MAGNETIC INTERACTIONS BETWEEN Mn$^{3+}$ IONS IN PEROVSKITES

by E. E. HAVINGA

Abstract

Paramagnetic Curie temperatures $\Theta$ and unit-cell dimensions of a number of perovskites with the general formula $A_2(B\text{Mn})O_6$ have been measured ($A = \text{La, Y, Ca, Sr, Ba, Pb}$; $B = \text{Ti, Nb, Ta}$). Besides cubic perovskites rhombohedral and orthorhombic perovskite structures were found. The interbond angles $\gamma$ in the latter structures could be calculated with the aid of a very simple model. The analysis of the magnetic data shows clearly an increasing ferromagnetic interaction with decreasing interionic distances and a decrease of $\Theta$ with decreasing values of $\gamma$. At about $\gamma = 150^\circ$ the magnetic interaction even tends to become antiferromagnetic. Reported data of $\text{LaMnO}_3$ and $\text{BiMnO}_3$ also fit the explanation.

1. Introduction

During an investigation of ferroelectric perovskites containing manganese ions $^1$ we observed that the strength of the ferromagnetic interaction between the Mn$^{3+}$ ions is markedly dependent on the lattice parameters. In this paper we will present the results of a somewhat more extensive study of this phenomenon.

Variations in the magnetic interaction between Mn$^{3+}$ ions in perovskites have been reported previously by Jonker $^2$ and by Watanabe $^3$. They found ferromagnetic interactions at relatively large interionic distances, as contrasted with antiferromagnetic interactions at smaller distances. Watanabe's estimates of the strength of the magnetic interactions in the Mn$^{3+}$-O-Mn$^{3+}$ configuration in compounds $\text{La}_{1-x}\text{Sr}_x\text{MnO}_y$, if plotted versus the interionic distance Mn$^{3+}$-Mn$^{3+}$, could be represented by a single curve.

The present investigations supplement the results cited above in two respects. In the first place the range of interionic (Mn$^{3+}$-Mn$^{3+}$) distances is extended upwards from 3·97 Å to 4·10 Å. This is made possible by the use of diluted compounds $A_2(B\text{Mn})O_6$ rather than $A\text{MnO}_3$. After a brief record of experimental particulars this procedure will be justified in a separate section of this paper. Secondly, the change in bond angles at smaller distances, together with its influence on the magnetic interactions, will be considered in detail.

2. Experimental

The compounds were prepared using conventional ceramic techniques. Details may be found in ref. 1. The final firing temperature and atmosphere were adjusted until a maximum d.c. resistivity (or minimum loss tangent) was reached. A chemical analysis of the manganese content and of the oxygen content.
for some samples showed that this criterion is sufficient to ensure that at least 95% of the manganese ions are in the trivalent state.

The paramagnetic susceptibility was measured at 9000 Oe by a Faraday method, generally in the temperature region from 300 °K to 800 °K. The linear high-temperature parts of the $\chi^{-1}$ vs $T$ curves were extrapolated to $\chi^{-1} \rightarrow 0$ in order to determine the paramagnetic Curie temperatures $\Theta$. However, the reproducibility of the results was rather modest, possibly on account of the occurrence of a partial ordering of the Mn$^{3+}$ and B ions, varying with the sample preparation (see also next section). As variations up to 15 °K were observed (the mean deviation being about ±4 °K) the values of $\Theta$ are given only to the next 5 °K. The slopes of the straight lines in the $\chi^{-1}$ vs $T$ plots were used to determine the effective magnetic moment $p$ of the manganese ions. All values were within the range $4•85 < p < 5•1$, in reasonable agreement with the expected spin-only value for Mn$^{3+}$ ions: $p = {S(S + 1)}^{1/2} = 4•90$.

The lattice constants of the perovskite phases were determined from CuKα X-ray powder diagrams. The relative accuracy for cubic and rhombohedral compounds is about ±0•1%, for orthorhombic compounds it amounts to ±0•25%. The absolute accuracy may be two or three times worse. No attempts to improve this accuracy were made because of the poor reproducibility of the magnetic measurements. In all but two compositions second phases could not be detected in the X-ray diagrams; in the diagrams of the two compounds containing the largest amount of Y (see bottom table I) traces of Y$_2$O$_3$ were found.

