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On the structure of some manganites.

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A preliminary report on the crystal structure of the manganites ($A^{2+}Mn_2^{3+}O_4^{2-}$) of some bivalent metals (A) such as Cd, Mg, Co, Fe, Cu and Ni, prepared in this Laboratory, is given below.

The manganites were prepared by heating for several hours 1:1 mixtures of manganese sesquioxide with the bivalent metal oxides at temperatures between 700 and 900° C. The products were quenched in air to room temperature and examined by X-ray powder diffraction using a 14 cm. Debye–Scherrer camera and Mo $K\alpha$ radiation ($\lambda = 0.709$ Å). The lines in the diffraction patterns were indexed on the basis of crystal data set out in Table 1.

The crystals were found to possess either a tetragonally deformed spinel structure isomorphous with $Mn[Mn_2]O_4$ and $Zn[Mn_2]O_4$ (Mason, 1947; Romeijn, 1953), or a spinel structure isomorphous with $Mg[Al_2]O_4$ (Bragg, 1915a,b). There are eight molecules in the unit cell, where the 32 oxygen ions form a cubic close-packed arrangement with 8 of the 64 tetrahedral and 16 of the 32 octahedral sites occupied by the cations.

The intensities of the reflexions were estimated visually and compared with those calculated for the three models: normal, $A[Mn_2]O_4$; random $A_{\frac{1}{3}}Mn_{\frac{2}{3}}[A_{\frac{2}{3}}Mn_{\frac{4}{3}}]O_4$; and inverse $Mn[AMn]O_4$. The cations in the octahedral sites are conventionally indicated by enclosing them in square brackets. The distribution of cations is sensitive to the intensities of 220, 400 and 422 reflexions (Bertaut, 1950) and is determined from a correlation of these intensities and also from overall agreement index $R = \Sigma||I_o - \sqrt{I_c| \div \Sigma|\sqrt{I_o}|}$, the latter varying between 10 and 25% in different cases.

Owing to the relatively low scattering power, the oxygen-ion parameter, u, could not be determined accurately from the X-ray data. For the manganites of Cu, Ni and Cd, u is within 1% of 0.389, 0.381 and 0.400, respectively. In other cases also, the steric factors (size of cations and tetrahedral hole) suggest (Table 2) a similar increase from the value 0.375 corresponding to the ideal close-packing of oxygen ions.

The distortion of the lattice and the distribution of the cations are explained on the basis of their bond-forming properties and relative affinities for a particular site. The distortion of cubic symmetry is brought about by coplanar square-bond-forming cations such as Mn^{3+} in the octahedral site (Goodenough & Loeb, 1955). A group of four equivalent dsp^2 covalent coordinate bonds are formed in a plane defined by the a and b axes and two ionic bonds parallel to the c axis. Since the covalent bonds are the stronger, the a and b axes are shorter than c, i.e. c/a is greater than unity.

The cationic arrangement is influenced in the first place by the strong tendency of the Mn^{3+} ions to form dsp^2 bonds (Table 2). They are therefore accommodated preferentially in octahedral sites where the geometrical factors favour the formation of square coplanar bonds.

In the manganites of Cd, Mn and Zn, the normal arrangement is stabilized by the strong tendency of these ions to form sp^3 bonds (regular or distorted) in the tetrahedral sites. The Mg^{2+} ion, which is unlikely to form covalent bonds, is stabilized in the tetrahedral holes through the formation of electrovalent bonds. The random structure in the case of cobalt manganite indicates that Co^{2+} shows more or less equal affinity for both types of

Table 1. *Crystallographic data*

Compound	Symmetry*	a (Å)	c (Å)	c/a	Cation arrangement†
$Cd[Mn_2]O_4$	T	8·22	9·87	1·20	Normal
$Mn[Mn_2]O_4$‡	T	8·15	9·44	1·16	Normal
$Mg[Mn_2]O_4$	T	8·07	9·28	1·15	Normal
$Zn[Mn_2]O_4$‡	T	8·10	9·25	1·14	Normal
$Co_xMn_{1-x}[Co_{1-x}Mn_{1+x}]O_4$	T	8·04	9·04	1·12	Random
$Fe_xMn_{1-x}[Fe_{1-x}Mn_{1+x}]O_4$	T	8·31	8·85	1·05	Random
$Cu[Mn_2]O_4$	C	8·33	8·33	1·00	Normal
$Mn[NiMn]O_4$	C	8·37	8·37	1·00	Inverse

* T: tetragonal; C: cubic.

† Nomenclature according to Barth & Posnjak (1932).

‡ Mason (1947); Romeijn (1953).

