

Place and Valence of the Cations in  $Mn_3O_4$   
and Some Related Manganates

F. C. M. Driessens\*

Received February 23, 1967

A high-temperature X-ray diffractometer has been used to investigate the transition of  $Mn_3O_4$  from the tetragonal hausmannite to the cubic spinel structure. In air the transition was found to take place at  $1,130 \pm 10^\circ C$  and in  $CO_2$  at  $1,110 \pm 10^\circ C$  [ $\log P_{O_2}$  (atm) = -4]. The degree of distortion below the temperature of transition and the dependence of the transition temperature on the oxygen partial pressure are discussed in connection with the defect structure of  $Mn_3O_4$ . The cation arrangements in the structure of  $Cu_xMn_{3-x}O_4$  ( $0 \leq x \leq 1.03$ ) and  $Zn_xMn_{3-x}O_4$  ( $0 \leq x \leq 1.5$ ) have been determined with X-rays after the method of Bertaut (1951). Cu and Zn have a preference for tetrahedral sites and the degree of inversion found in quenched samples of  $CuMn_2O_4$  and  $ZnMn_2O_4$  is only about 10% in either compound. Oxygen-deficient samples  $Cu_xMn_{3-x}O_{4-\gamma}$  ( $0 \leq x \leq 0.5$  and  $-0.08 \leq \gamma \leq 0.00$ ) probably contain copper ions between two oxygen ions as in the structure of  $Cu_2O$ . The investigated cation distributions are discussed in connection with the valencies of the cations and with their interaction.

## Introduction

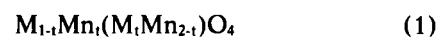
A number of compounds of the formula  $MMn_2O_4$  have been found or synthesized in which M is a metal ion. Some of these have the tetragonally deformed spinel structure of hausmannite,  $Mn_3O_4$ , at room temperature ( $M = Mn, Mg, Zn, Cd, Co$  and  $Fe$ ), others have the cubic spinel structure ( $M = Li, Cu, Ni, Ti, Sn$ ), and three substances of this kind are known which have an orthorhombic structure ( $M = Ca, Ge, Si$ ).

On heating the substances with hausmannite structure it has been found that their structure changes to that of a cubic spinel. This transition is of the first kind. A specific transition temperature has been found for the compound  $Mn_3O_4$  in air. In the presence of one more component ( $M = Mg, Zn, Cd, Co, Fe$ ) a temperature range has been found for this transition: at any temperature in this range two solid phases are present,  $M_xMn_{3-x}O_4$  with hausmannite structure, and  $M_xMn_{3-x}O_4$  with spinel structure. Generally the spinel phase is poorer in manganese than the hausmannite phase in the two-phase region.

The hausmannite- and the spinel-like substances  $MMn_2O_4$  form solid solutions with the low-temperature hausmannite form and the high-temperature spinel form of  $Mn_3O_4$  respectively. The kinds of metal ions M, and the maximum values of  $x_1$  and  $x_2$  of solid solutions stable in air at high temperatures, are summarised in Table I.

The disproportioning of the solid solutions which are stable at high temperatures, into a cubic spinel and a tetragonal hausmannite phase is rather slow and they therefore can be obtained as a metastable single phase by quenching from high temperatures. Therefore the lowest value of x, at which these solid solutions of the type  $M_xMn_{3-x}O_4$  have the cubic structure at room temperature can also be given in Table I.

In the structure of hausmannite and spinel the cations can occupy (deformed) tetrahedral sites (A-sites) or deformed octahedral sites (B-sites). Thus the structure of a manganite  $MMn_2O_4$  can be written as



where the brackets indicate octahedral sites. In these substances of type  $MMn_2O_4$  there seems to be a certain relation between place and valence of the cations, on the one hand, and the degree of distortion on the other. If M is mainly  $M^+$  and this cation occupies mainly tetrahedral sites ( $M = Li, Cu$ ), there is no distortion. If M is mainly  $M^{2+}$  and this cation occupies mainly tetrahedral sites ( $M = Mg, Co, Zn, Cd$ ), the distortion  $c/a$  is great. If M is mainly  $M^{3+}$ , the distortion is slight, irrespective of whether this cation occupies mainly octahedral sites ( $M = Cr$ ) or tetrahedral sites ( $M = Fe$ ). If M is  $M^{4+}$  and this cation occupies mainly octahedral sites ( $M = Ti, V, Sn$ ), there is no distortion.

Distortions have been studied on many more manganites by the introduction of two or more different cations in  $Mn_3O_4$ .<sup>24</sup> From these purely crystallographic studies the following conclusions have been drawn: (a) The formula of  $Mn_3O_4$  may be  $Mn^{2+}(Mn_2^{3+})O_4$  at room temperature. (b) The limit  $(x)_{min}$  from Table I seems to be related to a concentration of about 60% of  $Mn^{3+}$  ions in the octahedral sites. (c) With increasing concentration of  $Mn^{3+}$  the distortion increases non-linearly from about 1.03 to about 1.15. The minimum

(24) (a) A. Miller, *J. Appl. Phys.*, **31**, 261 S-262 S (1960). (b) M. O'Keefe, *J. Phys. Chem. Solids*, **21**, 172-178 (1961). (c) D. G. Wickham and W. J. Croft, *J. Phys. Chem. Solids*, **7**, 351-360 (1958).

(\* Previous address: Institute of Physical Chemistry, Technical University, Eindhoven.

**Table 1.** Some thermodynamic and crystallographic data of manganites derived from  $Mn_3O_4$ 

M	Phase diagram in air			Cubic structure		Crystallographic data for $x=1$		
	$(x_1)_{max}$	$(x_2)_{max}$	Ref.	$(x)_{min}$	Ref	$(c/a)_{x=1}$	$(t)_{x=1}$	Ref
Li	?	~4/3	1	0.5 < $x$ < 1.0	1	1	< 0.05	1
Mg	< 1.0	> 1.0	2b	> 1	17	1.15	0.00 < $t$ < 0.5	2a
Al	~0.7	2.5	3	> 0.9	3	?	?	
Ti	?	1 < $x_2$ < 2	4	< 1	4,13	1	1.0	18
V	< 0.1(?)	< 1	5	< 1	14	1	1.0	19
Cr	0.3	2.0	6	~1.1	17	1.05	1.0	17
Mn	—	—	—	—	—	1.16	—	51
Fe	~0.2	3	7	1.02	12	1.06	0.1	20, 49
Co	~0.9	3	8	1.8	8,15	1.14	0.2	8
Ni	0.105	1.275	9	0.42	16	1	0.88	21
Cu	< 0.2	1.03	10	0.95	10	1	0 < $t$ < 1	22
Zn	1.01	1.48	11	1.48	11	1.14	0.0	23
Ga	?	?	?	< 2	51	?	?	
Ge	?	?	?	?	?	orthorhombic		51
Rh	?	?	?	< 2	51	?	?	
Cd	?	?	?	> 1	51	1.20	0.0	23
In	?	?	?	< 2	51	?	?	
Sn	?	?	?	< 1	13	1	1.0	13

M = kind of metal ion introduced for Mn in  $Mn_3O_4$ .  $(x_1)_{max}$ : maximum value of  $x_1$  in  $M_{x_1}Mn_{3-x_1}O_4$  with hausmannite structure stable in air.  $(x_2)_{max}$ : maximum value of  $x_2$  in  $M_{x_2}Mn_{3-x_2}O_4$  with spinel structure stable in air.  $(x)_{min}$ : minimum value of  $x$  in  $M_xMn_{3-x}O_4$ , having the cubic spinel structure at room temperature (quenched, metastable state).  $(c/a)_{x=1}$ : ratio of c and a axes or the distortion at room temperature for the composition  $x=1$ .  $(t)_{x=1}$ : amount of M ions in B-sites, or the degree of inversion of the structure at  $x=1$  according to the formula  $M_{1-t}Mn_t(M_1Mn_{2-t})O_4$ .