3. Effects of a dilution of the Mn$^{3+}$ lattice

We have determined the strength of the magnetic interaction of the configuration Mn$^{3+}$ - O - Mn$^{3+}$ in a series of diluted compounds A$_2$(BMn)O$_6$, rather than in a series of normal compounds AMnO$_3$. This choice was prompted by the much greater degree of freedom in diluted compounds to vary the lattice dimensions by chemical substitutions.

According to a — rather crude — empirical rule perovskites ABO$_3$ are stable only if the Goldschmidt tolerance factor $t$, defined by $(r_o + r_A) = t(r_o + r_B)$, lies within the range 0•8 < $t$ < 1 ($r$ = Goldschmidt ionic radius). If $t$ > 0•9 the perovskites are cubic, but if 0•8 < $t$ < 0•9 distorted perovskite structures are found 4). These rules indicate that the only non-magnetic A$^{3+}$ ions that can give rise to the formation of perovskites AMnO$_3$ are Bi$^{3+}$, La$^{3+}$ and Y$^{3+}$. The largest unit cell is obtained for BiMnO$_3$ ($a = 3•95$ Å 5)). Moreover, all perovskites AMnO$_3$ are distorted, not only because $t$ < 0•9 but also because of the Jahn-Teller effect of Mn$^{3+}$ ions in oxygen octahedra.

The range of lattice constants as well as that of $t$ is extended upwards considerably in the case of compounds A$_2$(BMn)O$_6$. Maximum values were obtained for Ba$_2$(NbMn)O$_6$, a cubic perovskite with $a = 4•09$ Å. The possibility of cubic
compounds arises not only because $t > 0.9$, but also because of a decrease of the Jahn-Teller effect (larger unit cell and lack of cooperation in the diluted Mn$^{3+}$ lattice). In cubic perovskites the angles $\gamma$(Mn$^{3+}$-O$^2$--Mn$^{3+}$) are exactly 180°. Therefore these compounds are especially favourable for studying the dependence of the strength of the magnetic interaction on the interionic distance. In the distorted perovskites $\gamma$ differs appreciably from 180°, which gives a second influence on the strength of the magnetic interactions.

Having indicated some advantages of the use of diluted compounds it remains to show that such compounds indeed give useful information about the strength of the magnetic interaction. Theoretically the situation is fairly clear.

According to the molecular-field theory randomly diluted ferromagnetic systems obey at high temperatures a Curie-Weiss law:

$$\chi = \frac{C(T - \Theta)^{-1}}{1}.$$  

The Curie constant $C$ referring to one mole of magnetic ions is independent of the degree of dilution. The paramagnetic Curie point $\Theta$ is proportional to the concentration $x$ of magnetic ions ($0 \leq x \leq 1$):

$$\Theta = x\Theta',$$

where $\Theta'$ indicates the paramagnetic Curie point of the non-diluted compound. In this approximation the compound becomes ferromagnetic at $\Theta$ °K.

More sophisticated theories (B.P.W., Ising model), but involving only nearest-neighbour interactions, leave these results unaltered except for a lowering of the ferromagnetic-transition temperature with respect to the Curie temperature $\Theta$ 6). Therefore the $\chi$-values near $\Theta$ are changed and only high-temperature parts of the $\chi^{-1}$ vs $T$ curves are linear and can be used to calculate $\Theta$ and $C$ (or $\rho$).

