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The Crystal Structure of Cadmium Manganite, $Cd[Mn_2]O_4$

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Zusammenfassung

Die Kristallstruktur des durch Reaktion von CdO und Mn_2O_3 *im* festen Zustand gewonnenen Cadmiummanganits $Cd[Mn_2]O_4$ wurde mittels Pulveraufnahmen bestimmt. Die Gitterkonstanten der tetragonalen Zelle sind $a = 5{,}81$ Å, $c = 9{,}87$ Å, $c:a = 1{,}69_9$, Z = 4, die Raumgruppe $I\,4_1/amd\text{-}D_{4h}^{19}$. Die Metallionen nehmen spezielle Lagen entsprechend den normalen Spinellen ein.

Aus Betrachtungen über Elektronenkonfigurationen der Kationen wird geschlossen, daß die Mn^{3+}-Ionen mit größerer Wahrscheinlichkeit als die Cd^{2+}-Ionen die oktaedrischen Lücken besetzen und daß die Verringerung der Symmetrie von der kubischen der Spinelle zur tetragonalen auf der Natur und Verteilung der Mn^{3+}-Bindungen beruht.

Abstract

The crystal structure of cadmium manganite $Cd[Mn_2]O_4$, formed by reaction in the solid state between CdO and Mn_2O_3, has been determined from the X-ray powder diffraction pattern. The dimensions of the tetragonal unit cell are $a = 5.81$ Å, $c = 9.87$ Å and $c/a = 1.69_9$; $Z = 4$. The metal ions occupy special sites, as in a "normal" spinel.

From a consideration of the electronic configuration of the cations and their *d*, *s* and *p* hybrid bond-forming powers it is deduced that Mn^{3+}, but not Mn^{2+} or Mn^{4+} ions, occupy the octahedral interstices of the cubic close-packed oxygen anions in preference to Cd^{2+} ions. The distortion of the crystal lattice from cubic to tetragonal symmetry is attributed to the nature and distribution of the bonds associated with the Mn^{3+} ions.

Introduction

Several metal oxides and many binary oxide systems, having the general formula AB_2O_4, have the same general crystal structure as the mineral spinel $MgAl_2O_4$. This can be considered as an ordered mixture of the zinc-blende and sodium-chloride types of structures, where the much larger oxygen ions form a cubic close-packed assemblage stabilised by the cations A and B distributed among the tetrahedral and octahedral interstices (W. H. BRAGG, 1915).

In the unit cell of a spinel there are 8 molecules of AB_2O_4, with 64 tetrahedral and 32 octahedral holes. The simplest distribution of the cations is the one in which A ions occupy 8 of the tetrahedral and B ions 16 of the octahedral holes; this is known as the normal spinel structure. However, other distributions are possible. Thus BARTH and POSNJAK (1932) have shown that the A and B ions may be distributed randomly among the two types of interstices (random spinel structure), or that half the B ions may lie in tetrahedral interstices, while the A ions together with the rest of the B ions are randomly distributed over the 16 octahedral holes (inverse spinel structure). Other intermediate structures, partly normal and partly inverse, are also possible.

The spinels and spinel-like compounds are of great interest in view of their unusual physical and crystallographic properties. Although many spinels have been prepared and studied (ROMEIJN, 1953) much remains to be done in elucidating the factors influencing the distribution of cations in spinel structures and the effects of such distributions on their physical and crystallographic properties. For this reason we have been studying the mechanism of formation in the solid state of certain spinels and spinel-like compounds with a view to correlating structure with physical properties. While the aluminates, chromites and ferrites have been extensively studied, the manganites have received little attention. So far only $Mn[Mn_2]O_4$ and $Zn[Mn_2]O_4$ have been reported (BRIAN MASON, 1947; ROMEIJN, 1953) as possessing the normal spinel structure. A preliminary report of several manganites prepared in this laboratory has been given elsewhere (SINHA, SANJANA and BISWAS, 1957) and in what follows, a detailed account is given of the structure determination of cadmium manganite, formed by reaction in the solid state, from X-ray powder patterns.

