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Crystallographic Studies of Perovskite-Like Compounds. III. La $(M_x, \mathrm{Mn}_{1-x})\mathrm{O}_3$ with M = Co, Fe and Cr

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The ferromagnetic compound $\mathrm{La(Co_{0\cdot2}, Mn_{0\cdot8})O_3}$ is isostructural with antiferromagnetic compounds of the $\mathrm{GdFeO_3}$ structure. The structure is orthorhombic with four distorted perovskite units in a unit cell; the lattice constants are $a = 5{\cdot}525$, $b = 5{\cdot}530$, $c = 7{\cdot}819$ Å, all $\pm 0{\cdot}005$ Å. The most probable space group is D_{2h}^{16}–$Pbnm$. The seven structure parameters have been determined from intensity data obtained with a Norelco diffractometer using Ni-filtered Cu K radiation. Although the lattice constants closely approach the relationship for a cubic structure ($a = b = c/\sqrt{2}$), the displacement of the $\mathrm{La^{3+}}$ and $\mathrm{O^{2-}}$ ions from cubic positions is substantial. This structure persists in compounds of the formula $\mathrm{La}(M_x, \mathrm{Mn}_{1-x})\mathrm{O}_3$ with M = Cr for $0{\cdot}33 < x \leq 1$, with M = Fe for $0{\cdot}5 < x \leq 1$ and with M = Co for $0{\cdot}1 < x < 0{\cdot}4$. $\mathrm{LaMnO_3}$ ($x = 0$) is almost certainly orthorhombic. If it is isostructural with $\mathrm{GdFeO_3}$ the above limits may extend to $x = 0$. Ferromagnetism has been observed at liquid-nitrogen temperature for M = Co and Cr but not for M = Fe.

Introduction

Physical research in recent years has established that not only can ferroelectric compounds be found in the perovskite structure system, but also ferromagnetic compounds. Consequently chemical and structural knowledge of compounds in this system is important to the understanding of the origin of ferroelectricity and ferromagnetism.

Ferromagnetism in this structure system was first observed in $\mathrm{LaMnO_3}$ (Jonker & van Santen, 1950). It was possible to associate ferromagnetism with ferromagnetic interaction only between $\mathrm{Mn^{3+}}$ and $\mathrm{Mn^{4+}}$ ions in compounds of the general formula $(\mathrm{La}^{3+}_{1-x}, Me^{2+}_x)(\mathrm{Mn}^{3+}_{1-x}, \mathrm{Mn}^{4+}_x)\mathrm{O}_3$, where Me^{2+} is an alkaline-earth ion. Similar behavior was found when manganese was entirely replaced by cobalt (Jonker & van Santen, 1953). From these observations it is evident that the electronic configuration of the transition-metal ions is an important factor in the magnetic interaction. Therefore an investigation of magnetism in compounds of the type $\mathrm{La}(M_x, \mathrm{Mn}_{1-x})\mathrm{O}_3$, where M is a transition-metal ion, was undertaken at these Laboratories.

However, in the theories of interaction between magnetic (transition-metal) ions which arises from ‘excited states’ of intervening oxygen ions, the interionic distances and the M–O–M angles are important as well as the electronic configuration of M. Since interionic distances and angles are obtainable only if the atomic coordinates are available it is important that the crystal structure of these compounds be known.

We have now established that $\mathrm{La(Co_{0\cdot2}, Mn_{0\cdot8})O_3}$ is isostructural with $\mathrm{GdFeO_3}$ (Geller, 1956) and the structure parameters have been evaluated from powder diffractometer data. Powder photographs have shown that compounds of the general formula $\mathrm{La}(M_x, \mathrm{Mn}_{1-x})\mathrm{O}_3$ with M = Cr for $0{\cdot}33 < x \leq 1$, with M = Fe for $0{\cdot}5 < x \leq 1$ and with M = Co for $0{\cdot}1 < x < 0{\cdot}4$ are isostructural with $\mathrm{GdFeO_3}$. Ferromagnetism is present at liquid-nitrogen temperature for M = Cr and Co but not for M = Fe.

The crystal structure of $\mathrm{GdFeO_3}$ has been determined (Geller, 1956) from X-ray data from single crystals grown by Remeika (1956). Magnetic data from a single crystal have also been reported (Gilleo, 1956). Crystallographic work (Geller & Wood, 1956 (I); Geller & Bala, 1956 (II); Geller, 1957 (IV)) has also established that a large number of rare-earth–aluminum perovskites are isostructural with $\mathrm{GdFeO_3}$. Recently work on similar compounds has been reported by Bertaut & Forrat (1956) (see IV of this series).

Stoichiometric (antiferromagnetic) $\mathrm{LaMnO_3}$ and compounds for which x is less than the lower limit of the range given above are probably also isostructural with $\mathrm{GdFeO_3}$. However, it is felt that single-crystal data are required to confirm this possibility for reasons to be given later.