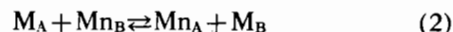
concentration of  $Mn^{3+}$  ions necessary in octahedral sites for a distortion to occur at room temperature depends on the nature of the other cations in octahedral<sup>24</sup> and tetrahedral sites.

Theoretical treatment has also been used in an approach of the phenomenon of distortion in manganite structures. According to both ligand field theory<sup>25</sup> and crystal field theory<sup>26</sup> the octahedron of oxygen ions around an  $Mn^{3+}$  ion, with its  $(3d)^4$  configuration, will be distorted so that the four oxygen neighbours in one plane are strongly bound and thus attracted to the cation, whereas the two oxygen neighbours above and below this plane are less strongly bound and will therefore be pushed away by the four more strongly bound neighbours.

At low temperature the interaction of the individually distorted octahedra of oxygen ions may lead to a long-range effect, once the concentration of distorting cations has reached a certain minimum.

Finch, Sinhã and Sinhã<sup>27</sup> have treated the problem by taking into account the interaction of a rightly (c-axis) or wrongly (a or b axis) distorted octahedron with the

lattice and by calculating the degree of distortion from the concentration of distorting ions in a way analogous to that of long-range order in an alloy.<sup>28</sup> This treatment implies that the high-temperature transition of  $Mn_3O_4$  from the tetragonal hausmannite to the cubic spinel structure is of the second kind. Actually it has been found to be of the first kind, as was pointed out by Wojtowicz,<sup>29</sup> who developed a theory taking into account nearest-neighbour interaction between the distorting ions via their surrounding oxygen ions; only one parameter has been used for this interaction energy. A more general theory in terms of nearest-neighbour interaction has been given recently by Robbrecht and de Clerck.<sup>30</sup> Moreover, these authors have taken into account the possibility of intermediate spinel structures as given in equation (1). For equilibrium (2)



where  $M_A$  means a cation M in an A-site, etc. an equilibrium constant can be formulated as for other chemical equilibria. Studies on  $MgFe_2O_4$ <sup>31</sup> and  $CuFeO_4$ <sup>32</sup>

- (1) (a) G. Blasse, *Philips Res. Repts.*, 18, 400-404 (1963). (b) G. Blasse, *Philips Res. Repts.*, 20, 528-555 (1965).  
 (2) (a) R. Manaila and P. Pausescu, *Phys. Stat. Solidi*, 9, 385-394 (1965). (b) P. V. Riboud and A. Muan, *J. Am. Ceram. Soc.*, 46, 33-36 (1963).  
 (3) T. Ranganathan, B. E. MacKean and A. Muan, *J. Am. Ceram. Soc.*, 45, 279-281 (1963).  
 (4) A. Lecerf, *Ann. Chim.*, (Paris), 7, 513-535 (1962).  
 (5) C. Brisi, *Aun. Chim.*, (Roma), 48, 270-275 (1958).  
 (6) D. H. Speidel and A. Muan, *J. Am. Ceram. Soc.*, 46, 577-578 (1963).  
 (7) A. Muan and S. Somyia, *Am. Mineralogist*, 46, 364-378 (1961).  
 (8) I. Aoki, *J. Phys. Soc. Japan*, 17, 53-61 (1962).  
 (9) D. G. Wickham, *J. Inorg. Nucl. Chem.*, 26, 1369-1377 (1964).  
 (10) F. C. M. Driessens and G. D. Rieck, *Z. Anorg. Allgem. Chem.* (in press).  
 (11) F. C. M. Driessens and G. D. Rieck, *J. Inorg. Nucl. Chem.*, 28, 1593-1600 (1966).  
 (12) F. C. M. Driessens, Thesis, Eindhoven 1964.  
 (13) M. A. Gilileo and D. W. Mitchell, *J. Phys. Chem. Solids*, 10, 182-184 (1960).  
 (14) B. Reuter, *Bull. Soc. Chim. France*, Sér. 5, 1053-1056 (1965).  
 (15) D. G. Wickham and W. J. Croft, *J. Phys. Chem. Solids*, 7, 351-360 (1958).  
 (16) E. G. Larson, R. J. Arnott and D. G. Wickham, *J. Phys. Chem. Solids*, 23, 1771-1781 (1962).  
 (17) P. F. Bongers, Thesis, Leiden (1957).  
 (18) A. Lecerf, M. Rault, J. Portier and G. Villers, *Bull. Soc. Chim. France*, 1210 (1965).  
 (19) J. C. Bernier, P. Poix and A. Michel, *Bull. Soc. Chim. France*, 1724-1728 (1963).  
 (20) A. Murasik and G. Roult, *J. Phys.*, (Paris), 25, 522 (1964).  
 (21) (a) B. Boucher, *Compt. Rend.*, 249, 514-516 (1959). (b) B. Boucher, *Compt. Rend.*, 263, 344-347 (1966).  
 (22) (a) A. P. B. Sinhã, N. R. Sanjana and A. B. Biswas, *J. Chem. Phys.*, 62, 191-194 (1958). (b) C. Delorme, *Bull. Soc. Franc. Minéral. et Cristal.*, 81, 79-102 (1958). (c) A. J. Zaslavskii, Z. V. Karachentseva and A. J. Zharinova, *Sov. Phys. Crystallography*, 7, 835-843 (1962). (d) I. Aoki, *J. Phys. Soc. Japan*, 20, 871 (1965). (e) S. Asbrink, *Acta Chem. Scand.*, 19, 1766 (1965).  
 (23) Inferred from the strong tetragonal distortion. See also Bongers.<sup>17</sup>  
 (25) J. B. Goodenough and A. L. Loeb, *Phys. Rev.*, 98, 391-408 (1955).  
 (26) (a) J. D. Dunitz and L. E. Orgel, *J. Phys. Chem. Solids*, 3, 20-29 and 318-323 (1957). (b) D. S. McClure, *J. Phys. Chem. Solids*, 3, 311-317 (1957).  
 (27) G. F. Finch, A. P. B. Sinhã and K. P. Sinhã, *Proc. Roy. Soc. London*, A242, 28-35 (1957).  
 (28) H. A. Bethe, *Proc. Roy. Soc. London*, A150, 552-575 (1935).  
 (29) P. J. Wojtowicz, *Phys. Rev.*, 116, 32-45 (1959).  
 (30) G. G. Robbrecht and E. F. de Clerck, *Physica*, 31, 1033-1045 (1965).  
 (31) F. Bertaut, *J. Phys. Radium*, 12, 252-255 (1951).  
 (32) L. Neel, *Compt. Rend.*, 230, 190-192 (1950).

have shown that this constant may have the form:

$$K = \frac{t^2}{(1-t)(2-t)} = \exp \left[ -\frac{E}{RT} \right] \quad (3)$$

This formula can give a good approximation for a certain composition at low values of  $t$ , but the energy term  $E$  may depend on the value of  $t$ , as has been found with some other ferrites.<sup>33</sup>

The primary purpose of the present study was to provide information about the defect structure of  $Mn_3O_4$  at high temperatures. According to the theory given by Robbrecht and de Clerck such information can be gained from the temperature dependence of the distortion of this compound, if the defect structure is of the kind indicated by equilibrium (2). This idea can be tested further by the introduction of other cations for  $Mn^{2+}$ .

