The author thanks Mr H. A. Plessius and Dr S. Harkema for their help during the early stages of the investigation. Mr P. A. Kroon of the Rijksuniversiteit Groningen is thanked for performing part of the refinement and Dr J. P. Dougherty of North American Philips, for carrying out the test with the second harmonic analyser.

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A Powder Neutron Diffraction Investigation of the Oxygen Vacancy Distribution in $4H$ $\mathrm{Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}}$ and the Magnetic Structure of $4H$ $\mathrm{Ba_{0\cdot1}Sr_{0\cdot9}MnO_{2\cdot96}}$

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(*Received* 21 *June* 1975; *accepted* 18 *July* 1975)

The structure and O vacancy distribution in $4H$ $\mathrm{Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}}$ and the magnetic structure of $4H$ $\mathrm{Ba_{0\cdot1}Sr_{0\cdot9}MnO_{2\cdot96}}$ have been determined by profile analysis of powder neutron diffraction data. In $\mathrm{Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}}$ the O vacancies are found in hexagonal $\mathrm{(Ba,Sr)O_3}$ layers which suggests that the $\mathrm{Mn^{3+}}$ ions are coordinated by O in edge-sharing trigonal bipyramids. The antiferromagnetic structure of $\mathrm{Ba_{0\cdot1}Sr_{0\cdot9}MnO_{2\cdot96}}$ has alternate Mn atoms along **c** with opposite spin and the spin direction in the basal plane. The sublattice magnetization was found to be $gS = 2\cdot42$ (4) at $4\cdot2K$.

Introduction

Perovskite related $\mathrm{ABO_3}$ mixed metal oxides have structures which are ideally based on close-packing of $\mathrm{AO_3}$ layers with B cations in octahedral sites and which differ in the ratio of the number of cubic to hexagonal layers. Relationships between such structures have been discussed by Katz & Ward (1964).

The $\mathrm{BaMnO_{3-x}}$ and $\mathrm{SrMnO_{3-x}}$ systems are of particular interest in that they exhibit a wide variety of structure types and extensive ranges of non-stoichiometry. Negas & Roth (1970, 1971) have investigated in detail the phase relationships and O composition for both compounds and their main experimental conclusions are summarized in Table 1. In both the amount of cubic stacking increases and the O content decreases with increasing temperature.

Table 1. $\mathrm{BaMnO_{3-x}}$ *in air* (*after Negas & Roth*, 1971) *and* $\mathrm{SrMnO_{3-x}}$ *in air* (*after Negas & Roth*, 1970)

$\mathrm{BaMnO_{3-x}}$ Layer sequence	Temperature (°C)	Oxygen content	% cubic stacking
$2H$	1150	$x=0$	0
$15H$	1150–1300	$0<x<0\cdot02$	20
$8H$	1300–1350	$0\cdot03<x<0\cdot05$	25
$6H$	1350–1475	$0\cdot10<x<0\cdot15$	$33\frac{1}{3}$
$10H$	1475–1550	$0\cdot175<x<0\cdot20$	40
$4H$	1550	$x\sim0\cdot25$	50
$\mathrm{SrMnO_{3-x}}$			
$4H$	1035	$x=0$	50
$4H$	1035–1400	$0<x<0\cdot11$	50
$3C$	1400–1740	$0\cdot26<x<0\cdot38$	100

Negas (1973) also studied the solid solutions $\mathrm{Ba_{1-y}Sr_yMnO_{3-x}}$ and showed that the $2H$, $15H$ and

8*H* phases of $BaMnO_{3-x}$ can accommodate only small amounts of Sr ($y<0\cdot06$) but that the 6*H* and 10*H* phase fields are extended to $y=0\cdot15$ and $y=0\cdot20$, respectively, and to 1250 °C. However, the 4*H* structure with which we are concerned in this work, dominates the phase diagram, existing for example at $y=0\cdot5$ from 1150–1600 °C and at $y=0\cdot9$ up to 1500 °C. Only one layer sequence (9*R*) not found for the end members is reported for $0\cdot09<y<0\cdot14$ below 1300 °C in accord with the high-pressure phase studies of Chamberland, Sleight & Weiher (1970).