Experimental

Preparation of materials

The materials employed in this work were prepared in ceramic form. Appropriate sesquioxides were mixed in proportions based on analysis of the raw materials for weight percent of metal. These oxides were ball-milled in water for about 24 hr. in porcelain jars with alundum balls.* Pills about one-half inch in diameter by about three-sixteenths inch thick were pressed

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* Impurities of as much as 1% of aluminum and silicon were introduced by ball milling.

Table 1. *Comparison of calculated with observed intensities and d values of reflections of* $La(Co_{0.2}, Mn_{0.8})O_3$ *for* Cu *Kα radiation*

Orthorhombic indices	$I_{(cal)}$	$\Sigma I_{(cal)}$	$I_{(obs)}$	$d_{(cal)}$	$d_{(obs)}$
101	2.62	2.6	<1.2	4.5122	
110	10.97			3.9085	3.9086
002	8.18	19.2	18.2	3.9095	
111	1.57	1.6	1.9	3.4961	3.4957
200	22.29			2.7625	2.7648
020	20.11			2.7650	
112	82.95	125.4	118.9	2.7641	
021	1.78	1.8	1.4	2.6068	2.6047
120	0.03			2.4726	
210	0.22	0.2	<1.2	2.4713	
121	0.01			2.3576	2.3600
211	0.83			2.3564	
103	0.49	1.3	1.6	2.3572	
202	11.05			2.2561	2.2566
022	10.48	21.5	23.7	2.2575	
113	1.15	1.2	1.7	2.1684	2.1659
122	0.11			2.0898	
212	0.26	0.4	<1.2	2.0889	
220	26.31			1.9543	1.9549
004	11.22	37.5	40.2	1.9547	
221	1.76			1.8959	1.8960
023	1.09	2.8	3.5	1.8966	
123	0.98			1.7938	
213	0.26			1.7933	
301	0.08	1.3	<1.2	1.7926	
130	0.80			1.7486	1.7490
310	1.22			1.7473	
222	3.34			1.7480	
114	2.84	8.2	9.2	1.7483	
131	2.60			1.7064	1.7059
311	0.51	3.1	2.7	1.7053	
132	13.68			1.5962	1.5959
312	15.59			1.5952	
024	9.93			1.5962	
204	10.51	49.7	51.4	1.5957	
223	0.60	0.6	<1.2	1.5636	
124	0.00			1.5334	
214	0.00			1.5331	
230	0.11			1.5333	
320	0.04	0.2	<1.2	1.5328	
303	0.35			1.5041	
231	0.15			1.5047	
321	0.41			1.5042	
105	0.23	1.1	<1.2	1.5047	
115	0.08			1.4519	
313	0.01			1.4513	
133	1.08	1.2	<1.2	1.4521	
232	0.00			1.4275	
322	0.01	0.0	<1.2	1.4270	
040	3.09			1.3825	1.3822
400	3.47			1.3813	
224	11.84	18.4	19.0	1.3820	
025	0.18			1.3612	
041	1.11	1.3	<1.2	1.3614	
140	0.06			1.3412	
410	0.11	0.2	<1.2	1.3401	
141	0.09			1.3218	
411	0.35			1.3208	
125	0.04			1.3217	
215	0.12			1.3215	
233	0.16			1.3216	
323	0.02	0.8	<1.2	1.3212	
330	0.40			1.3028	1.3033
206	0.75			1.3032	
042	0.33			1.3034	
402	0.77			1.3024	
134	0.68			1.3032	
314	1.00	3.9	3.7	1.3027	
331	0.68	0.7	<1.2	1.2851	
142	0.00			1.2686	
412	0.02	0.0	<1.2	1.2677	
332	5.12			1.2360	1.2352
116	6.49			1.2363	
240	2.55			1.2363	
420	3.31	17.5	18.2	1.2357	
241	1.09			1.2212	1.2214
421	0.30			1.2205	
225	0.43			1.2210	
043	0.46	2.3	2.7	1.2213	
234	0.02			1.2064	
324	0.02	0.0	<1.2	1.2062	
143	0.01			1.1925	
413	0.30			1.1918	
305	0.00	0.3	<1.2	1.1920	
242	1.09			1.1788	1.1782
422	1.43			1.1782	
026	0.45			1.1788	
206	0.54	3.5	3.8	1.1786	
333	0.93			1.1654	1.1661
135	0.75			1.1656	
315	0.22	1.9	1.9	1.1653	
126	0.00			1.1529	
216	0.00	0.0	<1.2	1.1527	
044	2.49			1.1287	1.1290
404	3.10	5.6	5.6	1.1280	
243	1.15			1.1170	1.1170
423	0.28	1.4	1.2	1.1165	
340	0.01			1.1056	