A further purpose of the present study was to provide additional information about the valencies of the cations and their distributions in manganites containing transition metal cations. The tentative cation distributions are given in Fig. 1. They are derived from

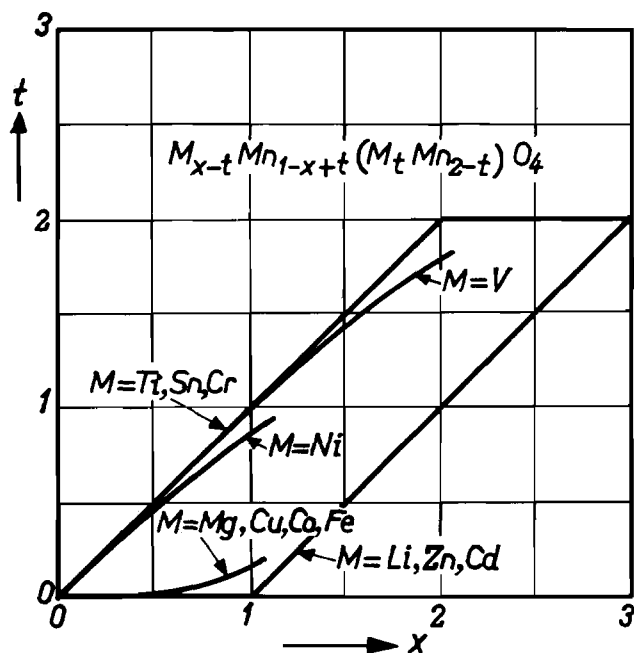


Figure 1. Cation distribution in manganites  $M_xMn_{3-x}O_4$  according to literature data (see also Table I).

X-ray measurements, neutron diffraction, magnetic susceptibility etc., as given in the literature (see also Table I). The roughly estimated valencies of the cations  $M$  of the first series of transition metals at the composition  $MMn_2O_4$  may be  $Ti^{4+}$ ,  $V^{4+}$ ,  $Cr^{3+}$ ,  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{1+}$  and  $Zn^{2+}$ , as was assumed above in considering the distortions of these compounds, but the redox couples  $Fe^{3+}/Fe^{2+}$  and  $V^{4+}/V^{3+}$  may compete

with  $Mn^{3+}/Mn^{2+}$ , and the couples  $Co^{3+}/Co^{2+}$  and  $Cu^{2+}/Cu^{1+}$  may compete with  $Mn^{4+}/Mn^{3+}$ . Evidence for this competition can be obtained from the oxygen equilibrium pressures of these compounds and from thermodynamic activity data, as shown in a previous paper<sup>34</sup> for solid solutions of  $Mn_3O_4-Fe_3O_4$  and  $Mn_3O_4-Co_3O_4$ . An analogous treatment will be given in the present paper for  $Cu_xMn_{3-x}O_4$ , of which the equilibrium oxygen pressure has been given in a preceding paper<sup>10</sup> and the cation distribution is dealt with now.

*Literature data referring to the present experiments.*  $Mn_3O_4$ . Hausmannite,  $Mn_3O_4$ , has a tetragonally deformed spinel structure at room temperature. At 1200°C there is no distortion and the substance has the cubic spinel structure.<sup>35</sup> Van Hook and Keith<sup>36</sup> have found the transition temperature on heating at 1165°C and on cooling at 1135°C by means of DTA and high-temperature X-ray diffraction in air. About the same values have been found by Rosenberg *et al.*<sup>37</sup> with electrical conductivity measurements.

Table II. Cell dimensions  $a$  and  $c$  (Å), cell volume  $V$  (Å<sup>3</sup>) and degree of distortion ( $c/a$ ) for some manganites  $MMn_2O_4$  at room temperature

M	a	c	V	c/a
Zn <sup>2+</sup>	8.08	9.23	602	1.142
Mg <sup>2+</sup>	8.07	9.28	604	1.150
Mn <sup>2+</sup>	8.14	9.42	613	1.158
Cd <sup>2+</sup>	8.22	9.87	667	1.200

$Zn_xMn_{3-x}O_{4+\gamma}$ . Mixed oxides of the composition  $Zn_xMn_{3-x}O_{4+\gamma}$  have been found to be stable in air<sup>11</sup> in the ranges  $0 \leq x \leq 1.48$  and  $0.000 \leq \gamma \leq 0.025$ . The structure of only  $ZnMn_2O_4$  has been reported.<sup>45</sup> This has been derived from visually estimated intensities on a Debye-Scherrer radiograph. The cation distribution is probably that of a normal spinel:  $Zn(Mn_2)O_4$ .

$Cu_xMn_{3-x}O_{4+\gamma}$ . In a previous study<sup>10</sup> we have determined the stability field of the tetragonal and of the cubic phase of the general formula  $Cu_xMn_{3-x}O_{4+\gamma}$ . In air the tetragonal phase was found to be stable in the range  $0 \leq x \leq 0.2$  with  $0 \leq \gamma \leq 0.02$  and the cubic phase in the range  $0 \leq x \leq 1.03$  with  $-0.08 \leq \gamma \leq 0.02$ . It was also found that in air  $Cu_{0.95}Mn_{2.05}O_4$  ( $a = 8.34$  Å) was stable between 980 and 1010°C,  $CuMn_2O_4$  ( $a = 8.31$  Å) between 800 and 920°C, and  $Cu_{1.02}Mn_{1.98}O_4$ , between 650 and 780°C. Furthermore,  $CuMn_2O_4$  was tetragonal ( $c/a = 1.03$ ) at room temperature when quenched from the low-temperature boundary of the spinel field ( $a = 8.24$ ,  $c = 8.51$ ).

The structure of only  $CuMn_2O_4$  has been reported in the literature. A survey of the data is given in Table III. The mean of the reported values of the temperature coefficient  $B$  and the oxygen parameter  $u$  are  $0.5$  Å<sup>2</sup> and  $0.39$ , respectively. With these values

(34) F. C. M. Driessens, «Thermodynamics and defect chemistry of some oxide solid solutions», to be published.

(35) H. F. McMurdie and E. Golovato, *J. Res. NBS*, 41, 589-600 (1948).

(36) H. J. van Hook and M. L. Keith, *Am. Mineralogist*, 43, 69-83 (1958).

(37) M. Rosenberg, P. Nicolau, R. Manaila and P. Pausescu, *J. Phys. Chem. Solids*, 24; 1419-1434 (1963).

(33) (a) H. B. Callen, S. E. Harrison and C. J. Kriessmann, *Phys. Rev.*, 103, 851-865 (1956). (b) C. J. Kriessmann and S. E. Harrison, *J. Appl. Phys.*, 32, 392S-393S (1961).

