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The Crystallographic and Magnetic Structures of $La_{1-x}Ba_xMn_{1-x}Me_xO_3$ (Me = Mn or Ti)

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The crystallographic and magnetic structures of the distorted perovskites $La_{1-x}Ba_xMn_{1-x}Me_xO_3$ (Me = Mn or Ti) have been determined by neutron powder diffraction. The MnO_6 octahedra are distorted and rotated from their ideal positions. The magnetic space group *Pn'ma'* allows for the ferromagnetism observed in these compounds. It is not possible to decide whether, in addition to long range magnetic order, local spin distortions as proposed by De Gennes are present.

Introduction

The magnetic structure of the series of perovskite-type compounds $La_{1-x}Ca_xMnO_3$ $(0 \leqslant x \leqslant 1)$ has been reported by Wollan and Koehler (*1*). These compounds are slightly distorted cubic but due to the limited resolving power of their neutron powder diffractometer Wollan and Koehler were not able to observe the line splitting caused by the distortion. As a consequence it was not possible to determine the directions of the spins in the lattice.

Recently, magnetic and electrical measurements on $La_{1-x}Ba_xMnO_3$ and $La_{1-x}Ba_xMn_{1-x}Ti_xO_3$ with $0 \leqslant x \leqslant 0.25$ were performed by Lotgering (*2*). As some of these compounds were available in powder form in sufficient amounts to enable neutron diffraction work it was decided to undertake an investigation of these samples with a higher resolving power than was used by Wollan and Koehler (*1*).

Experimental

The compounds which were investigated are listed in Table I. The preparation of the samples is described in Ref. (*2*). The oxidizing power in percentage by weight of oxygen as determined by titration (*3*) and the values calculated for the ideal composition are shown in Table II. Also shown in Table II is the spontaneous magnetization μ_s (*3*) found from the σ–H curve at 4.2°K by extrapolation to $H = 0$. It may be noted that also in pure $LaMnO_3$ evidence is obtained for the presence of a weak ferromagnetic component.

Of all compounds CuK_α X-ray diagrams were taken on a Philips diffractometer. Neutron diagrams at room temperature and at 4.2°K were collected on the powder diffractomer at the High Flux Reactor (HFR) at Petten. The neutron wavelength employed was 2.58 Å, obtained from the (111) planes of a Cu monochromator. A second order filter of 10 cm of pyrolytic graphite was used. Soller slits of 30′ angular divergence were placed between reactor and monochromator and in front of the BF_3 counter.

For the refinement of the structural and the magnetic parameters from the neutron diffractograms the line-profile method described by Rietveld (*4*) was applied. This program determines the values for the parameters that minimize the function:

$$\chi_\nu^2 = \sum_i w_i \frac{[y_i(\text{obsd}) - y_i(\text{calcd})]^2}{\nu},$$

where y_i(obsd) and y_i(calcd) are the observed and calculated values of the i-th intensity and w_i is its statistical weight. ν is the number of observed intensities minus the number of parameters. For

TABLE I

STRUCTURAL PARAMETERS AND MAGNETIC MOMENTS IN THE COMPOUNDS ABO_3

M_x and M_y are the antiferromagnetic and ferromagnetic moment per Mn atom respectively. Standard deviations in units of the last decimal are given in parentheses.