430	0.00			1.1054	
144	0.01			1.1059	
414	0.01	0.0	<1.2	1.1053	
501	0.12			1.0941	
235	0.04			1.0948	
325	0.24			1.0946	
341	0.05			1.0947	
431	0.23			1.0945	
107	0.00	0.7	<1.2	1.0948	
150	0.08			1.0845	1.0845
510	0.29			1.0836	
334	0.39			1.0841	
226	1.34	2.1	2.5	1.0842	
151	1.19			1.0742	1.0735
511	0.02			1.0733	
117	0.08	1.3	1.5	1.0740	
342	0.08			1.0639	
432	0.12	0.2	<1.2	1.0637	
152	2.47			1.0450	1.0441
512	3.77			1.0442	
136	3.49			1.0449	
316	3.98			1.0446	
244	3.97			1.0449	
424	4.73	22.4	23.0	1.0445	
027	0.12			1.0357	
045	0.52	0.6	<1.2	1.0358	
520	0.01			1.0261	
250	0.00	0.0	<1.2	1.0268	
521	0.17			1.0174	
251	0.05			1.0180	
217	0.05			1.0179	
127	0.05			1.0180	
433	0.09			1.0176	
343	0.13			1.0178	
503	0.07			1.0173	
415	0.14			1.0176	
145	0.07	0.8	<1.2	1.0180	
335	0.26			1.0010	1.0009
513	0.19			1.0006	
153	1.20	1.6	1.5	1.0013	
522	0.03			0.9925	
252	0.07			0.9931	
326	0.02			0.9928	
236	0.03	0.2	<1.2	0.9930	
440	2.01			0.9771	0.9772
008	0.99	3.0	3.0	0.9774	
441	0.73			0.9696	0.9699
227	0.18			0.9698	
245	0.57			0.9698	
425	0.17	1.6	1.5	0.9695	
434	0.03			0.9622	
344	0.01	0.0	<1.2	0.9624	
523	0.25			0.9548	
253	0.02			0.9553	
307	0.06	0.3	<1.2	0.9551	
350	0.02			0.9482	0.9481
530	0.10			0.9478	
442	0.35			0.9480	
118	0.56			0.9482	
154	0.11			0.9483	
514	0.47			0.9477	
046	0.38			0.9483	
406	0.55	2.5	2.8	0.9479	
351	1.14			0.9413	0.9403
531	0.51			0.9409	
137	0.42			0.9413	
317	0.02	2.1	2.3	0.9411	
416	0.04			0.9343	
146	0.03	0.1	<1.2	0.9346	
352	2.60			0.9214	0.9208
532	3.36			0.9211	
028	2.71			0.9215	
208	2.79			0.9214	
060	0.53			0.9217	
600	1.12			0.9208	
336	3.44	16.6	15.7	0.9214	
443	0.62			0.9149	0.9162
061	0.67	1.3	1.7	0.9153	
218	0.02			0.9089	
128	0.01			0.9089	
610	0.01			0.9083	
160	0.00			0.9091	
524	0.02			0.9085	
254	0.04	0.1	<1.2	0.9090	
505	0.13			0.9024	
611	0.40			0.9023	
161	0.00			0.9030	
435	0.24			0.9026	
345	0.01			0.9028	
327	0.04			0.9027	
237	0.06	0.9	<1.2	0.9028	
062	0.15			0.8971	0.8968
602	0.44			0.8963	
246	0.38			0.8969	
426	0.69	1.7	1.5	0.8968	
353	0.86			0.8910	0.8903
533	0.21			0.8907	
155	1.05			0.8912	
515	0.00	2.1	1.8	0.8907	
612	0.07			0.8848	
162	0.08	0.2	<1.2	0.8855	
260	1.72			0.8743	0.8736
620	2.35			0.8737	
444	4.02			0.8740	
228	4.20	12.3	10.3	0.8741	
261	1.74			0.8689	0.8679
621	0.21			0.8683	
047	0.38			0.8688	
063	1.04	3.4	3.2	0.8689	
540	0.07			0.8632	
450	0.14	0.2	<1.2	0.8633	
541	0.20			0.8580	
451	0.11			0.8581	
109	0.00			0.8582	
613	0.40			0.8577	
163	0.08			0.8584	
525	0.16			0.8579	
255	0.08			0.8583	
417	0.22			0.8580	
147	0.00	1.2	<1.2	0.8583	
262	0.09			0.8532	0.8536
622	0.80			0.8526	
534	0.35			0.8528	
354	0.12			0.8531	
318	0.69			0.8530	
138	0.48	2.5	1.6	0.8531	

from the dried and sieved oxides and fired on a platinum sheet in an alundum tube at a temperature of 1300° C. for about 16 hr., except as noted. The firing atmosphere was a 300 cm.^{3}/min. stream of nitrogen which had been dried over magnesium perchlorate (Dehydrite). The pills were moved in and out of the firing zone in 20–30 min.