An important conclusion of Negas & Roth's work is that transformations between structures are not truly polymorphic because of associated changes in the O content and that the increasing amount of cubic stacking as either the Sr content or the temperature is increased is related to the number of O vacancies. It was further suggested that the composition limits of phases with different stacking sequences could be rationalized in terms of a preferred coordination scheme for the Mn^{3+} ions.

Magnetic susceptibility measurements have been made for 4*H* $SrMnO_3$ ($T_N\sim350$ K), 2*H* and 4*H* $BaMnO_3$ and the high-pressure phases 6*H* $SrMnO_3$ ($T_N\sim90$ K) and 9*R* $BaMnO_3$ ($T_N\sim350$ K) (Chamberland, Sleight & Weiher, 1970). No Néel temperatures were detected for 2*H* and 4*H* $BaMnO_3$ but both showed antiferromagnetic Curie–Weiss behaviour.

More recently, Nørlund Christensen & Ollivier (1972) reported a Néel temperature of <2·4 K for 2*H* $BaMnO_3$ and determined the antiferromagnetic structure by neutron diffraction. The structure is collinear with the spin direction along **c**. The magnetic and chemical unit cells are related by $a_{\rm mag}=a_{\rm chem}\sqrt{3}$ and $c_{\rm mag}=c_{\rm chem}$.

In this work we have determined the structure and vacancy ordering in 4*H* $Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}$ and the magnetic structure of 4*H* $Ba_{0\cdot1}Sr_{0\cdot9}MnO_{2\cdot96}$. The particular compositions were chosen to facilitate quenching of large samples for neutron diffraction (~20 g) of suitable O content.

Experimental

Sample preparation

The starting materials $BaCO_3$, $SrCO_3$ and Mn_3O_4 were obtained 'Specpure' from Johnson Matthey Chemicals Ltd. The $BaCO_3$ and $SrCO_3$ were prefired at 950 and 850 °C respectively in CO_2 and the Mn_3O_4 at 1100 °C in air. Stoichiometric mixtures of starting materials were hand-mixed in an agate mortar and fired in Pt crucibles in air at 1400 °C. The $Ba_{0\cdot5}Sr_{0\cdot5}MnO_{3-x}$ mixture was fired for successive periods of 168, 96, and 96 h and $Ba_{0\cdot1}Sr_{0\cdot9}MnO_{3-x}$ for two periods of 96 h. Between firings the samples were quenched, reground and examined on a Philips X-ray diffractometer. Intermediate firings showed small amounts of 2*H* phase but all lines in the final diffractometer traces could be indexed on 4*H* unit cells with lattice parameters $a=5\cdot573$ (3), $c=9\cdot181$ (5) Å (Ba:Sr = 1:1) and $a=5\cdot466$ (3), $c=9\cdot094$ (9) Å (Ba:Sr = 1:9). The compositions of the products calculated from the weight loss on reaction were $Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot86}$ and $Ba_{0\cdot1}Sr_{0\cdot9}MnO_{2\cdot96}$. The average Mn oxidation state in the two compounds was determined by dissolving in HCl containing an excess of KI and titrating the liberated I_2 with $Na_2S_2O_3$. The compositions were $Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot82(2)}$ and $Ba_{0\cdot1}Sr_{0\cdot9}MnO_{2\cdot96(2)}$ in good agreement with the thermogravimetric results.

Neutron diffraction

The neutron diffraction measurements were made at room and liquid He temperatures on a powder diffractometer at the reactor PLUTO, AERE, Harwell. The samples were contained in thin-walled V cans. Wavelengths of 1·318 and 1·324 Å, obtained from the (511) planes of a Ge monochromator with a take-off angle of 75° were used to collect the room temperature and the 4·2 K data respectively. The wavelengths were calibrated against a Ni standard. The counter was stepped every 0·02° and total counts accumulated at 0·1° intervals.

$Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}$

For $Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}$ structural parameters were refined from data collected at room temperature in the range $5°<2\theta<111°$ by the profile analysis method (Rietveld, 1967). The refinement was based on $P6_3/mmc$ with the starting parameters taken as those corresponding to ideal close-packing of the $(Ba,Sr)O_3$ layers with stacking sequence *chch*. A random distribution of Ba and Sr was assumed. One Ba and one Sr were placed in position 2(*a*), one Ba and one Sr in position 2(*c*),

Table 2. *Atomic positional parameters for* $Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}$ *obtained from neutron refinement at room temperature*

$Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}$ ($P6_3/mmc$)

	Positions	*x*	*y*	*z*	*B*
(Ba, Sr) (1)	2(*a*)	0	0	0	1·6 (1)
(Ba, Sr) (2)	2(*c*)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0·5 (1)
Mn	4(*f*)	$\frac{1}{3}$	$\frac{2}{3}$	0·6090 (5)	0·2 (1)
O(1)	6(*g*)	$\frac{1}{2}$	0	0	1·1 (1)
O(2)	6(*h*)	−0·1854 (3)	−0·3708 (6)	$\frac{1}{4}$	0·9 (1)

Occupation numbers

O(2)	6(*h*)	2·68 (3)
O(1)	6(*g*)	3·00 (4)
Total occupation		5·68 (7)

four Mn in 4(*f*) and 12 O in 6(*g*) and 6(*h*). The scattering lengths used were: $b_{\mathrm{Ba}}=0{\cdot}52\times10^{-12}$, $b_{\mathrm{O}}=0{\cdot}58\times10^{-12}$ (Neutron Diffraction Commission, 1972), $b_{\mathrm{Sr}}=0{\cdot}692\times10^{-12}$ (Cooper & Rouse, 1972) and $b_{\mathrm{Mn}}=-0{\cdot}372\times10^{-12}$ cm (Jacobson, Tofield & Fender, 1973). Background contributions were estimated by hand and 16 parameters including individual isotropic temperature factors were refined. The reliability index defined as

$$R_p=\frac{100\sum w\left(y_{\mathrm{obs}}-\frac{1}{c}\,y_{\mathrm{calc}}\right)^2}{\sum w{y_{\mathrm{obs}}}^2},$$

where y is the number of counts at a point in 2θ, c is a scale factor and $w=1/\sigma^2$, converged to 11·4% compared with an idealized minimum of 4·1%. R based on integrated intensities was 6·6%. The data were refined until all parameter shifts were less than $0{\cdot}3\sigma$ and in the final refinement a constraint on the O occupation numbers was removed.

The atom positions are given in Table 2 and some important interatomic angles and distances in Table 3. The O composition, 2·84, determined from the total O occupancy (Table 2) is in good agreement with the stoichiometry determined thermogravimetrically and by chemical analysis. The experimental and calculated profiles, a difference plot and the positions of the Bragg reflexions are shown in Fig. 1. There are no major discrepancies but the strong low-angle reflexions have difference profiles which indicate small errors in the half-width parameters. This is probably associated with departures from Gaussian peak shapes assumed in the analysis, but may possibly be a consequence of residual stacking disorder. A somewhat larger than expected R_p results, although R based on integrated intensities is little affected. The lattice parameters obtained from the neutron refinement were 5·5705 (6) and 9·1887 (15) Å.