Experimental

An equimolecular mixture of CdO and Mn_2O_3 (prepared by the decomposition of "Analar" MnO_2 at 900 °C), was heated at different temperatures and quenched in air to room temperature. The products obtained at various stages were examined at room temperature in a 14 cm. DEBYE-SCHERRER camera using $MoK\alpha_1$ radiation ($\lambda = 0.709$ Å) filtered through Zr foil.

Results

The powder patterns for finely divided and intimately mixed samples heated progressively at 650, 700, 750 and 800 °C revealed a gradual fading of the diffractions due to the components and their replacement by a new set of reflections. Heating at 850 °C for 45 hours eliminated all diffractions due to the components.

A list of the new reflections observed, together with the observed and calculated spacings and observed intensities are set out in Table 1. The intensities of the lines (measured in more than one photograph) were estimated by eye and also checked from the diffractometer patterns. The intensity of the strongest reflection at 2.87 Å, has been arbitrarily assigned the value of 100.

All the reflections could be indexed (column 1, Table 1) on the basis of a tetragonal unit cell having the dimensions $a = 5.81$ Å, $c = 9.87$ Å, $c/a = 1.69_9$; observed density measured by displacement in a specific gravity bottle = 5.52 g/cm^3, whence $Z = 4$, and the density calculated on this basis is 5.67 g/cm^3 which, having regard for

Table 1

hkl	$d_{calc.}$	$d_{obs.}$	$I_{obs.}$	$I_{calc.}$ Normal $x = .200$ $z = .400$	$I_{calc.}$ Inverse $x = .250$ $z = .375$	$I_{calc.}$ Random $x = .250$ $z = .375$
101	5.00		<3	1	51	12
112	3.16	3.15	95	137	28	61
200	2.90_5	2.87	100	40	8	17
103	2.86			84	88	101
211	2.51	2.51	100	115	121	138
202	2.50			6	39	25
004	2.47			2	37	23
220	2.05	2.04	24	1	40	24
213	2.04			12	11	2
301	1.90	1.86_5	66	5	4	1
204	1.88			19	4	10
105	1.87			40	25	29
312	1.72	1.72	24	31	7	15
303	1.67	1.66	15	10	18	20
321	1.59	1.57	100	45	29	33
224	1.58			57	77	83
215	1.57			1	5	1
116	1.53	1.51	30	9	2	5
314	1.47	—	–	1	<1	<1

Table 1. *(continued)*

hkl	$d_{calc.}$	$d_{obs.}$	$I_{obs.}$	$I_{calc.}$		
				Normal $x = .200$ $z = .400$	Inverse $x = .250$ $z = .375$	Random $x = .250$ $z = .375$
400	1.45	1.45	36	22	30	32
323	1.44_5			1	4	1
206	1.43	1.41	10	6	10	7
411	1.40			1	4	1
402	1.39			1	<1	<1
305	1.38	1.37	25	11	10	11
107	1.37			2	2	1
332	1.32	1.29	39	5	1	3
413	1.30			17	15	17
420	1.30			5	1	3
422	1.25_5	1.25	12	4	14	10
404	1.25			1	14	8
325	1.25			3	5	2
217	1.24	1.22	33	10	14	16
008	1.23			1	8	8
316	1.22			13	2	5
431	1.15	1.14	24	2	2	1
501	1.15			1	1	1
424	1.15			10	2	4
415	1.15			13	10	12
307	1.14			1	1	1
208	1.13_5			4	1	2
512	1.11	1.11	10	9	2	3
433	1.09_5	1.09	15	7	9	10
503	1.09_5			6	4	5
406	1.09			1	<1	<1
109	1.08	1.07	14	1	1	1
521	1.07			6	8	9
327	1.06			8	8	9
228	1.06			1	8	4
336	1.05	1.04_5	15	5	1	2
514	1.03_5			1	<1	<1
440	1.03	1.02	14	5	9	9
523	1.02_5			2	1	1
318	1.02			1	<1	<1
426	1.02			3	11	8
219	1.01	0.99_5	18	9	7	8
435	1.00			6	4	7
505	1.00			6	2	4
417	0.99_7			1	1	1
			$R =$	15%	35%	23%