Diffraction data

The X-ray diffraction data for $La(Co_{0.2}, Mn_{0.8})O_3$ were obtained with a Norelco diffractometer. Cu *K* radiation was employed with a Ni filter in front of the counter tube. The areas of the recorded reflections were measured with a polar planimeter. The sample consisted of powdered ceramic material mixed with a small amount of petrolatum as a binder. An attempt to employ Cr *K* radiation with a V filter yielded less satisfactory results, presumably as a consequence of air absorption, lower radiation intensity and smaller counter sensitivity, even though manganese fluorescence was eliminated. However, increased dispersion by the *L*-shell of La would have made calculation of structure factors more difficult on account of the necessity of including an imaginary part.

In the powder photography work, Cr *K* radiation was used in preference to Cu *K* because it yielded the clearest films with good contrast. Straumanis-type Norelco cameras of 114·59 mm. diameter were employed. A V filter was placed along one edge of the film to aid in identification of Cr *Kβ* reflections.

Structure calculations for $La(Co_{0.2}, Mn_{0.8})O_3$

From knowledge of the structure of $GdFeO_3$ (Geller, 1956) it was possible to index the reflections of $La(Co_{0.2}, Mn_{0.8})O_3$ on the proper orthorhombic basis and to observe that all reflections of the type (*h*0*l*) with $(h+l)$ odd and $(0kl)$ with k odd were absent (Table 1). The intensities of the lines present (Table 1) were also in accord with the observations on $GdFeO_3$ (I). Consequently it is concluded that D_{2h}^{16}-$Pbnm$ is the most probable space group for $La(Co_{0\cdot2}, Mn_{0\cdot8})O_3$.

In view of the nearly cubic relationship $(a=b=c/\sqrt{2})$ of the lattice constants of this compound it is necessary that the reflections be selected carefully for lattice-constant determination to avoid cases of multiple overlap. For this purpose groups of reflections were chosen in which one component is of dominant intensity, such as (243) and (153), or in which there are only two components of comparable intensity, as in the (440), (008) pair in which the contributions may be weighted. The lattice constants are

$$a = 5\cdot525,\ b = 5\cdot530,\ c = 7\cdot819\ \text{Å},\ \text{all}\ \pm0\cdot005\ \text{Å}\ .$$

The calculated d values agree well with those observed (Table 1).

In evaluation of the seven atomic parameters the accuracy of the $f_a(\theta)$ employed, as well as of the data obtained, is important. Therefore the f_a data given for the elements La, Co, and Mn in the *Internationale Tabellen zur Bestimmung von Kristallstrukturen*, vol. 2, were corrected for ionicity and for dispersion for Cu $K\alpha$ radiation. Ionicity corrections were carried out by smoothly joining the atomic scattering factor, $f_a(\theta)$, curves for La, Co, and Mn to the Xe, Cr, and Ti curves respectively at low angles. In the case of La, Co, and Mn, corrections for K-shell dispersion (James, 1948) were carried out.* For La the L-shell correction was also applied in approximation by taking as a lower limit a correction based on the L-shell dispersion known for W in Zr $K\alpha$ radiation (James, 1948).

The temperature correction for atomic scattering factors was omitted since it would be of most consequence for oxygen ions which make minor contributions to the intensity of reflections, except at lower angles.

The $f_a(\theta)$ values thus obtained were used in the calculation of $p|F_{hkl}|^2$ values, where p is the multiplicity and F_{hkl} is the structure amplitude. These calculations were carried out on IBM machines; the best solution was obtained on a trial-and-error basis. For the best set of parameters (Table 2) the $I_{(\text{cal.})}$* values (see Table 1) yield an $R = 0\cdot07$.† As a consequence of the high sensitivity of most of the reflections observed to the La(y) parameter, it is the most precisely known ($\pm0\cdot002$). The remaining parameters are probably not better than $\pm0\cdot01$‡.

Table 2. *Coordinates of ions in* $La(Co_{0\cdot2}, Mn_{0\cdot8})O_3$

Ion	Position	Coordinates x	y	z
La^{3+}	4(c)	$-0\cdot01$	0·023	$\frac{1}{4}$
$(Co, Mn)^{3+}$	4(b)	$\frac{1}{2}$	0	0
O_{I}^{2-}	4(c)	0·01	0·50	$\frac{1}{4}$
O_{II}^{2-}	8(d)	$-0\cdot29$	0·27	0·06

Positions:
4(c): $\pm(x, y, \frac{1}{4};\ \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4})$.
4(b): $(\frac{1}{2}, 0, 0;\ \frac{1}{2}, 0, \frac{1}{2};\ 0, \frac{1}{2}, 0;\ 0, \frac{1}{2}, \frac{1}{2})$.
8(d): $\pm(x, y, z;\ \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z;\ \bar{x}, \bar{y}, \frac{1}{2}+z;\ \frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$.