Table 3. *Bond distances* (Å) *and angles* (°) *in* $\mathrm{Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}}$

(Ba,Sr) (1)–O(2)	2·912 (2)	Mn—O(2)	1·928 (4)
(Ba,Sr) (1)–O(1)	2·785 (1)	Mn—O(1)	1·894 (3)
(Ba,Sr) (2)–O(2)	2·791 (3)	O(2)–O(2)	3·100 (3)
(Ba,Sr) (2)–O(1)	2·804 (1)	O(2)–O(2)	2·471 (4)
(Ba,Sr) (1)–Mn	3·368 (5)	O(1)–O(1)	2·785 (1)
(Ba,Sr) (2)–Mn	3·298 (3)	O(2)–O(1)	2·758 (3)
		Mn–Mn	2·593 (9)
O(2)–Mn–O(2)	79·71 (20)	Mn–O(2)–Mn	84·54 (21)
O(2)–Mn–O(1)	92·36 (3)	Mn–O(1)–Mn	180·0 (16)
O(1)–Mn–O(1)	94·67 (20)		

$\mathrm{Ba_{0\cdot1}Sr_{0\cdot9}MnO_{2\cdot96}}$

Data collected at 4·2 K in the range $5°<2\theta<114°$ were initially refined in $P6_3/mmc$ with starting positions as in $\mathrm{Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}}$. The best R_p obtained was 16% and extra intensity was observed for the low-angle reflexions 002, 101, 103, 112 and 201 suggesting an ordered magnetic structure. All observed reflexions could be indexed without enlargement of the chemical unit cell. The magnetic susceptibility measurements of Chamberland, Sleight & Weiher (1970) indicate antiferromagnetic interactions in 4*H* $\mathrm{SrMnO_3}$ and 4*H* $\mathrm{BaMnO_{2\cdot85}}$ and consequently a magnetic structure in which the Mn atoms ideally at $(\frac{1}{3},\frac{2}{3},\frac{5}{8})$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{8})$ are of opposite spin to those at $(\frac{1}{3},\frac{2}{3},\frac{7}{8})$ and $(\frac{2}{3},\frac{1}{3}\frac{3}{8},)$ is proposed. The magnetic structure factor calculated for this model is:

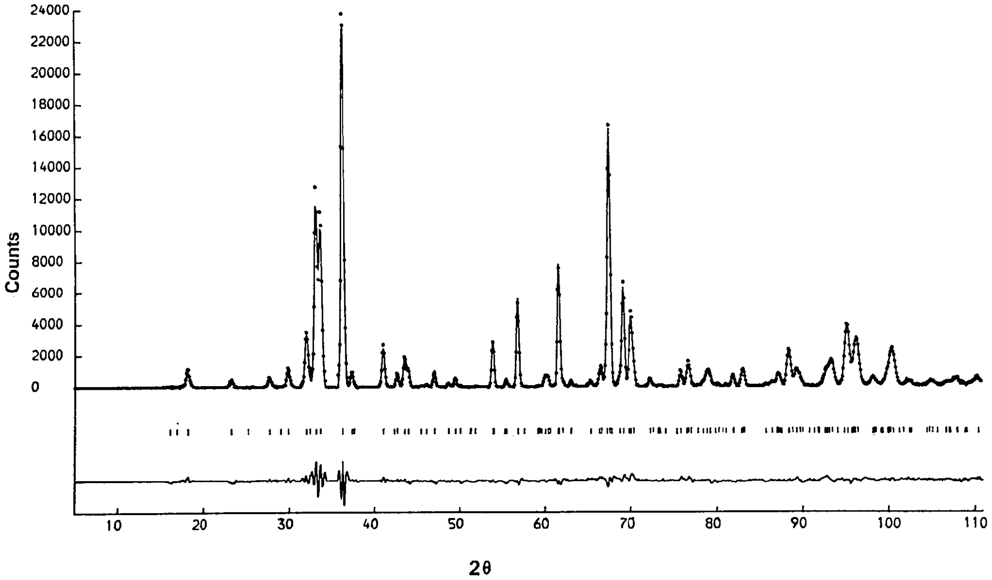

Fig. 1. Powder neutron diffraction profile for $\mathrm{Ba_{0\cdot5}Sr_{0\cdot5}MnO_{2\cdot84}}$. Small circles are the experimental points, and the continuous line passes through the calculated points. The small vertical lines mark the positions of the Bragg reflexions and the bottom trace is the difference profile.