A	La		$La_{.95}Ca_{.05}$		$La_{.95}Ba_{.05}$		$La_{.95}Ba_{.05}$		$La_{.90}Ba_{.10}$		$La_{.875}Ba_{.125}$	
B	Mn		Mn		Mn		$Mn_{.95}Ti_{.05}$		$Mn_{.90}Ti_{.10}$		$Mn_{.875}Ti_{.125}$	
Temp (°K)	293	4.2	293	4.2	293	4.2	293	4.2	293	4.2	293	4.2
a (Å)	5.537(2)	5.742(2)	5.666(1)	5.673(1)	5.638(2)	5.648(2)	5.682(2)	5.685(2)	5.618(3)	5.632(3)	5.570(2)	5.567(2)
b	7.695(2)	7.668(2)	7.712(1)	7.676(1)	7.737(2)	7.695(2)	7.738(2)	7.695(2)	7.798(3)	7.743(3)	7.854(2)	7.834(2)
c	5.743(1)	5.532(1)	5.535(1)	5.528(1)	5.548(2)	5.548(2)	5.560(2)	5.548(2)	5.571(2)	5.565(2)	5.574(2)	5.569(2)
$x(La_{1-x}Me_x)$	0.550(1)	0.549(1)	0.541(1)	0.541(1)	0.535(1)	0.538(1)	0.540(1)	0.541(1)	0.530(1)	0.536(1)	0.521(1)	0.525(1)
$z(La_{1-x}Me_x)$	0.009(1)	0.010(1)	0.007(1)	0.008(1)	0.004(1)	0.006(1)	0.006(1)	0.009(1)	0.003(1)	0.003(2)	0.000(3)	0.003(2)
x(O I)	−0.011(1)	−0.014(1)	−0.011(1)	−0.013(1)	−0.008(1)	−0.008(1)	−0.009(1)	−0.009(1)	−0.007(1)	−0.003(2)	−0.007(1)	−0.004(2)
z(O I)	−0.071(1)	−0.070(1)	−0.069(1)	−0.065(2)	−0.067(1)	−0.065(1)	−0.067(1)	−0.065(1)	−0.068(1)	−0.065(2)	−0.079(2)	−0.065(2)
x(O II)	0.309(1)	0.309(1)	0.301(1)	0.303(1)	0.295(1)	0.297(1)	0.299(1)	0.302(1)	0.290(1)	0.291(1)	0.278(1)	0.277(2)
y(O II)	0.039(1)	0.039(1)	0.038(1)	0.038(1)	0.037(1)	0.036(1)	0.037(1)	0.038(1)	0.035(1)	0.035(1)	0.029(1)	0.036(1)
z(O II)	0.225(1)	0.224(1)	0.224(1)	0.225(1)	0.228(1)	0.228(2)	0.229(1)	0.229(1)	0.237(1)	0.238(1)	0.240(3)	0.226(3)
M_x (μ_B)	—	3.7(1)	—	3.4(1)	—	3.2(1)	—	3.6(1)	—	2.9(1)	—	1.0(1)
M_y	—	0.0(5)	—	0.9(1)	—	1.0(1)	—	0.0(5)	—	1.2(1)	—	2.9(1)
M	—	3.7(1)	—	3.5(1)	—	3.4(1)	—	3.6(1)	—	3.2(1)	—	3.1(1)
χ_v^2	2.6	6.2	4.6	4.1	4.3	6.3	3.3	5.8	3.3	5.2	2.9	3.5

TABLE II

B–O DISTANCES AND O–B–O ANGLES IN THE BO_6-OCTAHEDRA IN ABO_3 COMPOUNDS AT 4.2°K

x, y, and z are the oxygen parameters given in Table I. μ_f is the ferromagnetic moment in μ_B per Mn atom from magnetization measurements. w(obsd) and w(calcd) are the observed and calculated percentages by weight of oxygen.

A	La	$La_{.95}Ca_{.05}$	$La_{.95}Ba_{.05}$	$La_{.95}Ba_{.05}$	$La_{.90}Ba_{.10}$	$La_{.875}Ba_{.125}$
B	Mn	Mn	Mn	$Mn_{.95}Ti_{.05}$	$Mn_{.90}Ti_{.10}$	$Mn_{.875}Ti_{.125}$
B(0, 0, 0) – O1(x, y, z) (Å)	1.959(1)	1.956(2)	1.960(2)	1.958(1)	1.970(2)	1.991(2)
B(0, 0, 0) – O2(x, y, z) (Å)	2.187(5)	2.144(6)	2.120(7)	2.155(5)	2.119(11)	2.011(13)
B(0, 0, 0) – O2($\frac{1}{2}-x$, $\bar{y}$, $z-\frac{1}{2}$) (Å)	1.905(6)	1.910(7)	1.920(8)	1.900(6)	1.899(13)	1.986(14)
O1(x, y, z) – B(0, 0, 0) – O2(x, y, z) (°)	90.7(2)	90.2(3)	89.8(3)	89.8(2)	89.9(3)	89.1(4)
O1(x, y, z) – B(0, 0, 0) – O2($\frac{1}{2}-x$, $\bar{y}$, $z-\frac{1}{2}$) (°)	91.1(3)	91.4(3)	90.7(3)	91.1(2)	90.0(3)	90.3(4)
O2(x, y, z) – B(0, 0, 0) – O2($\frac{1}{2}-x$, $\bar{y}$, $z-\frac{1}{2}$) (°)	90.5(1)	90.8(1)	90.9(1)	90.9(1)	91.0(1)	91.2(1)
μ_f (μ_B)	0.1	0.5	0.5	0.2	0.6	2.9
w(obsd)	3.26(3)	3.53(3)	3.48(3)	3.14(3)	2.93(3)	2.87(3)
w(calcd)	3.31	3.55	3.48	3.15	2.98	2.90