$La(M_x, Mn_{1-x})O_3$ *compounds*

A series of compounds of the general formula $La(M_x, Mn_{1-x})O_3$ has been prepared and examined by powder-photographic methods for M = Cr, Fe and Co. In each case these compounds were found to be clearly isostructural with $GdFeO_3$ for a certain range of x. However, this structure did not unambiguously persist for x approaching zero ($LaMnO_3$).

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* More accurate correction data, which subsequently became available (Dauben & Templeton, 1955), are comparable.

* $I_{(\text{cal.})} \equiv p|F_{hkl}|^2 LP \times 10^{-5};\ LP = (1+\cos^2 2\theta)/\sin^2\theta \cos\theta$.

† The best solution was selected on the basis of a minimum value for

$$\mathscr{R} \equiv \frac{1}{n} \sum^{n} \frac{||F_o|^2 - |F_c|^2|}{|F_o|^2},$$

which was 0·15.

This requirement is more stringent than that of minimum

$$R \equiv \frac{\Sigma||F_o|^2 - |F_c|^2|}{\Sigma|F_o|^2}.$$

‡ The intensity calculated for the (101) reflection depends sensitively on the O_{II}^{2-} parameters; presumably it could be reduced by adjustment of these parameters with a slight improvement of R.

Table 3. $La(Fe_x, Mn_{1-x})O_3$

x	Firing temperature (°C.)	Firing atmosphere	a (Å)	b (Å)	c (Å)	$c/\sqrt{2}$ (Å)	V (Å³)	a_0 (Å)
0*	1300	N_2	5·529	5·662	7·713	5·454	241·5	3·923
0·2*	1500	Air	5·532	5·644	7·756	5·485	242·2	3·927
	1300	N_2	5·535	5·647	7·758	5·486	242·5	3·928
0·5	1400	N_2	5·542	5·580	7·840	5·544	242·4	3·928
	1300	N_2	5·544	5·560	7·840	5·544	241·7	3·924
0·8	1400	N_2	5·552	5·563	7·851	5·552	242·5	3·928
	1300	N_2	5·545	5·554	7·848	5·549	241·7	3·924
1·0†	—	—	5·556	5·565	7·862	5·559	243·1	3·932

* The lattice constants are given on the same basis as the others even though these compounds may not be isostructural, as discussed in the text.

† See I.

For M = Fe we find that the structure remains the same from $x = 1$ to $x = 0{\cdot}50$. Through the entire range of x, a_0* tends to decrease with increase in Mn content $(1-x)$ (Fig. 1 and Table 3). Although for $x = 0$ and $x = 0{\cdot}2$ the powder patterns may still be indexed on the same basis, they are distinctly different from all compounds isostructural with $GdFeO_3$ for which $a < c/\sqrt{2} < b$ since for $x = 0$ ($LaMnO_3$) and for $x = 0{\cdot}2$ we find that $c/\sqrt{2} < a < b$.

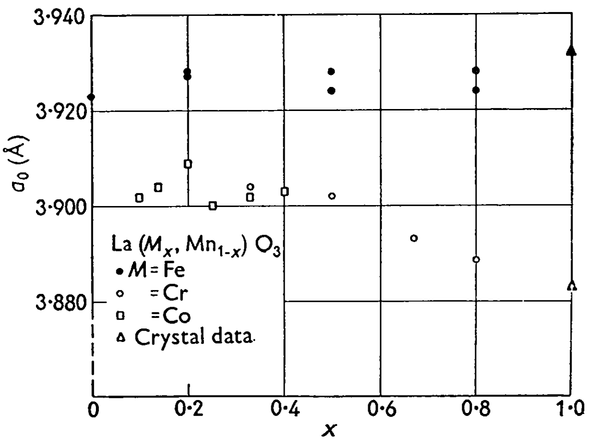

Fig. 1. a_0 versus x for compounds of general formula $La(M_x, Mn_{1-x})O_3$ with M = Cr, Fe and Co.

For M = Cr the structure again remains the same over the range $1 \geq x > 0{\cdot}33$. In this compound a_0 increases with increase of Mn content $(1-x)$ (Fig. 1). In the case of M = Co the isostructural range is more restricted, $0{\cdot}1 < x < 0{\cdot}4$ (Fig. 1).

The structural similarity of these three series of compounds can be brought out clearly by tabulation of the d values and intensities of reflections indexed on an orthorhombic basis. These data coincide completely with those reported for $GdFeO_3$ (Geller, 1956) and other isostructural compounds (I, II, IV); variations in the intensity of reflections with $h+k$ odd or l odd are greatest, of course, as a result of parameter variations among the compounds.