$$F(hkl)^2_{\mathrm{mag}} = \langle q^2\rangle\{p[1-\exp(\pi il/2)]\,[\exp(2\pi i(2h/3+k/3+l/8))+\exp(2\pi i(h/3+2k/3+5l/8))]\}^2$$

where $\langle q^2\rangle$ is the spin orientation factor: p is the magnetic scattering length

$$p=\frac{e^2\gamma}{2mc^2}\,gSf(\mathbf{Q})$$

where S is the effective transition metal ion spin: $f(\mathbf{Q})$ is the magnetic form factor for Mn^{4+}, and $Q=4\pi\sin\theta/\lambda$. The spin orientation factor $\langle q^2\rangle$ for a powder sample with hexagonal symmetry has been given by Shirane (1959) as

$$\langle q^2\rangle = 1-\{\tfrac{1}{2}(h^2+hk+k^2)a^{*2}\sin^2\varphi + l^2c^{*2}\cos^2\varphi\}d^2$$

where φ is the angle between the spin direction and $\langle 0001\rangle$.

The magnetic structure factor is compatible with the observed absences and the presence of the 002 reflexion indicates that the spin direction cannot be exactly along $\langle 0001\rangle$.

The magnetic structure proposed is non-centrosymmetric and the data were refined in $P6_3mc$ with the atoms constrained to the centrosymmetric positions. The spin direction was taken perpendicular to **c** and the Mn^{4+} form factor was interpolated from the values for other d^3 ions tabulated by Watson & Freeman (1961). 11 parameters including the cation magnetic moment were refined. The refinement converged to give $R_p=11{\cdot}2\%$ and R based on integrated intensities of 5·6 and 7·6% for the nuclear and magnetic intensities respectively. The final parameter shifts were less than $0{\cdot}3\sigma$. The O vacancy distribution is random and the spin direction is perpendicular to $\langle 0001\rangle$ within the statistical errors. The atom positions and gS are given in Table 4 and interatomic distances and angles in Table 5. The experimental and calculated profiles, a difference plot, and the positions of the Bragg reflexions are shown in Fig. 2. Again the difference profile indicates small errors in the half-width parameters for the strong low-angle reflexions. The lattice parameters at 4·2 K determined from the refinement are 5·4472 (6) and 9·0554 (12) Å.

Table 4. *Atomic positional parameters for* $Ba_{0.1}Sr_{0.9}MnO_{2.96}$ *obtained from refinement at* 4·2 K

$Ba_{0.1}Sr_{0.9}MnO_{2.96}$ ($P6_3/mmc$)

	Positions	x	y	z
(Ba,Sr) (1)	2(a)	0	0	0
(Ba,Sr) (2)	2(c)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$
Mn	4(f)	$\frac{1}{3}$	$\frac{2}{3}$	0·6123 (6)
O(1)	6(g)	$\frac{1}{2}$	0	0
O(2)	6(h)	−0·1800 (3)	−0·3600 (6)	$\frac{1}{4}$

$gS=2{\cdot}41$ (4)

Table 5. *Bond distances and angles in* $Ba_{0.1}Sr_{0.9}MnO_{2.96}$

(Ba,Sr) (1)–O(2)	2·830 (2)	Mn—O(2)	1·910 (4)
(Ba,Sr) (1)–O(1)	2·723 (1)	Mn—O(1)	1·873 (3)
(Ba,Sr) (2)–O(2)	2·726 (2)	O(2)–O(2)	2·941 (3)
(Ba,Sr) (2)–O(1)	2·756 (1)	O(2)–O(2)	2·506 (4)
(Ba,Sr) (1)–Mn	3·281 (5)	O(1)–O(1)	2·724 (1)
(Ba,Sr) (2)–Mn	3·305 (2)	O(2)–O(1)	2·723 (2)
		Mn—Mn	2·494 (8)
O(2)–Mn–O(2)	81·99 (21)	Mn–O(2)–Mn	81·52 (21)
O(2)–Mn–O(1)	92·09 (4)	Mn–O(1)–Mn	180·00 (17)
O(1)–Mn–O(1)	93·31 (19)		