**Table III.** Cell dimension  $a$  (Å) and distribution parameter  $t$  of  $\text{CuMn}_2\text{O}_4$  according to the formula  $\text{Cu}_{1-t}\text{Mn}_t(\text{Cu}_t\text{Mn}_{2-t})\text{O}_4$ 

Ref.	$a$	Literature data $t$	Preparation Conditions	Evaluation	Evaluation of literature data about intensities after Bertaut <sup>31</sup>
22a	8.33-8.25	$\sim 0$	45 h 900° C air	trial and error	$0.1 < t < 0.2$
22b	8.31	0.34	in air at 750°C	ref. 31	—
22c	8.30	$0.67 < t < 1$	24 h 900°C air	Fourier-anal.	$0.2 < t < 0.4$
22d	?	0.12	240 h 700°C air	ref. 31	—
22e	8.37-8.34	0.42	45 days 1050°C air*	trial and error	no data available

\* Quartz glass is permeable to oxygen and nitrogen at this temperature.

and the reported<sup>22a, 22c</sup> intensities for the reflections 220, 400, 422 and 440 we calculated the  $t$  values, given in the last column of Table III after the method of Bertaut,<sup>31</sup> just as will be done below in the case of zinc manganites. The result is a diversity of numbers between 0.12 and 0.42. The reported cell constants do not agree either. The causes may be the smallness of the temperature range of stability, the sensitivity of this range to small compositional deviations and the complication that annealed or slowly cooled samples may have a small tetragonal distortion of their structure, which can be discovered only tediously. Furthermore, none of the authors reported deviations from stoichiometry with respect to the oxygen content.

## Experimental Section

$\text{Mn}_3\text{O}_4$ . In the present study a modification of the high-temperature X-ray diffractometer, described by Smith,<sup>38</sup> was used to determine the high-temperature transition of this substance in different atmospheres.  $\text{Mn}_3\text{O}_4$  was made from  $\text{MnCO}_3$ , which had a purity of 99.97%.

In air, the transition of  $\text{Mn}_3\text{O}_4$  was found at 1150°C on heating and at 1125°C on cooling, with slow step-wise temperature variation. If, however, the temperature was kept constant at 1140°C for four hours the sample always had the cubic spinel structure, irrespective of pre-heating above or below this temperature. The absolute accuracy was estimated to be  $\pm 10^\circ\text{C}$ . In Fig. 2 our own results for the cell dimensions of  $\text{Mn}_3\text{O}_4$  in air are compared with those of others.<sup>36, 39</sup>

In  $\text{CO}_2$ , the cubic structure was found to be stable at 1120°C. At this temperature the partial dissociation of  $\text{CO}_2$  into  $\text{CO}$  and  $\text{O}_2$  has the result that  $\log P_{\text{O}_2}$  (atm) =  $-4.1$ .<sup>40</sup>

$\text{Zn}_x\text{Mn}_{3-x}\text{O}_{4+\gamma}$ . We investigated the structure of substances of this type which were stoichiometric with respect to the oxygen content. Moreover, an attempt was made to determine the structure of the substance  $\text{ZnMn}_2\text{O}_4$  if quenched from different temperatures (varying between 600 and 1225°C). Accurate integrated intensities were measured on powders with a Philips X-ray diffractometer using  $\text{FeK}\alpha$  (Fe radiation and Mn filter) from a tube on a highly stabilised high-power generator, counting being performed with a

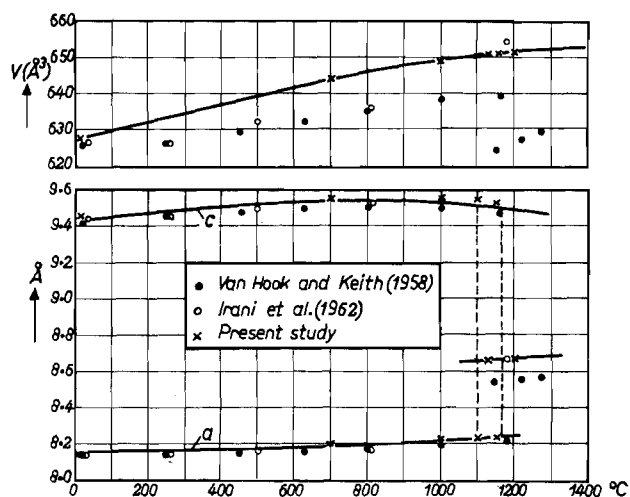
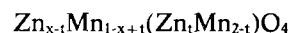


Figure 2. Cell dimensions  $a$  and  $c$  (Å) and cell volume  $V$  (Å<sup>3</sup>) of  $\text{Mn}_3\text{O}_4$  in air as a function of the temperature.

proportional counter and electronic one-channel discrimination. The intensities of the reflections (220), (202), (400), (004), (422) and (224) are particularly sensitive<sup>31</sup> to the distribution parameter  $t$  in the formula



whereas the intensities of the reflections 440 and 404 are completely insensitive to  $t$ . Theoretical curves for the intensity ratios

$$\begin{array}{cccc} (220)/(004) & (202)/(004) & (422)/(004) & (224)/(004) \\ (220)/(400) & (202)/(400) & (422)/(400) & (224)/(400) \\ (220)/(404) & (202)/(404) & (422)/(404) & (224)/(404) \\ (220)/(440) & (202)/(440) & (422)/(440) & (224)/(440) \end{array}$$

as a function of the parameter  $t$  where derived, using oxygen parameters  $x$ ,  $y = 0.383$  and  $z = 0.395$  and a temperature coefficient of  $B = 0.5 \text{ \AA}^2$ . Comparison with actual intensity ratios gave sixteen values for  $t$ , all with different degree of reliability. The statistical weight of one value was taken to be inversely proportional to the corresponding standard deviation of that value. In this way the results given in Fig. 7 were found for specimens having a negligibly small deviation from stoichiometry ( $0 \leq \gamma \leq 0.003$ ). The absolute deviation in the mean value of  $t$  is estimated to be  $\pm 0.03$ .

(40) J. Smiltens, *J. Chem. Phys.*, 20, 990-994 (1952).

(38) D. K. Smith, *Norelco Reporter*, 10, 19-29 (1963).

(39) K. S. Irani, A. P. B. Sinha and A. B. Biswas, *J. Phys. Chem. Solids*, 23, 711-727 (1962).

$\text{Cu}_x\text{Mn}_{3-x}\text{O}_{4+\gamma}$ . The distribution parameter  $t$  is defined by the formula

$$\text{Cu}_{x-t}\text{Mn}_{1-x+t}(\text{Cu}_t\text{Mn}_{2-t})\text{O}_4$$

Determinations of the value of  $t$  were carried out by X-ray diffraction on nearly stoichiometric samples ( $0.000 \leq \gamma \leq 0.005$ ) in the whole composition range  $0 \leq x \leq 1.03$ .

The same method with respect to experiments and mathematical evaluation was used as for zinc manganites. The adopted values for oxygen parameter and temperature coefficient were 0.39 and  $0.5 \text{ \AA}^2$  respectively. The result is given in Fig. 9. The temperature of stability of these nearly stoichiometric compounds varied greatly at high copper contents:

composition (x)	0.1	0.2	0.3	0.4	0.6	0.8	1.0	1.03
quenching temperature ( $^{\circ}\text{C}$ )	1150	1150	1150	1150	1100	1050	870	750

Therefore, one can expect a certain temperature dependence in the cation distribution of these spinels, as shown by the broken curves in Fig. 9.

## Discussion

$\text{Mn}_3\text{O}_4$ . The system Mn-O may be described by Fig. 3. Data for the other transitions in this system were compiled by Klingsberg and Roy.<sup>41</sup>

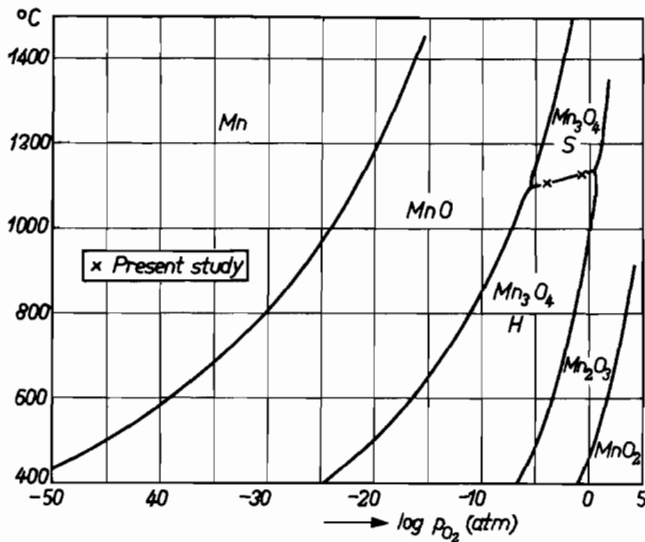


Figure 3. Phase equilibria in the system Mn-O.