the magnetic formfactor of Mn, the one given by Watson and Freeman (*5*) for Mn^{3+} was used.

Crystal Structures

From the appearance of the X-ray and neutron diagrams at room temperature it was concluded that all compounds were isostructural, though the orthorhombic distortion becomes smaller with increasing x. For $x = 0.125$ no orthorhombic line splitting was observable but from line broadening and the presence of super-lattice reflections it was obvious that the symmetry was still orthorhombic.

The space group was found to be *Pnma* (D_{2h}^{16}) and the structures proved to be isostructural with $GdFeO_3$. Both findings are in accordance with the suggestions of Gilleo (*6*) for this type of compounds. By systematic consideration of all possible deviations from the ideal structure and by refinement of all these models based on the X-ray data at room temperature the structures were determined to be

4 $La_{1-x}Ba_x$ or 4 $La_{1-x}Ca_x$ in 4(c):
x, $\frac{1}{4}$, z with $x \approx 0.54$, $z \approx 0.01$

4 Mn or 4 $Mn_{1-x}Ti_x$ in 4(a):
0, 0, 0

4 O I in 4(c):
x, $\frac{1}{4}$, z with $x \approx -0.01$, $z \approx -0.07$

8 O II in 8(d):
x, y, z with $x \approx 0.30$, $y \approx 0.03$, $z \approx 0.22$

The precise values of the parameters for the different compounds, resulting from a profile refinement with the neutron data, are collected in Table I.

Magnetic Structures

The neutron diagrams at 4.2°K of all compounds showed a number of extra intensities which could be indexed on the basis of the crystallographic unit-cell. The reflection condition of the extra reflections in $LaMnO_3$ is $h + l = 2n$, $k = 2n + 1$. Clearly in this compound the spin ordering consists of ferromagnetic a–c planes with antiferromagnetic coupling of spins in adjacent planes, in conformity with Ref. (*1*). The moments were found to be aligned along the a axis. This defines the magnetic space group uniquely as *Pn'ma'*. In this space group a ferromagnetic component along the b axis is allowed. From magnetization measurements (*3*) it was known that in $La_{0.875}Ba_{0.125}Mn_{0.875}Ti_{0.125}O_3$ the ferromagnetic component takes an appreciable value (~2.9 μ_B/Mn atom). Though in this compound the orthorhombic line splitting is extremely small the direction of this component was confirmed to be along the b axis. It is emphasized that also in this "ferromagnetic" compound an antiferromagnetic component is present with a magnitude of about 1/4 of that in $LaMnO_3$.

In the compounds $La_{0.95}Ca_{0.05}MnO_3$, $La_{0.95}Ba_{0.05}MnO_3$, and $La_{0.90}Ba_{0.10}Mn_{0.90}T_{0.10}O_3$ a ferromagnetic component had also been observed by magnetization measurements (*3*). As in these compounds the ferromagnetic component is much

smaller (~0.5 μ_B/Mn atom) it did not show up as pronounced contributions to the nuclear peaks in the neutron diagrams. However, a refinement of a ferromagnetic component along the *b* axis together with the other parameters resulted for all three compounds in a final value for this component of about 1 μ_B with a standard deviation of 0.1 μ_B, which can be considered to be in good agreement with the earlier observations.