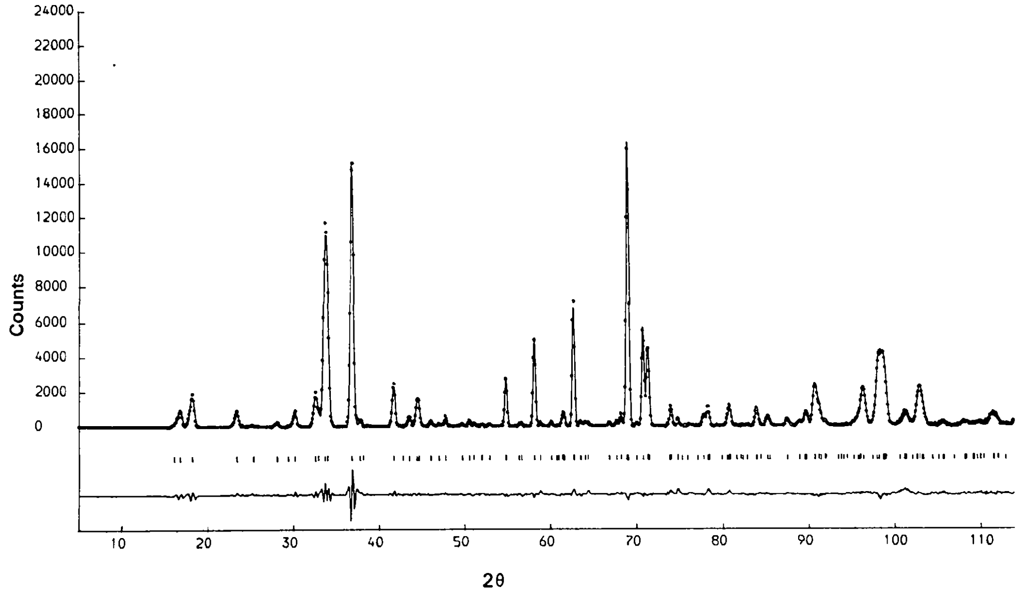

Fig. 2. Powder neutron diffraction profile for $Ba_{0.1}Sr_{0.9}MnO_{2.96}$ at 4·2 K.

Discussion

In $Ba_{0.5}Sr_{0.5}MnO_{2.84}$ the O vacancies (5·4 %) are found in the face-sharing positions; the O sites which corner-link MnO_6 octahedra are fully occupied. The disruption of the face-sharing leads to a local environment which may be described as two edge-sharing trigonal bipyramids if one O is lost from each pair. Both Mn atoms in such a pair are expected to be Mn^{3+} and 32 % of the pairs are coordinated in this way. The pairs may share corners with other such pairs or with face-sharing pairs of octahedra containing Mn^{4+}. Stabilization of $Mn^{3+}(d^4)$ in trigonal bipyramidal coordination is not uncommon and is found, for example, in $YMnO_3$ (Yakel, Koehler, Bertaut & Forrat, 1963).

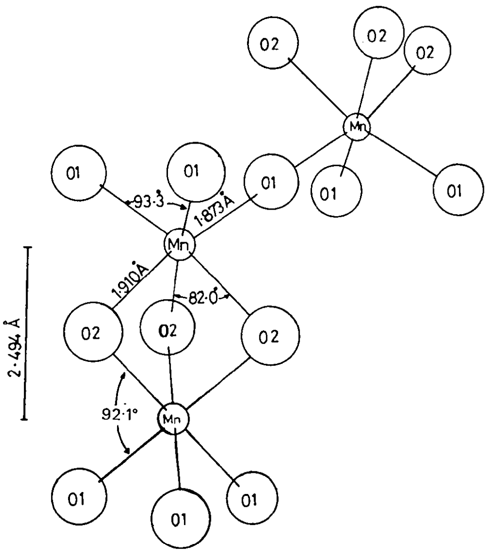

Fig. 3. Mn environment in $Ba_{0.5}Sr_{0.5}MnO_{2.84}$.