The small effect of the oxygen pressure on the temperature of transition points to a small influence of the oxygen pressure on the oxygen content of hausmannite. Furthermore it may indicate that the influence of the oxygen pressure on the concentration of the majority point defects is also small (compare to ref. 50). This is probably the case, as will be seen below.

(41) C. Klingsberg and R. Roy, *J. Am. Ceram. Soc.*, 43, 620 (1960).

More information about the defect structure may be obtained if we consider its relation to the degree of distortion as a function of the temperature. In the introduction it was mentioned that the theory of Robbrecht and de Clerck<sup>30</sup> gave the distortion of a manganite with intermediate cation distribution as a function of the temperature. A typical solution on a relative scale is given in Fig. 4a.

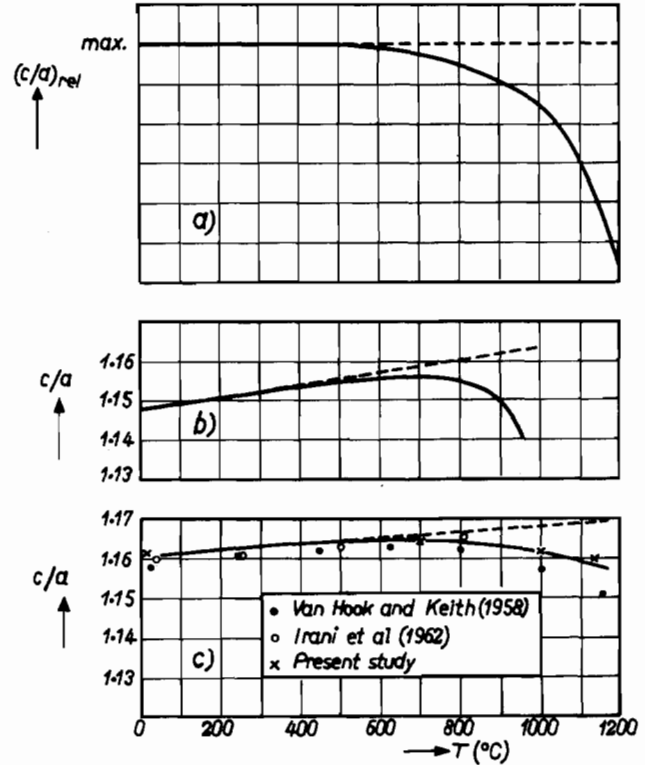
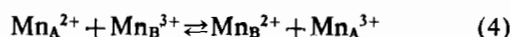


Figure 4. Degree of distortion of a manganite as a function of the temperature (a) theoretical curve of Robbrecht and de Clerck<sup>30</sup> (b) experimental curve<sup>23</sup> for  $\text{MgMn}_2\text{O}_4$ , (c) experimental curve for  $\text{Mn}_3\text{O}_4$ .

The result of Manaila and Pausescu<sup>2</sup> with  $\text{MgMn}_2\text{O}_4$  is a typical practical example. These authors have determined both the distortion and the cation distribution of  $\text{MgMn}_2\text{O}_4$  as a function of the temperature (see Fig. 4b and Fig. 5, respectively). It will be seen that the deflection of the curve in Fig. 4b from a straight line is noticeable at the temperature at which the value of  $t$  in Fig. 5 begins to differ distinctly from zero. This is in accordance with the theory of Robbrecht and de Clerck.<sup>30</sup>

In disagreement with their theory is the fact that the experimental straight line at low temperatures both for  $\text{MgMn}_2\text{O}_4$  (Fig. 4b) and for  $\text{Mn}_3\text{O}_4$  (Fig. 4c) is not horizontal but slightly inclined. The reason for this may be that the interaction energies of the distorting cations depends on their distance from each other and thus on the temperature because of the expansion of the lattice. The same effect of increasing distortion is demonstrated by the compounds  $\text{MMn}_2\text{O}_4$  at room temperature in the order  $\text{M} = \text{Mg}, \text{Zn}, \text{Mn}^{2+}, \text{Cd}$  of gradually increasing cell volumes (Table II).

If the defects on the right hand side of the equilibrium



are the majority defects in  $\text{Mn}_3\text{O}_4$ , then the degree of inversion of  $\text{Mn}_3\text{O}_4$  can be estimated to be  $15 \pm 5\%$ , at the temperature of transition, from a comparison of Fig. 4c with Figs. 4b and 5.

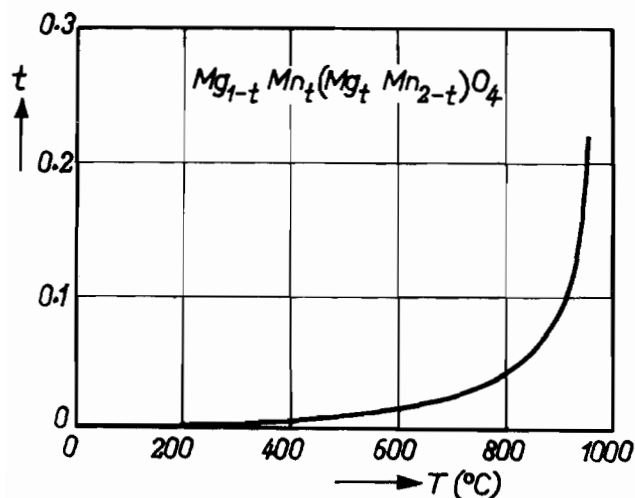


Figure 5. Cation distribution in  $\text{MgMn}_2\text{O}_4$  with the hausmannite structure as a function of the temperature.

From the phase diagrams of the systems  $\text{M}-\text{Mn}-\text{O}$  in air, where  $\text{M} = \text{M}^{2+}$  ( $\text{Mg}^{2+}$ ,<sup>42</sup>  $\text{Ni}^{2+}$ ,<sup>9</sup>  $\text{Zn}^{2+}$ ,<sup>11</sup>), it may be concluded that another type of defect equilibrium competes with equilibrium (4). Let us therefore consider the upper boundary of the spinel field, where these spinel solid solutions are stoichiometric with respect to the oxygen content.<sup>9,11</sup> If  $\text{M}^{2+}$  is gradually substituted for  $\text{Mn}^{2+}$  in the substance  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}^{2+}$  and  $\text{Mn}^{3+}$  will be present, until the composition  $\text{MMn}_2\text{O}_4$  is reached. If  $\text{M}^{2+}$  is further substituted for  $\text{Mn}^{3+}$  in the compound  $\text{MMn}_2\text{O}_4$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  will necessarily be present. Therefore at the composition  $\text{MMn}_2\text{O}_4$  the high-temperature boundary of the spinel-phase field might be expected to be of the form given in Fig. 6a, if the concentrations of  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  present simultaneously are low, and of the form given in Fig. 6b, if both concentrations are appreciable.