Small amounts of oxygen in the firing atmosphere have been observed by us to have a great influence on the structure when the Mn content becomes large ($x < 0{\cdot}5$), as would be expected as a consequence of the behavior of $LaMnO_3$ with respect to oxygen content (see also Yakel, 1955; Harwood, 1955). However, the partial pressure of oxygen in the nitrogen firing atmosphere employed was low enough to prevent the formation of more than a few percent Mn^{4+}, as judged from the small spontaneous magnetization observed in $LaMnO_3$ at liquid-nitrogen temperature (Jonker & van Santen, 1950; Wollan & Koehler, 1955).

Discussion

The extensive occurrence of the orthorhombic structure (space group D_{2h}^{16}–$Pbnm$) in ABO_3 compounds with trivalent A and B ions has been clearly established (I, II, IV). In particular, $LaFeO_3$ and $LaCrO_3$ are known to crystallize in this structure. Therefore it would be expected that the substitution of at least a small amount of Mn for Cr or Fe would not lead to a change of structure. However, the initial structure clearly persists even though the B ion may be two-thirds Mn, which implies that $LaMnO_3$ may also be isostructural with $GdFeO_3$. The decrease of a_0 from that of $LaFeO_3$ and the increase of a_0 from that of $LaCrO_3$ with Mn substitution are to be expected purely on a steric basis since Mn^{3+} should reasonably fall between Cr^{3+} and Fe^{3+} in size as it does in atomic number (within this given structure system an increase in a_0 implies an increase in B-ion size).

The structure of stoichiometric $LaMnO_3$, which is antiferromagnetic (Wollan & Koehler, 1955), cannot be known definitely in the absence of single-crystal data. Yakel (1955) found that it was possible to account for the reflections shown in a powder photograph on the basis of an orthorhombic (or monoclinic) cell containing 16 units of $LaMnO_3$ ($a \simeq \sqrt{2}.b \simeq c$), or, if a few weak reflections are neglected, 4 units with the a and c axes half as large. We have found that $LaMnO_3$ powder-photograph data can be completely accounted for on the same orthorhombic basis as other compounds isostructural with $GdFeO_3$, except that in this case $c/\sqrt{2} < a < b$, rather than $a < c/\sqrt{2} < b$ as is found in all other cases reported in this series of papers. The relative intensities of the reflections observed are substantially in accord with those computed for $La(Co_{0{\cdot}2}, Mn_{0{\cdot}8})O_3$. Furthermore, a_0 varies quite smoothly with x as it should if all compositions are isostructural. Consequently it is felt that it is quite possible that $LaMnO_3$ also is isostructural with $GdFeO_3$.

The appearance of a structure nearly identical with $LaFeO_3$ in $La(Co_x, Mn_{1-x})O_3$ with $0{\cdot}1 < x < 0{\cdot}4$ is somewhat unexpected since $LaCoO_3$ has been observed to have a rhombohedral-type structure by Askham, Fankuchen & Ward (1950) and by Yakel (1955). $LaMnO_3$ also exhibits a similar structure when heavily oxidized according to Yakel (1955) and Harwood (1955); this behavior has also been observed by us. Although Bertaut & Forrat (1956) report observation of orthorhombic and rhombohedral structures in $LaMnO_3$ they do not specify the conditions under which a given structure appears.

A careful study of the compound $La(Co_{0{\cdot}2}, Mn_{0{\cdot}8})O_3$ was necessary to establish that D_{2h}^{16}–$Pbnm$ is the most probable space group for it and, accordingly, for the other compounds considered. We find that, despite the nearly cubic relationship of the lattice constants ($a = b = c/\sqrt{2}$), the structure parameters for O_{II}^{2-} are comparable to those for $GdFeO_3$; for La^{3+} and O_I^{2-}

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* $a_0 \equiv (V/4)^{\frac{1}{3}}$ is the lattice constant of a cubic pseudo-cell with a volume of one formula unit.

Table 4. *Interionic distances and angles*

Ion*	Position	Angles† (°)	Distances‡ (Å)
$M_1(\frac{1}{2}, 0, 0)$	4(*b*)	$(M_1\text{–O}_1\text{–}M_2) = 150$	$M_1\text{–O}_1 = 1\cdot95$
$M_2(1, \frac{1}{2}, 0)$	4(*b*)	$(M_1\text{–O}_2\text{–}M_3) = 177$	$M_2\text{–O}_1$ } = 2·10
$M_3(\frac{1}{2}, 0, \frac{1}{2})$	4(*b*)	$(\text{O}_1\text{–}M_1\text{–O}_2) = 77$	$M_1\text{–O}_3$
$\text{O}_1(x+1, y, z)$	8(*d*)	$(\text{O}_2\text{–}M_1\text{–O}_3) = 78$	$M_1\text{–O}_4$
$\text{O}_2(\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{4})$	4(*c*)	$(\text{O}_1\text{–}M_1\text{–O}_3) = 88$	$M_1\text{–O}_2$ } = 1·96
$\text{O}_3-(\frac{1}{2}+x-1, \frac{1}{2}-y, \bar{z})$	8(*d*)	$(\text{O}_1\text{–}M_1\text{–O}_4) = 92$ $= 180° - (\text{O}_1\text{–}M_1\text{–O}_3)$	$M_3\text{–O}_2$
$\text{O}_4(\frac{1}{2}+x, \frac{1}{2}-y, \bar{z})$	8(*d*)		

* See Table 2 for x, y, and z.