If, on the other hand, all B and Mn$^{3+}$ ions in our compounds A$_2$(BMn)O$_6$ were completely ordered, no nearest-neighbour Mn$^{3+}$-O-Mn$^{3+}$ interaction would be present, but only interactions in configurations Mn$^{3+}$-O-B-O-Mn$^{3+}$ that are probably smaller by an order of magnitude 7). Therefore one would expect much lower values of $\Theta$ in ordered compounds than in randomly disordered compounds. In the discussion of our results we will assume that our samples are practically at the limit of a completely random structure. This is plausible for the following reasons. The compounds are certainly not completely ordered as no indication for ordering could be found in the X-ray diagrams. The absence of long-range order is a general property of perovskites containing a mixture of trivalent ions and tetravalent or pentavalent ions 8), unless size effects or covalent bonding play an important part 9). Hence the difference in Coulomb energy between ordered and disordered structures is very small indeed. Moreover, our samples were quenched from rather high temperatures (about 1200 °C).
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With the assumption of a randomly disordered structure the measured value of $\Theta$ of a compound A$_2$(BMn)O$_6$ is just half the value of $\Theta$ of a compound AMnO$_3$, with an otherwise identical lattice. In a non-diluted lattice each Mn$^{3+}$ ion has six nearest neighbours Mn$^{3+}$, hence $\Theta = 3\Theta_1$, if $\Theta_1$ denotes the strength of the magnetic interaction in a single configuration Mn$^{3+}$-O-Mn$^{3+}$. We therefore have the relation $\Theta = \frac{3}{2}\Theta_1$, applying to compounds A$_2$(BMn)O$_6$.

Experimental verification of the linear relation between $\Theta$ and concentration $x$ is very difficult to obtain. In several systems (see e.g. ref. 1) $\Theta$ indeed increases linearly with $x$, but in all cases a change in $x$ is accompanied by a small change in lattice constants. However, it will be seen in the discussion (sec. 6) that the magnetic properties of BiMnO$_3$ and LaMnO$_3$ can be explained nearly quantitatively with the results of the analysis of the measurements on our diluted compounds. So the basic assumptions are more or less justified afterwards by the results.

The fluctuations in the observed Curie temperatures (up to 15 °K, see sec. 2) may be due to a partial short-range ordering in some of the samples, varying with the sample preparation. However, the effect of 15 °K is fairly small and does not invalidate the assumption completely, but shows that it will be fulfilled only as a first approximation. On the other hand, we do not intend to give very accurate quantitative values of the strength of the interaction involved, but only its general behaviour as a function of interionic distances and angles. As is borne out by the results, the data indeed enable this information to be obtained with reasonable accuracy.

4. Results

The results of the X-ray and magnetic measurements are summarized in table I. Besides cubic perovskites (C), rhombohedral (R) and orthorhombic (O) distorted perovskites were found, isomorphous with LaAlO$_3$ and GdFeO$_3$, respectively. Only "pseudo"-cell dimensions are given, corresponding to the unit cell of the cubic compounds because these are relevant to the discussion in sec. 5. In addition to the compounds of table I some compounds A$_2$(TaMn)O$_6$ were prepared. Their properties are almost indistinguishable from those of the corresponding Nb compounds in table I and are therefore not listed.

Some rhombohedral perovskites become cubic at higher temperatures. The transition temperatures, determined by X-ray diffraction, are given in table I. At about 400 °C LaAlO$_3$ shows a transition, probably higher than first order, to the cubic perovskite structure. In our compounds too, therefore, the observed transition probably be of higher than first order. This explains the very non-linear $\chi^{-1}$ vs $T$ curves measured for SrLa(TiMn)O$_6$ (R ⇔ C at 400 °C) and for Ba$_{0.33}$Sr$_{0.67}$La(TiMn)O$_6$ (R ⇔ C at 700 °C), which prevented the determination of a paramagnetic Curie point $\Theta$ for these compounds. Three other compounds, showing a similar transition just above room temperature,
Crystallographic data and paramagnetic Curie temperatures $\Theta$ of perovskites with the general formula $A_2(BMn)O_6$