the nature of the material, is in fair agreement with the observed value. The space group is $I4_1/amd\text{-}D_{4h}^{19}$, and the atomic coordinates for the unit cell are $(0\ 0\ 0;\ \frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}) +$ metal ions at 4(a) — $0\ 0\ 0;\ 0\ \frac{1}{2}\ \frac{1}{4}$; 8(d) — $0\ \frac{1}{4}\ \frac{5}{8};\ 0\ \frac{3}{4}\ \frac{5}{8};\ \frac{1}{4}\ 0\ \frac{3}{8}$; and $\frac{3}{4}\ 0\ \frac{3}{8}$; oxygen ions at 16(h) — $0\ x\ z;\ 0\ \bar{x}\ z;\ 0\ \frac{1}{2}+x\ \frac{1}{4}-z;\ 0\ \frac{1}{2}-x\ \frac{1}{4}-z;\ x\ 0\ \bar{z};\ \bar{x}\ 0\ \bar{z};\ x\ \frac{1}{2}\ \frac{1}{4}+z$; and $\bar{x}\ \frac{1}{2}\ \frac{1}{4}+z$.

In order to determine the distribution of metal ions over the 4(a) and 8(d) positions, and also the values of the oxygen parameters x and z, the relative intensities of all non-zero reflections down to 1.00 Å were calculated for various models using the formula

$$I \propto |F|^2 . \ p \cdot \frac{1+\cos^2 2\theta}{\sin^2\theta \cdot \cos\theta}$$

where p is the multiplicity factor. Atomic structure factors have been taken from the International Tables (1935); and corrections for the opposing effects of absorption and thermal vibrations were not applied. The values I_c normalised with respect to the observed intensities, are given in Table 1 for normal, inverse and random distributions of cations for the models which give the best overall agreement with particular values of x and z. Intensity ratios of certain lines are included in Table 2.

Table 2

Reflection ratios	Observed intensity ratios	Calculated intensity ratios		
		Normal $x = .200$ $z = .400$	Inverse $x = .250$ $z = .375$	Random $x = .250$ $z = .375$
101	absent	1	51	12
112/200, 103/ 211, 202, 004	vs/vs/vs	137/124/123	28/96/197	61/118/186
220, 213/ 301, 204, 105	w/s	13/64	51/33	26/40
312/303	ms/w	31/10	7/18	15/20
332, 413, 420/ 422, 404, 325	ms/vw	27/7	17/33	23/20

From a comparison of the observed and calculated intensities set out in Table 1 a choice can now readily be made of the most probable coordinates of the metal ions, because, they largely determine the reflection intensities which are relatively insensitive to the oxygen parameter ($f_{Cd^{2+}} : f_{Mn^{3+}} : f_{O^{2-}} = 46 : 22 : 10$).

The agreement is easily the best with the normal spinel structure at $x \cong 0.200$, $z \cong 0.400$, and the inverse and random structure models are ruled out. Thus, whereas the 101 reflection is not actually observed, for the inverse and random structures it should be strong and medium respectively. The 112 reflection is very strong, but the inverse structure requires that this be medium and weaker than 101, and for the random structure it is strong. Again, ratios of intensities of lines or group of lines listed in Table 2 clearly rule out the inverse and random structures and give a good fit in the case of normal structure. Furthermore, the usual reliability index $\left(R = \frac{\Sigma \mid \sqrt{I_o} - \sqrt{I_c} \mid}{\Sigma \mid \sqrt{I_o} \mid}\right)$ has been calculated to check overall agreement for all the models examined. The normal structure shows the best agreement. However, owing to the presence of heavy atoms and the relatively few reflections, this index must not be relied on implicitly (DONOHUE and TRUEBLOOD, 1956; LIPSON and COCHRAN, 1953).

In view of the above considerations a normal structure may reasonably be assigned to cadmium manganite with the Cd^{2+} ions in 4(a) and Mn^{3+} ions in 8(d) positions. It should be noted that a small degree of disorder could not be revealed by a powder pattern analysis. It will be shown later, however, that in this case the existence of disorder is unlikely.