† Angles are not better than ±3° for parameter tolerances cited in text.

‡ Distances are not better than ±0·06 Å for parameter tolerances cited in text.

they are about one-third as large as in GdFeO$_3$. For this reason the approach of La(Co$_{0\cdot2}$, Mn$_{0\cdot8}$)O$_3$ to a cubic structure is not as close as might at first have been supposed.

Knowledge of the atomic coordinates allows us to see that the magnetic interaction between B ions will not be equivalent in the ⟨110⟩ and ⟨001⟩ directions of the –M–O–M–O– chains (Fig. 2), or between the chains, since the M–O distances and M–O–M angles are not equivalent (Table 4); the magnetic coupling is also a function of the O–M–O angles. Consequently, appreciable magnetic anisotropy would be expected in a ferromagnetic case. Complicated anisotropy of susceptibility and of parasitic antiferromagnetism has been observed in isostructural GdFeO$_3$ (Gilleo, 1956).

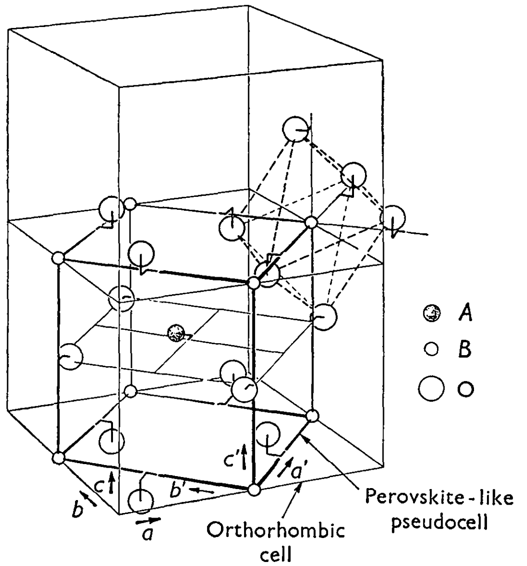

Fig. 2. Schematic representation of displacements of ions from ideal positions in compounds isostructural with GdFeO$_3$.

There is evidence that the orthorhombic structure assumed by these compounds (with trivalent A and B ions) is principally a consequence of steric considerations; the diversity of electronic configurations and the variety of magnetic properties encountered among these isostructural compounds indicate that the nature of the bonding and of the interaction between magnetic ions seems to be of secondary importance (except perhaps in borderline cases such as in the galliates (Geller, 1957)).

There is the following evidence for the secondary importance of electronic configuration: Compounds isostructural with GdFeO$_3$ exist in which the A and B ions have closed $4p$ and $2p$ shells (YAlO$_3$ (II)); in which the A ion has a closed $5p$ shell and the B ion a partially filled $3d$ shell (LaMO$_3$ with M = Fe (I); with M = V and Cr (IV); also the compounds discussed in this paper); in which the A ion has a partly filled $4f$ shell and the B ion a partly filled $3d$ shell (e.g., rare-earth orthoferrites (I)); and finally in which the A ion has a partly filled $4f$ shell and the B ion a closed $2p$ shell (rare-earth (Gd, Eu, Sm) aluminates (II)).

The following data show the secondary importance of the influence of magnetic interaction between the positive ions on the structure and vice versa: In isostructural (D_{2h}^{16}–$Pbnm$) compounds we find YAlO$_3$ with no magnetic ions; we have observed ferromagnetism at liquid-nitrogen temperature in La(M_x, Mn$_{1-x}$)O$_3$ with M = Cr and Co but not with M = Fe; we know that LaCrO$_3$ (Koehler & Wollan, 1954) and LaFeO$_3$ (Forestier & Guiot-Guillain, 1952; Guiot-Guillain, 1953; Roth, 1954) are antiferromagnetic. Furthermore, compounds exist which are not isostructural with these but which exhibit similar magnetic properties. For example, Ca^{2+}Mn^{4+}O$_3$ is antiferromagnetic (Wollan & Koehler, 1955); LaCoO$_3$ is paramagnetic down to 4·2° K. (Koehler & Wollan, 1954); LaAlO$_3$ (space group D_{3d}^{5}–$R\bar{3}m$: II) contains no magnetic ions; and some (La$_{1-x}$, Me_x)MnO$_3$-type compounds are ferromagnetic (Jonker & van Santen, 1950; Wollan & Koehler, 1955).