In fact, boundaries have been found of the type of Fig. 6b.<sup>42,9,11</sup> Therefore an equilibrium has to be formulated to describe the non-negligible concentrations of  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  at the composition  $\text{MMn}_2\text{O}_4$ . This may be equilibrium (5),



Although about 17 eV are necessary for this reaction to occur between free ions, this energy is nearly completely compensated by the contribution of the polarisation of the crystal.<sup>43</sup> If the energy is about 1 eV or 23 kcal/mole,<sup>43</sup> then the product of the concentrations of  $\text{Mn}_B^{2+}$  and  $\text{Mn}_B^{4+}$  in  $\text{Mn}_3\text{O}_4$  at the temperature of transition has the value  $10^{-3}$ .

(42) G. H. Jonker, private communication.

(43) F. C. M. Driessens, Thesis, Eindhoven, pag. 14 (1964).

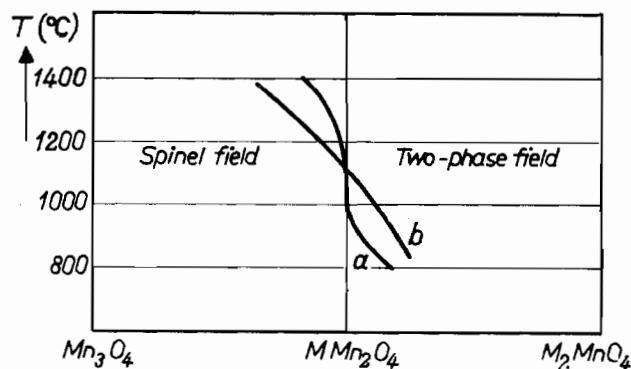


Figure 6. High-temperature boundary of the spinel phase field in an isobaric section of the phase diagram  $\text{MnO}-\text{M}^{2+}\text{O}$  (a) expected form for low concentrations of  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  in  $\text{MMn}_2\text{O}_4$  (b) expected form for appreciable concentrations of  $\text{Mn}^{2+}$  and  $\text{Mn}^{4+}$  in  $\text{MMn}_2\text{O}_4$ .

To sum up, the cubic structure of  $\text{Mn}_3\text{O}_4$  at high temperatures may be stabilised in the following ways:

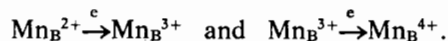
(a) Below the temperature of transition the structure is tetragonal and most of the  $\text{Mn}^{3+}$  ions have the fourth 3d electron in the  $d_{z^2}$  orbital, which has a lower energy in this tetragonally deformed state of the crystal ( $c/a > 1$ ) (Jahn-Teller effect). As the temperature rises an increasing number of  $\text{Mn}^{3+}$  ions will have the fourth 3d electron in the  $d_{x^2-y^2}$  orbital, which has a higher energy on account of the tetragonally deformed state of the crystal. The electron in the  $d_{x^2-y^2}$  orbital has, however, a tendency to deform the crystal in the opposite way ( $c/a < 1$ ), and the more electrons are in this state, the more will the tetragonal distortion of the crystal ( $c/a > 1$ ) decrease. This, in turn, has the consequence that the energy difference between the two orbitals decreases, which leads to an unexpectedly high number of electrons in the  $d_{x^2-y^2}$  state.

At a certain temperature a sudden transition to the cubic structure can occur, in which both orbitals have the same energy and the tendency of distortion by electrons in  $d_{z^2}$  orbitals is quenched by the tendency of contrary distortions by electrons in  $d_{x^2-y^2}$  orbitals in neighbouring cations. In a particular  $\text{Mn}^{3+}$  ion the fourth 3d electron will change continuously from one orbital to the other. This state is called the dynamic Jahn-Teller effect. An extra stabilisation of the cubic structure in comparison with the tetragonal structure results from the Madelung energy.<sup>44</sup>

(b) The similarity of the distortion as a function of the temperature for  $\text{Mn}_3\text{O}_4$ ,  $\text{ZnMn}_2\text{O}_4$  and  $\text{MgMn}_2\text{O}_4$  suggests a type of transition different from that described in (a), especially because of the initial increase of the distortion with increasing temperature. At further increases of the temperature the degree of inversion of the cation distribution may increase in accordance with equilibrium (4), and so the distortion may decrease by virtue of the decreasing number of  $\text{Mn}^{3+}$  ions in B-sites and an increase of the number of  $\text{Mn}^{3+}$  ions in A-sites,

(44) I. Aoki, *J. Coll. Arts Sci., Chiba Univ. Nat. Sci.*, Ser. 2, 115 (1957), cited by M. F. C. Ladd and W. H. Lee in *Progress in Solid State Chemistry*, vol. 1, pag. 44 (1964), Pergamon Press.

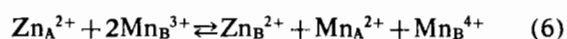
which have a tendency to distort the crystal in the opposite way ( $c/a < 1$ ). Especially in the cubic state above the temperature of transition a second defect equilibrium (5) will occur, for reasons given above. Both equilibria give rise to the possibility of another form of dynamism for the Jahn-Teller effect by a rapid exchange of electrons according to



The mobility of these electrons, together with the increasing concentration of  $\text{Mn}_B^{2+}$  and finally, the extra stabilisation due to the Madelung energy,<sup>44</sup> can cause a sudden transition from the tetragonal to the cubic structure.

Both mechanisms may in fact contribute to the transition of  $\text{Mn}_3\text{O}_4$ . Actually, only the first (a) has been proposed until now.

$\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ . The cation distribution shown in Fig. 7 may be described by



Taking a value of  $3.4 \times 10^{-4}$  for the equilibrium constant  $K_6$  (at a mean temperature of  $1100^\circ\text{C}$ ) one obtains a theoretical cation distribution curve, which is given by the solid line in Fig. 7. Equilibrium (6) explains the continuous decrease of the high-temperature boundary of the cubic spinel field (Fig. 6b) by the continuity of the increasing amount of  $\text{Mn}^{4+}$  ions with increasing zinc content. The assumption of a disproportionating according to equilibrium (5) does therefore not seem to be necessary.

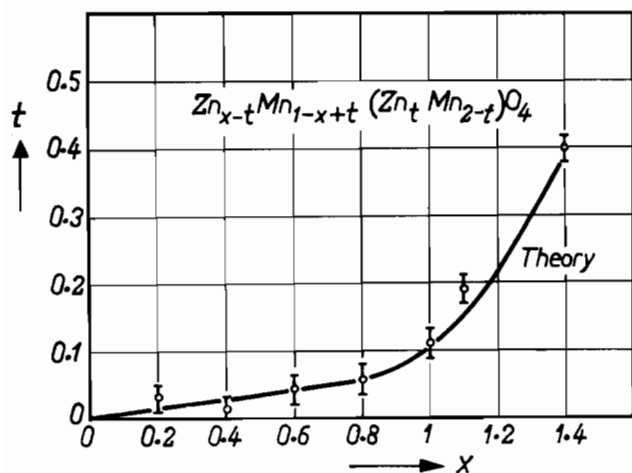


Figure 7. Cation distribution in nearly stoichiometric compounds of the formula  $\text{Zn}_x\text{Mn}_{3-x}\text{O}_4$ , determined with X-rays. The solid curve indicates calculated values (see text).

Samples having the tetragonal structure and quenched from a temperature below about  $1000^\circ\text{C}$  contain a non-negligible excess of oxygen ( $\gamma = 0.025$  was even found). The crystallographic equivalence of this chemically determined excess is probably the occurrence of some cation vacancies. The above mentioned intensity ratios are more sensitive to the place of these vacancies than to the distribution parameter  $t$ . This was the

reason why no temperature dependence could be determined for the cation distribution, although the temperature range of the stability of  $\text{ZnMn}_2\text{O}_4$  is very extended.