The parameters, x and z, of the oxygen atoms cannot be determined accurately because of their low scattering power. This is brought out by the small change in the values of R vs x and z which act as a useful guide in deciding whether any particular change in parameter improves the agreement. With x and z varying in the limits $0.25 \geqslant x \geqslant 0.20$ and $0.40 \geqslant z \geqslant 0.375$ respectively, the values of R were found to vary from 0.15 to 0.20 in normal, 0.23 to 0.28 in random, and 0.35 to 0.38 in inverse structures. It was not worthwhile to check models beyond the above stated limits as the structure becomes unreasonable from steric considerations. However, since the 101 reflection is too weak to be observed, and the group of 404, 422, 325 reflections also is very weak, we are led to assign $x \cong 0.20$ and $z \cong 0.40$ with the normal structure. These values are also supported by considerations of space (size of the interstices) and bond properties of the ions.

In analogy with cubic spinels regarded as of body-centered tetragonal structure, the ideal values of x and z are $^1/_4$ and $^3/_8$ respectively. However, from Table 3, it will be seen that corresponding radius of the tetrahedral hole is only 0.58 Å, which is too small to accomodate a

Cd^{2+} ion with its radius of 0.97 Å. By increasing z and correspondingly decreasing x, the size of the tetrahedral hole increases until at $x = 0.20$ and $z = 0.40$, the radius of the hole becomes 0.97 Å, which can accommodate a Cd^{2+} ion. On the other hand, if the Cd^{2+} ion is tetrahedrally and covalently linked with the neighbouring oxygen ions, a smaller value of z ($= .390$ with $x = .220$) would also satisfy steric restrictions, as the tetrahedral $Cd^{2+} - O^{2-}$ distance 2.14 Å (PAULING, 1945) is shorter than the ionic distance 2.37 Å. The interionic distances and bond angles are listed in Table 4.

Table 3. *Calculated radii of tetrahedral and octahedral holes in $CdMn_2O_4$*
($O^{2-} = 1.32$ Å)

x	z	Tetrahedral Å	Octahedral planar Å	Octahedral linear Å
0.250	0.375	0.58	0.73	1.15
0.240	0.380	0.66	0.70	1.10
0.230	0.385	0.74	0.66	1.06
0.220	0.390	0.82	0.63	1.01
0.210	0.395	0.90	0.59	0.97
0.200	0.400	0.97	0.56	0.92

Each Cd^{2+} ion is surrounded by four equidistant oxygen ions in a distorted tetrahedral arrangement. All the $O^{2-} - Cd^{2+} - O^{2-}$ angles

Table 4. *Interionic distances and bond angles*

$M - O^{2-}$	Observed (Å) $x = .200$ $z = .400$	Reported values*		Bond angle calculated from experimental data
		Ionic (Å)	Covalent (Å)	
$Cd^{2+} - O^{2-}$ (Tetrahedral)	2.29	2.37	2.14 (Tetrahedral)	$O^{2-} - Cd^{2+} - O^{2-}$ (99° 19′ and 114° 46′)
$Mn^{3+} - O^{2-}$ (linear)	2.24			
		2.02	1.86 (Octahedral)	
$Mn^{3+} - O^{2-}$ (coplanar)	1.88			

* Taken from PAULING (1945).

are not equivalent; two of them are 99° 19′ and the remaining four are 114° 46′. Manganese in the octahedral position is surrounded by four equidistant, coplanar oxygens in a square arrangement and by two equidistant, linear oxygens in a perpendicular plane, the respective distances being 1.88 Å and 2.24 Å. The assumption that the manganese is present as Mn^{3+} (and not as Mn^{2+} and Mn^{4+}) in the crystal lattice is justified by considerations of electronic configuration and lattice distortion which are discussed below.

Discussion

For convenience the unit cell so far used may be represented by another, comparable in dimensions and similar to that of a cubic spinel. Such an equivalent is a face-centered tetragonal cell with dimensions $a' = 8.22$ Å, $c' = 9.87$ Å and $c'/a' = 1.20$. This can be regarded as a distorted spinel with the c-axis elongated by about 20 per cent.