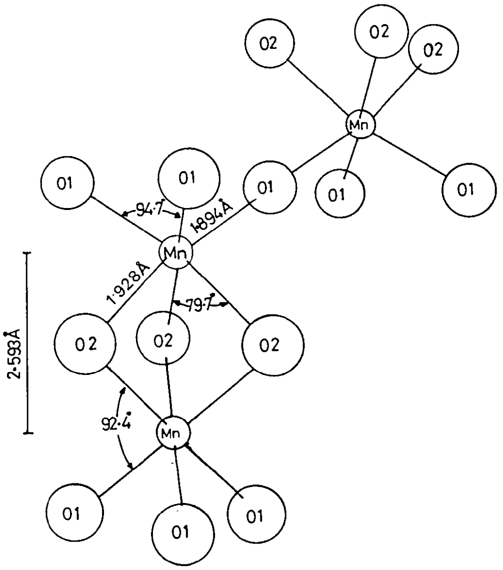

Fig. 4. Mn environment in $Ba_{0.1}Sr_{0.9}MnO_{2.96}$.

The neutron sample of $Ba_{0.5}Sr_{0.5}MnO_{2.84}$ and a sample which had been annealed in a sealed Au tube at 900°C for 340 h were examined by electron microscopy but no evidence was found for vacancy ordering within the hexagonal layers. However, Negas & Roth (1970) reported a structural distortion in 4*H* $SrMnO_{3-x}$ at the highest defect concentrations, before the 4*H*–3*C* transformation, which may be a consequence of incipient vacancy ordering.

The vacancy ordering found in the 4*H* structure supports the suggestion of Negas & Roth (1971) that the preferred method of incorporation of O vacancies in other manganate layer sequences which show substantial departures from stoichiometry is *via* the formation of pairs of edge-shared trigonal bipyramids. Thus in the 6*H* and 10*H* structures which have alternate strings of 4 and 2 and 3 and 2 face-shared octahedra respectively the limiting compositions predicted are 2·83 and 2·80 in close agreement with experiments (Table 1).

$Ba_{0.1}Sr_{0.9}MnO_{2.96}$ has been shown to have a simple collinear antiferromagnetic structure at 4·2 K. Alternate Mn atoms, along **c**, have parallel and antiparallel spins and the spin direction lies in the basal plane. The effective cation spin, 1·21 (2), is lower than the value of 1·5 expected for a pure d^3 system. The observed reduction may be attributed to the effects of zero point spin deviation and covalency. A zero point spin deviation of 5·2% is estimated from Anderson's (1952) formula and the covalency reduction (Jacobson, 1973) would be expected to be similar to the 13·2% (Tofield & Fender, 1970) for the orthorhombic perovskite, $CaMnO_3$. Taking these two factors into account we would expect an effective metal ion spin of approximately 1·23, in agreement with the observed value. However, uncertainties in the degree of saturation of the sublattice magnetization, the form factor extrapolation, and the presence of 8 % Mn^{3+} make a quantitative estimate of the covalency impracticable.