A refinement of a ferromagnetic component in $LaMnO_3$ and $La_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O_3$ resulted in values for these components of $(0.5 \pm 0.2)\mu_B$ and $(0.4 \pm 0.2)\mu_B$ respectively, while the value for this component from magnetization data was only about 0.1 μ_B. A calculation of the quantity χ_ν^2 as a function of the ferromagnetic moment, keeping all other parameters constant, showed that in these two cases one of the essential assumptions of the least-squares method, viz. the parabolic behaviour of the hypersurface χ_ν^2 versus all parameters in the vicinity of the minimum, is not fulfilled for M_y. The curves are rather flat and asymmetric which causes the resulting standard deviations of M_y to be too low. From these curves it was estimated that in these two compounds the neutron data are compatible with a ferromagnetic component of $(0 \pm 0.5)\mu_B$.

A listing of all parameters at 4.2°K is given in Table I. The distances and angles in the distorted MnO_6 octahedra are listed in Table II.

Discussion

The essential new results of this investigation are the determination of the oxygen parameters and the spin directions with respect to the crystallographic axes.

It is seen that Goodenough's model (*7*) for the crystallographic deformation is generally correct though the MnO_6 octahedra are not only deformed but also show a rotation from their ideal orientation.

Havinga (*8*) assumes that substitution of La by the smaller Ba ion at first leads to contraction of the unit-cell without rotation of the octahedra thus preserving cubic symmetry. At some critical value the Mn–O distances cannot decrease any more, and further substitution of La by Ba causes rotation of the MnO_6 octahedra from the ideal orientation. This leads to a deformation of the cubic structure and to a deviation of the interbond angles γ (Mn–O–Mn) from 180°. On the basis of this model Havinga calculates the angles γ in these compounds as a function of the cell dimensions and subsequently tries to correlate these angles with the paramagnetic Curie temperatures θ.

As the MnO_6 octahedra show a considerable deformation Havinga's model is certainly too simple. This is reflected by the values for the Mn–O–Mn angles in $LaMnO_3$. Havinga calculated for these angles 172° and 148° while the values found in this investigation are 156.5° and 154.2°. Therefore Havinga's conclusions are not valid quantitatively though a relationship as proposed by him, may well exist.

The aim of Lotgering's (*2*) investigation was to test the hypothesis that the occurrence of ferromagnetism and metallic conduction in these compounds are correlated through the mechanism of double exchange between Mn^{3+} and Mn^{4+} ions as described by De Gennes (*9*). As pointed out earlier by Jonker (*10*), Lotgering assumes that in compounds in which Mn and La have been substituted in equal amounts by Ti and Ba respectively no Mn^{4+} is present: $La^{3+}_{1-x}Ba^{2+}_xMn^{3+}_{1-x}Ti^{4+}_xO^{2-}_3$. Then double exchange cannot occur in these compounds, but it was found that they still show ferromagnetism. This observation rules out the presence of double exchange as the main cause for the occurrence of ferromagnetism. For small Ba contents, as present in the samples under investigation, the Ti-free materials are not metallic. According to De Gennes (*9*), the double exchange interactions are then localized and give local spin distortions with a resulting ferromagnetic moment. Lotgering (*2*) pointed out that double exchange is not essential for the formation of such locally distorted structures, which can therefore also occur in the Ti-containing substances. Although a long-range ordering of the magnetic moments has been observed in the present investigation, it cannot be excluded a priori that, superposed on this long-range order, local distortions of the arrangement exist. Observation of these local distortions in these compounds is beyond the possibilities of powder techniques.

As already mentioned, the magnetic space group *Pn'ma'* allows for the existence of a ferromagnetic component along the *b* axis in conformity with the observation. After completion of the work it came to the authors' attention that the occurrence of parasitic ferromagnetism in $LaMnO_3$, as reported in Ref. (*2*), has also been observed by Matsumoto (*11*, *12*). The latter author also mentions (*11*) as a private communication, a determination of the crystal structure of $LaMnO_3$ with X-ray and neutron diffraction by Will and Cox. In this determination the same space group and essentially the same deformed crystal structure have been found as in the present paper. The reported distances in the MnO_6 octahedra differ somewhat from those

found in our work. This may be due to slight differences in the stoichiometry of samples. Matsumoto (*11*) reports that for samples obtained in a strong reducing atmosphere an additional monoclinic distortion is observed.

From the observation of parasitic weak ferromagnetism and from the results of the earlier neutron work (*1*) combined with group-theoretical considerations of the same type as those given above, Matsumoto (*11*) deduces a model for the magnetic structure of these compounds which fully fits the result of the present work.

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