The cation distributions, and the resulting crystal system are, no doubt, influenced by the charge and steric factors, but they do not by themselves suffice to explain the distributions observed in many spinels and spinel-like compounds. It is necessary also to consider the effect of specific directional forces due to the covalent contribution to the bonds between the cations and anions (GOODENOUGH and LOEB, 1955).

It is reasonable to expect that those metals whose oxides have a wurtzite structure should also tend to occupy the tetrahedral sites in spinels as they do in their oxides. Similarly, metals the structures of whose oxides are of the rock-salt type should tend to occupy octahedral sites. On the other hand, both an A and a B metal ion might tend to occupy the same kind of site, in which case the relative affinities of the two ions for such similar sites must be compared before their distribution can be predicted.

CdO has the rock-salt type of structure, and the Cd^{2+} ions should accordingly occupy the octahedral sites in a spinel structure which is contrary to what we find in the cadmium manganite structure. This suggests that the Cd^{2+} ions are forced out of octahedral sites by the Mn^{3+} ions due to their greater affinity for these sites.

The formation and properties of various hybridised orbitals involving s, p and d electrons have been discussed by PAULING (1945). Thus a cation with a full d shell separated in energy by only a small interval from the next empty s and p shells can form empty, stable

sp^3 hybrid orbitals pointing towards the four corners of a tetrahedron. The outer electron configuration of Cd in the ground state is $4d^{10}5s^2$, so that Cd^{2+} ions (where $4d^{10}$, i. e. a full d shell remains) fulfil the above requirements. In fact Cd^{2+} is well known to form stable hybrid sp^3 orbitals in its compounds such as CdS, CdSe and CdTe. In the present case the four nearest neighbouring oxygen anions which have a $1s^2 2s^2 2p^6$ electron configuration perturb the cation in the tetrahedral site of the lattice to form stable, empty sp^3 hybrid orbitals which in turn overlap with the oxygen full p orbitals and accept electrons from the anions forming coordinate covalent bonds. Thus the Cd^{2+} ions are most likely to be accommodated in the tetrahedral interstices.

A comparison of the observed $Cd^{2+} - O^{2-}$ interionic distance with those of electrostatically and tetrahedrally bonded distances (Table 4) suggests that the binding takes place through a mixture of the two types. The deviation of the $O^{2-} - Cd^{2+} - O^{2-}$ angles from the ideal tetrahedral value (109° 28′) also indicates a distortion from the purely sp^3 hybrid bonding of Cd^{2+} in the site.

The outer electron configuration of manganese in the ground state is $3d^5 4s^2$ and we have assumed manganese to be present in the cadmium manganite structure as Mn^{3+} (with a $3d^4$ configuration). Such an ion with one completely vacant d orbital available for hybridization with empty s and p orbitals can easily form the square, coplanar (dsp^2) hybrid orbitals and be accommodated in an octahedral site. It could also form the d^2sp^3 type of orbitals by reversing an electron spin, but this would require extra energy. Bonds formed through a sp^3 orbital are weak in the case of Mn^{3+} which will in consequence have little tendency to go to the tetrahedral sites. Hence, the most stable site for Mn^{3+} is the octahedral, while the corresponding site for Cd^{2+} is the tetrahedral.

If, instead of Mn^{3+}, $Mn^{2+}(3d^5)$ were present then, according to HUND's rule, each of the five $3d$ orbitals would be occupied by one uncoupled electron, so that the Mn^{2+} ion would preferably form an empty sp^3 hybridised bond orbital. Thus the Mn^{2+} ion should occupy a tetrahedral site and in the present case, it would then compete with Cd^{2+} for the same site. In that case the structure should have been inverse or partly inverse according to their relative affinities for the same site. On the other hand, if Mn^{2+} has much less affinity than Cd^{2+} and is forced out to the octahedral site, where it is not likely to form dsp^2 or d^2sp^3 bond orbitals, it should form six equivalent ionic Mn — O bonds with its neighbouring oxygen ions. Similarly $Mn^{4+}(3d^3)$

has two unfilled $3d$ orbitals, which with the next s and p orbitals can form six equivalent d^2sp^3 hybridised bond orbitals and become stabilised in the octahedral site, forming only one type of bonds with the six neighbouring oxygens. On the contrary there are two types of Mn — O distances in the cadmium manganite structure, which, together with lattice distortion, would not have occurred if Mn^{2+} and Mn^{4+} only were present. YAKEL (1955) studied the structure of a few perovskite type manganites (ABO_3) containing both Mn^{3+} and Mn^{4+} ions which indicate that the distortion from the cubic form decreases with the increase of Mn^{4+} ions in the structure. These considerations rule out the occurrence of Mn^{2+} and Mn^{4+} ions in the cadmium manganite structure.