The local environments of Mn in $Ba_{0.5}Sr_{0.5}MnO_{2.84}$ and $Ba_{0.1}Sr_{0.9}MnO_{2.96}$ are shown in Figs. 3 and 4. The average Mn–O distances are 1·911 and 1·891 Å, respectively and may be compared with average distance in 8*H* $BaMnO_3$, 1·898 Å in the same element of structure (Potoff, Chamberland & Katz, 1973). The results for the two nearly stoichiometric compounds are in agreement with values predicted from ionic radii (Mn^{4+} = 0·54, O^{2-} = 1·35 Å; Shannon & Prewitt, 1969). The larger value for the more non-stoichiometric compound is also in agreement with a prediction based on the presence of Mn^{3+} (32 %) with a larger radius, 0·58 Å. The Mn–Mn distance for $Ba_{0.1}Sr_{0.9}MnO_{2.96}$ (2·494) is comparable with the corresponding value in 8*H* $BaMnO_3$ (2·507) and significantly longer than for Mn–Mn in a long face-sharing chain; 2·404 in 8*H* $BaMnO_3$ and 2·403 Å in 2*H* $BaMnO_3$ (Nørlund Christensen & Ollivier, 1972). The Mn–Mn distance in $Ba_{0.5}Sr_{0.5}MnO_{2.84}$ is also larger at 2·593 Å and this may arise from the presence of Mn^{3+} ions and the loss of O from the plane between the Mn which leads to increased cation–cation repulsions. It is also interesting to note that, in both compounds examined, the O–O distance in the hexagonal layer is short (2·471, $Ba_{0.5}Sr_{0.5}MnO_{2.84}$; 2·506 Å, $Ba_{0.1}Sr_{0.9}MnO_{2.96}$) and comparable with that in 8*H* $BaMnO_3$, 2·507 Å.

The relationships between structures with different stacking sequences and O deficiency in the manganate systems is in marked contrast to that found for other transition metal ions, *e.g.* $BaCoO_{3-x}$ and $BaFeO_{3-x}$. An experiment to investigate the consequences of a different preferred coordination scheme for the reduced ion is at present in progress for 6*H* $BaFeO_{3-x}$.

We thank the Science Research Council and AERE Harwell for the provision of neutron facilities and Dr J. L. Hutchison for the electron microscopy.

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Tris(tetramethylurea)trinitratoeuropium(III)

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(*Received* 16 *May* 1975; *accepted* 14 *July* 1975)

$EuH_{36}C_{15}N_9O_{12}$, monoclinic, $P2_1/c$, $a=9{\cdot}428\ (6)$, $b=16{\cdot}034\ (8)$, $c=18{\cdot}921\ (9)$ Å, $\beta=96{\cdot}0\ (3)^\circ$; $Z=4$; $D_m=1{\cdot}62$ (flotation), $D_x=1{\cdot}60$ g cm^{-3}; $\mu(\text{Mo } K\alpha)=22{\cdot}9$ cm^{-1}. Single crystals were obtained by mixing ethanolic solutions of europium nitrate and of tetramethylurea (TMU) in a mole ratio of about 1:8. Europium has a nominal coordination number of nine with the three nitrates symmetrically coordinated in a bidentate fashion and the three TMU's bonded through their oxygens. The mean Eu–O distances are 2·51 Å for the nitrate oxygens, and 2·33 Å for the oxygens of the TMU's.

Introduction

This structure determination is the first of a series to investigate the coordination geometry around lanthanoid atoms in complexes involving *N*-substituted ureas. TMU forms complexes with lanthanoid nitrates and perchlorates with stoichiometries of $Ln(NO_3)_3(TMU)_3$ and $Ln(ClO_4)_3(TMU)_6$ respectively (Burgess, 1970; Giesbrecht & Kawashita, 1970; Vicentini & Najjar, 1970). Inferrential evidence (electrical conductivity and infrared data) indicates differences between the two series of compounds and suggests that they should be formulated as $[Ln(TMU)_3(NO_3)_3]$ and $[Ln(TMU)_6](ClO_4)_3$ respectively (Burgess, 1970). Presumably the coordination number of the lanthanoid in the perchlorate series is 6 but in the nitrate series it could be 6, 7, 8 or 9 depending upon the manner in which the nitrate is bonded. On the basis of previous work it seemed probable that the nitrates would be functioning as bidentate ligands [see for example, Beineke & Delgaudio (1968), Al-Karaghouli & Wood (1968, 1973), Toogood & Chieh (1975)] and hence that the coordination number of the lanthanoid would be 9. With the current interest in the structures of compounds with higher coordination numbers, we report the X-ray study of $Eu[(TMU)_3(NO_3)_3]$.

The fine prismatic crystals are white with a slight