However, an indication for the temperature dependence of the cation distribution could be gained from ESR spectra. The spectrum of  $\text{ZnMn}_2\text{O}_4$ , quenched from  $1225^\circ\text{C}$ , contains a signal (Fig. 8a) of a certain defect (perhaps  $\text{Mn}^{2+}$  in tetrahedral sites) without a fine structure. The same signal, found in the spectrum of  $\text{ZnMn}_2\text{O}_4$  when it was quenched from  $705^\circ\text{C}$ , showed a marked fine structure (Fig. 8b), indicating that the defect had a lower concentration.

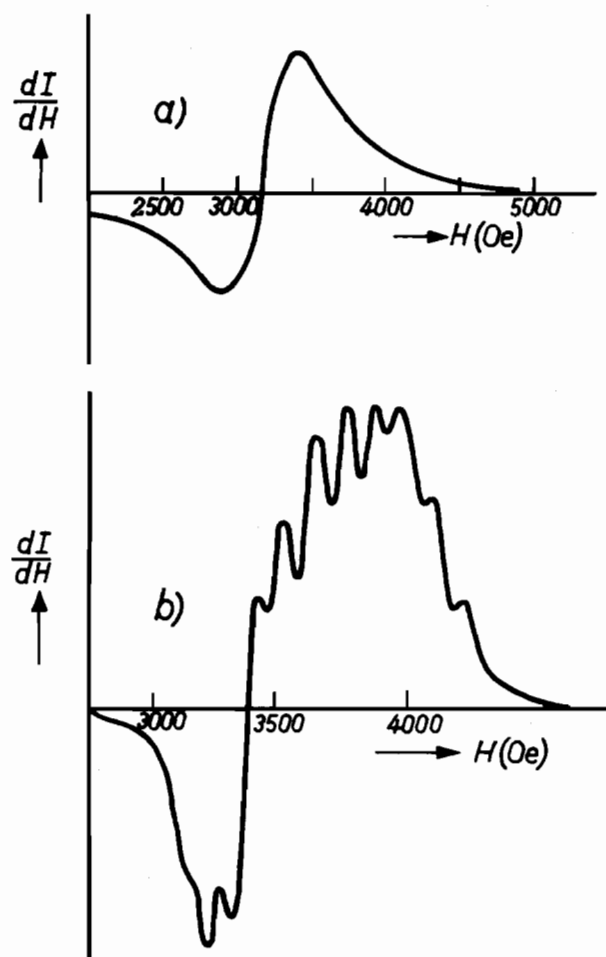


Figure 8. ESR differential spectra of  $\text{ZnMn}_2\text{O}_4$  at liquid-nitrogen temperature. (a)  $\text{ZnMn}_2\text{O}_4$  quenched from  $1225^\circ\text{C}$  (b)  $\text{ZnMn}_2\text{O}_4$  quenched from  $705^\circ\text{C}$ . Amplification of (b) twenty times that of (a).

$\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$ . The cation distributions expected to occur at  $1000^\circ\text{C}$  can be read from Fig. 9. The experimental equilibrium oxygen pressure at the same temperature on the low-pressure boundary of the spinel field in the isothermal section of the system  $\text{Cu-Mn-O}$  has already been given in a previous paper<sup>10</sup> (see also the solid line in Fig. 10). It may be possible to derive from these data a model for the defect structure of these compounds. For this purpose let us assume that the valence and distribution of the cations in  $\text{Cu}_x\text{Mn}_{3-x}\text{O}_4$  can be written in the form

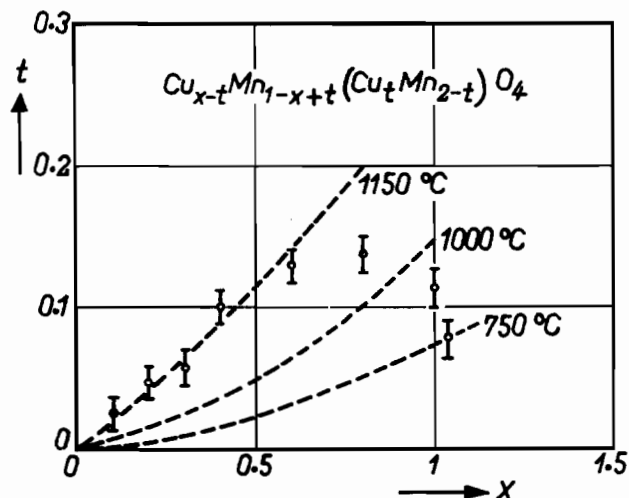


Figure 9. Cation distribution in nearly stoichiometric compounds of the formula  $\text{Cu}_x\text{Mn}_{1-x}\text{O}_4$ . The temperatures of preparation and quenching were necessarily different. See text. Interpolation for different quenching temperatures is given by the broken curves. The curve for 1000°C could be calculated (see text).

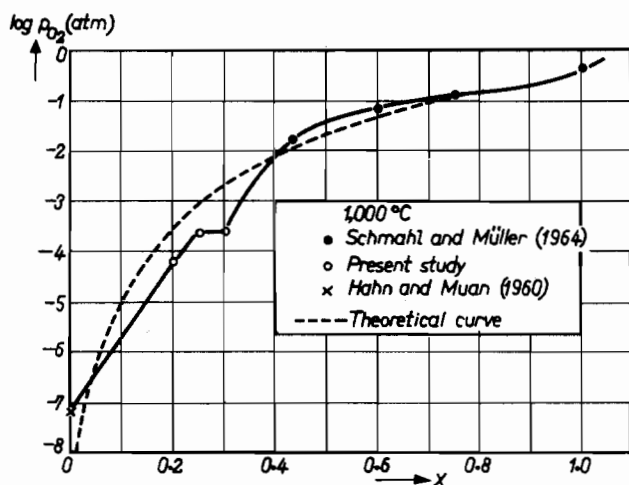
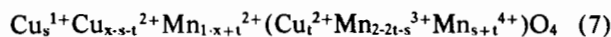


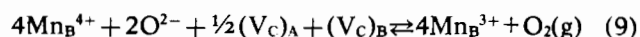
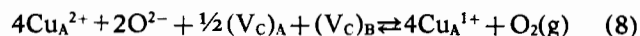
Figure 10. Low-pressure boundary of the spinel ( $0.3 < x$ ) and the hausmannite field ( $0 < x < 0.25$ ) in an isothermal (1000°C) section of the system Cu-Mn-O. (a) experimental curve<sup>10</sup> given by the solid curve (b) theoretical curve given by the broken curve. Compositional parameter  $x$  is taken from the formula  $\text{Cu}_x\text{Mn}_{1-x}\text{O}_4$ . The curves coincide above  $x=0.8$ .



Analogous to the treatment of some ferrite solid solutions by Schmalzried and Tretjakow<sup>46</sup> the assumption is made that the activity of the cation vacancies on the low-pressure boundary of the spinel field does not vary with composition. Then  $x$  is known from the composition and  $t$  from Fig. 9. Furthermore if we use the notation  $(V_C)_A$  to represent a cation vacancy at an A-site, etc., we can write

(45) A. P. B. Sinha, N. R. Sanjana and A. B. Biswas, *Acta Cryst.*, 10, 439-440 (1957).