Table 2

Cations	r (Å)	Outer electronic configuration	Most probable* bond formation
Cd^{2+}	0·97	$4d^{10}$	sp^3
Mn^{2+}	0·91	$3d^5$	sp^3
Mn^{3+}	0·62	$3d^4$	dsp^2
Mg^{2+}	0·78	$2p^6$	Electrovalent
Zn^{2+}	0·78	$3d^{10}$	sp^3
Co^{2+}	0·82	$3d^7$	sp^3; dsp^2
Fe^{2+}	0·82	$3d^6$	sp^3; d^2sp^3
Fe^{3+}	0·60	$3d^5$	sp^3
Cu^{1+}	0·96	$3d^{10}$	sp^3
Cu^{2+}	0·70	$3d^9$	dsp^2
Ni^{2+}	0·78	$3d^8$	dsp^2

* Goodenough & Loeb (1955).

sites, some Mn^{3+} ions being displaced from octahedral sites.

The occurrence of cubic symmetry with a normal cation arrangement of copper manganite is contrary to expectation since, of all the metals in the first transition series, Cu^{2+} has the strongest square (dsp^2) bond-forming power and should occupy an octahedral site, thus making the structure inverse and the symmetry tetragonal. The result can easily be explained on the basis of an electron transfer process

$$Cu^{2+}+Mn^{3+} \xrightarrow{\ e^-\ } Cu^{1+}+Mn^{4+}$$
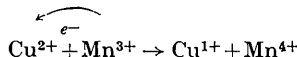
occurring under the experimental conditions and, as a result, the Cu^{1+} ions formed occupy tetrahedral sites (Table 2), the resulting structure being normal. Furthermore, in the unit cell of $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4^{2-}$, the $8 Mn^{4+}$ ions ($3d^3$) form six equivalent octahedral d^2sp^3 bonds and the 8 Mn^{3+} ions dsp^2 square bonds. The stress produced by the Mn^{3+} ions, which occupy only 25% of the octahedral lattice sites, is not sufficient to cause any observable distortion in the macro-crystal.

The inverse structure of nickel manganite shows the stronger tendency for Ni^{2+} ions to occupy octahedral sites. However, if the Ni^{2+} ions also form dsp^2 bonds, all the octahedral ions tend to distort the lattice, and the observed cubic symmetry is thus anomalous. This may,

however, be explained in one of the following ways: (i) Ni^{2+} ions form six equivalent bonds of the type $3d^24s4p^3$ by promoting two $3d$ electrons to higher $5s$ level or $4s4p^34d^2$ hybridized orbitals in the octahedral site; (ii) the group of four planar dsp^2 bonds due to Mn^{3+} and Ni^{2+} ions forming tetragonally distorted octahedra oriented in three mutually perpendicular directions; or (iii) a compound $Mn^{2+}[Ni^{2+}Mn^{4+}]O_4^{2-}$ formed as a result of the electron transfer process, $2 Mn^{3+} \to Mn_2^+ + Mn^{4+}$. The cubic symmetry can then be explained as in the case of $Cu^{1+}[Mn^{3+}Mn^{4+}]O_4^{2-}$.

In the case of iron manganite, it is not possible to determine the cation arrangement from the X-ray data because of the nearly equal scattering power of the two cations. However, since c/a is almost equal to unity, it can be inferred that at octahedral sites an appreciable portion of Mn^{3+} ions have been replaced by cations forming six equivalent bonds. It is likely that an electron transfer process

$$Fe^{2+}+Mn^{3+} \xrightarrow{\ e^-\ } Fe^{3+}+Mn^{2+}$$
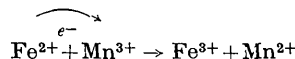
occurs so that a compound $Fe_{0.5}^{3+}Mn_{0.5}^{2+}[Fe_{0.5}^{2+}Mn_{1.5}^{3+}]O_4^{2-}$ with an almost random type of structure is formed.

Further work is under progress and the detailed results will be published later.

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Observations on pigeonite. By M. G. BOWN and P. GAY, *Department of Mineralogy and Petrology, Cambridge, England*

The most important rock-forming pyroxenes occur in the ternary system $MgSiO_3$–$FeSiO_3$–$CaSiO_3$, with less than 50% $CaSiO_3$; a minor amount of replacement by other cations, notably aluminium, is usual. Over most of this field the pyroxenes are monoclinic, although at less than 5% $CaSiO_3$ an orthorhombic modification is the more stable form. All clino-pyroxenes are very similar in structure to diopside, $CaMg(SiO_3)_2$, which has the space group $C2/c$ (Warren & Bragg, 1929; Warren & Biscoe, 1931). Those with compositions falling inside the trapezium $CaMgSi_2O_6$–$CaFeSi_2O_6$–$FeSiO_3$–$MgSiO_3$ are divided, on the basis of their optical properties, into augites and pigeonites: roughly speaking augites contain more than,

and pigeonites less than, 20% $CaSiO_3$. There is a solid-solubility gap at low temperatures between augite and pigeonite, the variation of the solubilities of one component in the other being temperature dependent; thus augite which has crystallized at a fairly high temperature may precipitate lamellae of pigeonite on slow cooling in the earth's crust, and similarly pigeonite crystals often contain augite lamellae. Morimoto (1956) has recently examined such a lamellar aggregate, and has found that the cell dimensions of the pigeonite are very similar to those of the augite, that the two phases have the directions of the x and y axes in common, and that whereas the space group of the augite is $C2/c$, that of the pigeonite