The $Mn^{3+} — O^{2-}$ distance in the C-plane where the ions are supposed to be bonded through dsp^2 orbital overlap is 1.88 Å but normal to this plane this distance is 2.24 Å. Taking the covalent radius of Mn^{3+} to be approximately the same as that of octahedrally bonded isoelectronic tetravalent Fe and adding the covalent radius of oxygen (PAULING, 1945) the $Mn^{3+} — O^{2-}$ distance becomes 1.86 Å, which is a little less than our observed value. Furthermore, the $Mn^{3+} — O^{2-}$ ionic bond length has been estimated to be 2.02 Å, which is smaller than the distance 2.24 Å observed by us. However, our values are in fair agreement with the Mn — O distances in manganite (BUERGER, 1936) where four oxygens surrounding a manganese ion are at a distance of 1.85 to 1.92 Å in a nearly square configuration, while the two other oxygen ions of the octahedron are at a distance of 2.30 Å. Also, the Mn — O distances in hollandite (1.94 Å in one plane, and 1.90 Å and 2.12 Å in a different plane) reported by BYSTROM and BYSTROM (1950) agree with our values. Further, in two of the modifications of MnO_2 whose structures have been fully determined the Mn — O distances are 1.88 Å (pyrolusite) and 1.89 Å (ramsdellite). Again, in groutite, $HMnO_2$, the $Mn^{3+} — O^{2-}$ bond has been found to be 2.06 Å (COLLINS and LIPSCOMB, 1950).

The agreement between our results and those cited above suggest that Mn^{3+} ions in cadmium manganite are located in the octahedral sites and formed bonds with the oxygen ions which are partially covalent and partially ionic.

Like $CdMn_2O_4$, hausmannite (Mn_3O_4) and hetaerolite ($ZnMn_2O_4$) also form spinel structures of tetragonal symmetry. It is reasonable to suppose that the cation distributions in all these three crystal structures are similar and may be represented in the conventional way as

$Cd^{2+}[Mn_2^{3+}]O_4^{2-}$, $Mn^{2+}[Mn_2^{3+}]O_4^{2-}$ and $Zn^{2+}[Mn_2^{3+}]O_4^{2-}$. The axial ratios of the last two have been reported as $c'/a' = 9.42$ Å/8.14 Å $= 1.16$, and $c'/a' = 9.23$ Å/8.08 Å $= 1.14$ respectively (BRIAN MASON, 1947) compared with $c'/a' = 9.87$ Å/8.22 Å $= 1.20$ for $CdMn_2O_4$. The larger c' and a' axial lengths and the correspondingly larger unit cell dimensions of $CdMn_2O_4$ are attributed to the larger radius of Cd^{2+} ($r_{Cd^{2+}} = 0.97$ Å, $r_{Zn^{2+}} = 0.83$ Å and $r_{Mn^{2+}} = 0.91$ Å).

The distortion to tetragonal symmetry may be ascribed to similar causes in all these manganites and explained as follows (GOODENOUGH and LOEB, 1955): Mn^{3+} is stabilized in the octahedral interstices forming a group of four equivalent covalent bonds, in a plane defined by the a' and b' axes and the two linear ionic bonds, parallel to the c'-axis. The covalent bonds are stronger than the ionic bonds; hence the a' and b' axes contract and the elementary octahedron becomes distorted to tetragonal symmetry with an axial ratio $c'/a' > 1$. The value of c'/a' should depend upon the ratio of the ionic to covalent bond lengths in the elementary octahedron and the net fraction of these distorted octahedra having their elongated axis aligned parallel to the crystal c-axis (FINCH, SINHA and SINHA, 1957).

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