than would have been obtained by difference from the rhenium determination. Unfortunately, removal of the inner tube from the outer without fracture was found to be difficult and furthermore, white specks in the preparation suggested the presence of potassium chloride, so no use was made of the weight increase to find the oxygen content.

These samples were analysed for rhenium by the nitron method and examined by X-rays.

The analyses showed varying amounts of oxygen to be present in the samples. The oxide corresponded to

$\text{ReO}_{1.6}$

The diffraction photographs were similar in all cases, but not identical. Faint lines due to the added metal oxide were observed in the zinc, magnesium, and iron preparations.

It was found not possible to index the rhenium oxide pattern; diametric symmetry appeared to be absent.

No published intensities or d values exist for rhenium dioxide, so those obtained for $\text{ReO}_{1.6}$ are included here for reference.

RHENIUM OXIDE, $\text{ReO}_{1.6}$

Powder Diffraction Data.

Intensity.	d .	Intensity.	d .	Intensity.	d .
3	3.62	1	1.374	5	1.094
4	2.842	3	1.341	1	1.084
5	2.386	2	1.275	10	1.072
1	2.284	1	1.256	2	1.062
3	2.094	0.5	1.213	1	1.049
4	1.936	2	1.198	4	1.034
8	1.691	1	1.175	7	0.9880
3	1.634	7	1.171		
3	1.622	4	1.154		
2	1.455	0.5	1.111		
3	1.406				

Conclusion.

It may be that some mixed oxide formation had taken place, accounting for the small differences in the patterns of the four preparations; on the other hand this may have been due only to the different oxygen content of each sample. Nevertheless, it can be stated that, under the conditions used, rhenium does not form mixed oxides structurally analogous to the manganites, bearing in mind that some formation of mixed oxide of lower symmetry is not precluded by the observations.

Further work is required, with more exact control of the oxygen content of the products, to clarify the position.

ACKNOWLEDGEMENTS.

The writer expresses his gratitude to both the Ministry of Education and the Department of Scientific and Industrial Research for the award of maintenance grants, the former (F.R.S. grant) for the first half, and the latter for the last half of the period during which the work just described was carried out.

Thanks are due to the Imperial College for the research facilities provided, and to Professor H. V. A. Briscoe, whose kind interest in the work has been much appreciated.

To Dr. A. J. E. Welch, who supervised this research, for his ever ready guidance, advice and encouragement, sincere thanks and the warmest appreciation are extended.

Extensive use has been made of the X-ray apparatus provided by a grant from the Royal Society to Professor Briscoe and Dr. Welch, for which grateful recognition is recorded.

Finally, acknowledgement must be made of the helpful discussion with, and criticism of these friends who were engaged in cognate studies at the time.

1st June, 1951.

J. B. Payne.