(46) H. Schmalzried and Yu. D. Tretjakow, *Ber. Bunsenges. Physik. Chem.*, 70, 180-189 (1966).



so that

$$P_{\text{O}_2} = k_1([\text{Cu}_A^{2+}]/[\text{Cu}_A^{1+}])^4 = k_2([\text{Mn}_B^{4+}]/[\text{Mn}_B^{3+}])^4$$

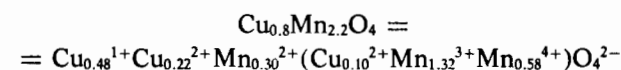
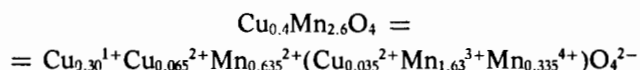
For  $x = 0.4$  we have  $P_{\text{O}_2} = 0.0068$  atm. and  $t = 0.035$  so that

$$0.0068 = k_1\{(0.365 - s_1)/s_1\}^4 = k_2\{(0.035 + s_1)/(1.94 - s_1)\}^4$$

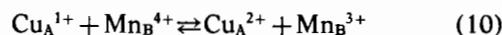
For  $x = 0.8$  we have  $P_{\text{O}_2} = 0.14$  atm. and  $t = 0.10$  so that

$$0.14 = k_1\{(0.70 - s_2)/s_2\}^4 = k_2\{(0.10 + s_2)/(1.80 - s_2)\}^4$$

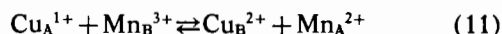
The unknowns  $k_1$ ,  $k_2$ ,  $s_1$  and  $s_2$  can be solved from these four equations. The results are:



These distributions and valencies may thus be valid at 1000°C. From these solutions it can be derived that the constant of equilibrium (10)



has the value 1.04. For the constant of equilibrium (11)



the same value is found with both the above solutions at  $x=0.4$  and  $x=0.8$  (0.047), although the equality does not follow from the mathematical treatment. Therefore the model of formula (7) may be supposed to be a good approximation of the real defect structure.

From the above values of the equilibrium constants the cation distribution can be calculated as a function of the composition. The calculated curve is the same as the broken curve shown in Fig. 9 for 1000°C. It is also possible to derive the oxygen pressure as a function of the composition. The result of this calculation is given by the broken curve in Fig. 10. Using the equilibria (10) and (11) and the model of formula (7) for the defect structure it is not possible to obtain a non-zero value for the oxygen pressure of  $\text{Mn}_3\text{O}_4$  in equilibrium with  $\text{MnO}$ . But, remembering equation (5) and applying the relation

$$\log P_{\text{O}_2} = 4 \log([\text{Mn}_B^{4+}]/[\text{Mn}_B^{3+}]) + 0.57$$

(which is valid for the copper containing substances with the cubic spinel structure according to equation (9)) to the result of Hahn and Muan<sup>47</sup> for the oxygen pressure of tetragonal  $\text{Mn}_3\text{O}_4$  in equilibrium with  $\text{MnO}$ , we find that the concentration of  $\text{Mn}^{4+}$  in B-sites at

(47) W. C. Hahn and A. Muan, *Am. J. Sci.*, 258, 66-78 (1960).



1000°C is about 0.03 in  $M_3O_4$ , if it should be cubic at that temperature and should have that oxygen pressure. We may assume that the oxygen pressure of the cubic form should not be very different from that of the tetragonal form. Then the conclusion may be that the disproportioning according to equilibrium (5) does not play an important role in  $Mn_3O_4$ .

Compositions fired at 1300°C in air showed an unexpectedly high content of copper oxide incorporated in  $Mn_3O_4$ . Single-phase products were obtained in the range  $0 \leq x \leq 0.45$ . The expected range of stability was only  $0 \leq x < 0.2$ . The compounds, especially those with higher copper content, had a marked deficiency of oxygen ( $-0.08 \leq \gamma \leq 0.00$ ).

When quenched, these samples had the tetragonal structure of hausmannite. For this structure the intensity of the reflection (400) is about one and a half times that of the reflection (004). In these samples, however, the intensity of the reflection (400) was only 30 to 20% of that of (004), depending on the copper content and the temperature of firing. This enabled us to infer that about half the copper ions were situated in certain interstitial sites, where they made a positive contribution to the structure factor of the (004) reflection (as do the cations in octahedral sites), and a negative contribution to the structure factor of the (400) reflection (as do the cations in tetrahedral sites). These interstitial sites are found between two oxygen ions in a (001) plane. Without this model, a value of 12 to 15% was found for the reliability factor R of the structure. With this model, the value of R decreased to 6 or 8%.

It should be noted that the  $Cu^{1+}$  ions in the structure of cuprite  $Cu_2O$  are also situated between two oxygen ions. It has already been reported<sup>10</sup> that the distance

between two oxygen ions in the cubic spinels  $Cu_xMn_{3-x}O_{4+\gamma}$  at these high temperatures is the same as that in  $Cu_2O$  at these temperatures. Therefore the defects may result from the tendency of  $Cu^{1+}$  ions to form two-ligand surroundings.

The formation of these defects can be partly understood on the basis of the spinel structure. If a deficiency of oxygen ions occurs, the close packing of oxygen ions remains and some cations have to be accommodated in interstitial sites. The largest interstitial sites in the spinel structure are the unfilled octahedral sites. A cation in such a site will, however, hinder two cations in neighbouring tetrahedral sites. The local strain of this hindering will largely vanish if these neighbours in tetrahedral sites move into interstitial positions, which, as shown above, were partly occupied.

## Conclusion

The defect structure of  $Mn_3O_4$  and manganites containing zinc or copper ions was deduced from structural and thermodynamic studies.  $Mn_3O_4$  is probably a partly inverse spinel at high temperatures. Partial disproportioning of the  $Mn^{3+}$  ions in B-sites into  $Mn^{2+}$  and  $Mn^{4+}$  ions does not play an important role. The cation distribution of zinc manganites could be explained by assuming  $Mn^{4+}$  ions in B-sites. The cation distribution and the equilibrium oxygen pressure of copper manganites could be explained by assuming  $Cu^{1+}$  ions in A-sites and  $Mn^{4+}$  ions in B-sites. The formula of  $CuMn_2O_4$  at 1000°C is expected to be



*Acknowledgement.* The author is indebted to Prof. Dr. G. D. Rieck for stimulating discussions. He also wishes to thank many of his colleagues for their interest and their critical reading of the manuscript. Thanks are given to Prof. Dr. G. C. A. Schuit and his co-workers for the opportunity to determine the ESR spectra.

Eindhoven, Aprile 1967.

(48) G. D. Rieck and F. C. M. Driessens, *Acta Cryst.*, 20, 521-525 (1966).

(49) (a) J. M. Hastings and L. M. Corliss, *Phys. Rev.*, 103, 328-331 (1956). (b) I. J. Yamzin, N. V. Belov and Yu. Z. Nozik, *J. Phys. Soc. Japan*, 17, Suppl. B111, 55-57 (1962). (c) H. A. Alperin, *J. Phys. Soc. Japan*, 17, Suppl. B111, 57 (1962). (d) A. Murasik and G. Roult, *J. Phys.* (Paris), 25, 522-525 (1964). (e) K. Kleinstück, E. Wieser, P. Kleinert and R. Perthel, *Phys. Stat. Sol.*, 8, 271-281 (1965).

(50) M. Balarin and M. Schenk, *Phys. Stat. Solidi*, 17, 91-99 (1966).

(51) R. W. G. Wyckhoff, *Crystal Structures*, 2nd. Ed., Interscience Publishers, New York (1965).