However, it is clearly evident that magnetic interaction is most highly dependent on the electronic configuration of the B ions present. This view has consistently been the theoretical one since its original formulation by Kramers (1934); it has recently been extended specifically to the (La$_{1-x}$, Me_x)MnO$_3$ system by Goodenough (1955). However, Goodenough has also correlated the structural symmetries observed in this system with the electronic configurations (semicovalent bonding) of the Mn ions (neglecting the electrostatic and steric changes caused by the valence change of Mn) and A-ion composition to an extent which now would appear to be only precariously tenable.

In connection with the importance of B-ion electronic configuration to magnetic interaction it should be noted that ferromagnetism has thus far been observed in compounds in the perovskite-structure system *only when the B ions are not all alike* (i.e., when all are not of the same valence or when all are not of the same atomic number).

More detailed data on the magnetic properties of $\mathrm{La}(M_x, \mathrm{Mn}_{1-x})\mathrm{O}_3$ compounds will be published elsewhere later.

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Discussions and correspondence with others engaged in related work have enhanced my interest in this problem and influenced its course. These others are Prof. E. Banks and Drs E. W. Gorter, W. L. Roth, W. C. Koehler, and E. Prince.

References

Askham, F., Fankuchen, I. & Ward, R. (1950). *J. Amer. Chem. Soc.* **72**, 3799.

Bertaut, F. & Forrat, F. (1956). *J. Phys. Radium*, **17**, 129.

Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* **8**, 841.

Forestier, H. & Guiot-Guillain, G. (1952). *C. R. Acad. Sci., Paris*, **230**, 1844.

Geller, S. (1956). *J. Chem. Phys.* **24**, 1236. [Abstract *Phys. Rev.* (1955), **99**, 1641.]

Geller, S. (1957). (IV). *Acta Cryst.* In the Press.

Geller, S. & Bala, V. B. (1956). (II). *Acta Cryst.* **9**, 1019.

Geller, S. & Wood, E. A. (1956). (I). *Acta Cryst.* **9**, 563.

Gilleo, M. A. (1956). *J. Chem. Phys.* **24**, 1239. [Abstract *Phys. Rev.* (1955), **99**, 1641.]

Goodenough, J. B. (1955). *Phys. Rev.* **100**, 564.

Guiot-Guillain, G. (1953). *C. R. Acad. Sci., Paris*, **237**, 1654.

Harwood, M. G. (1955). *Proc. Phys. Soc.* B, **68**, 586.

James, R. W. (1948). *The Optical Principles of the Diffraction of X-rays.* London: Bell.

Jonker, G. H. & Santen, J. H. van (1950). *Physica*, **16**, 337.

Jonker, G. H. & Santen, J. H. van (1953). *Physica*, **19**, 120.

Koehler, W. C. & Wollan, E. O. (1954). Conference on Ferrimagnetism, U.S. Naval Ordnance Laboratory, White Oak, Md.

Kramers, H. A. (1934). *Physica*, **1**, 182.

Remeika, J. P. (1956). *J. Amer. Chem. Soc.* **78**, 4259.

Roth, W. L. (1954). Pittsburgh Diffraction Conference, joint meeting with American Crystallographic Association.

Wollan, E. O. & Koehler, W. C. (1955). *Phys. Rev.* **100**, 545.

Yakel, H. L. (1955). *Acta Cryst.* **8**, 394.

Acta Cryst. (1957). **10**, 166

The Crystal Structure of U_2Mo*

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The crystal structure of the γ' phase in the U–Mo system has been determined to be the $C11b$ $\mathrm{MoSi_2}$ type. The unit cell is tetragonal and the space group D_{4h}^{17}–$I4/mmm$. The lattice parameters are $a_0 = 3{\cdot}427$ Å, $c_0 = 9{\cdot}834$ Å, $c/a = 2{\cdot}871$. The γ' phase is an ordered state of the body-centered cubic γ phase.

Introduction

The uranium–molybdenum system was first investigated by Pfeil (1950*a*). His results indicated that molybdenum was soluble in body-centered cubic γ-uranium to the extent of about 43 atomic % at 1280° C. The γ phase was considered to be stable at room temperature as no effects were found in thermal analysis or dilatometric experiments. Further work by Pfeil (1950*b*) and by Tucker (1950) showed that equilibrium conditions had not been obtained and that the γ phase transforms into a new tetragonal phase, γ'. Tucker found the unit cell to be body centered with the dimensions $a_0 = 3{\cdot}420$ Å, $c_0 = 3{\cdot}278$ Å. Pfeil found

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