<table>
<thead>
<tr>
<th>composition</th>
<th>symmetry *)</th>
<th>(pseudo)-cell dimensions at $25^\circ C$</th>
<th>$\Theta$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Ca_2(NbMn)O_6$</td>
<td>O</td>
<td>$a' = 3.885$ $b' = 3.875$ $c' = 91.2^\circ$</td>
<td>40</td>
</tr>
<tr>
<td>$Sr_2(NbMn)O_6$</td>
<td>R</td>
<td>$a' = 3.974$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>90</td>
</tr>
<tr>
<td>$Ba_2(NbMn)O_6$</td>
<td>C</td>
<td>$a' = 4.090$ $b' = 90^\circ$ $c' = 40^\circ$</td>
<td>40</td>
</tr>
<tr>
<td>$Pb_2(NbMn)O_6$</td>
<td>C</td>
<td>$a' = 4.060$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>40</td>
</tr>
<tr>
<td>$Pb_1.75La_{0.25}(Nb_{0.75}Ti_{0.25}Mn)O_6$</td>
<td>C</td>
<td>$a' = 3.995$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>90</td>
</tr>
<tr>
<td>$Pb_1.50La_{0.50}(Nb_{0.50}Ti_{0.50}Mn)O_6$</td>
<td>C</td>
<td>$a' = 4.024$ $b' = 90^\circ$ $c' = 85^\circ$</td>
<td>55</td>
</tr>
<tr>
<td>$Pb_1.25La_{0.75}(Nb_{0.25}Ti_{0.75}Mn)O_6$</td>
<td>R</td>
<td>$a' = 3.962$ $b' = 90^\circ$ $c' = 70^\circ$</td>
<td>105</td>
</tr>
<tr>
<td>$PbLa(TiMn)O_6$</td>
<td>C</td>
<td>$a' = 3.933$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>105</td>
</tr>
<tr>
<td>$BaLa(TiMn)O_6$</td>
<td>C</td>
<td>$a' = 3.960$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>105</td>
</tr>
<tr>
<td>$BaLaO_{0.67}SrO_{0.33}(TiMn)O_6$</td>
<td>R</td>
<td>$a' = 3.944$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>105</td>
</tr>
<tr>
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<td>R</td>
<td>$a' = 3.929$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>90</td>
</tr>
<tr>
<td>$SrLa(TiMn)O_6$</td>
<td>R</td>
<td>$a' = 3.912$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>105</td>
</tr>
<tr>
<td>$SrO_{0.67}CaO_{0.33}La(TiMn)O_6$</td>
<td>R</td>
<td>$a' = 3.900$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>105</td>
</tr>
<tr>
<td>$Sr_2Ca_{0.67}La(TiMn)O_6$</td>
<td>R</td>
<td>$a' = 3.885$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>100</td>
</tr>
<tr>
<td>$Ca_2La(TiMn)O_6$</td>
<td>R</td>
<td>$a' = 3.872$ $b' = 90^\circ$ $c' = 90^\circ$</td>
<td>100</td>
</tr>
<tr>
<td>$CaLaO_{0.75}Y_{0.25}(TiMn)O_6$</td>
<td>O</td>
<td>$a' = 3.87$ $b' = 3.85$ $c' = 90^\circ$</td>
<td>95</td>
</tr>
<tr>
<td>$CaLaO_{0.50}Y_{0.50}(TiMn)O_6$</td>
<td>O</td>
<td>$a' = 3.87$ $b' = 3.82$ $c' = 90^\circ$</td>
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</tr>
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<td>O</td>
<td>$a' = 3.85$ $b' = 3.80$ $c' = 90^\circ$</td>
<td>50</td>
</tr>
<tr>
<td>$CaY(TiMn)O_6$</td>
<td>O</td>
<td>$a' = 3.84$ $b' = 3.77$ $c' = 92^\circ$</td>
<td>10</td>
</tr>
</tbody>
</table>

*) C = cubic,  
R = rhombohedral,  
O = orthorhombic.

could be measured over a sufficiently broad temperature range to allow the determination of $\Theta$ in the cubic structure.

The variation of the paramagnetic Curie temperatures $\Theta$ with the average (pseudo)-cell edge $\bar{a}$ is shown in fig. 1. For comparison Watanabe's 3) curve is also given (with, of course, halved $\Theta$ values). The general trend of the two results is similar.

The symmetry of the compounds measured is indicated in fig. 1 by the use of different symbols for cubic, rhombohedral and orthorhombic compounds. The value of $\Theta$ increases with decreasing unit-cell edge for cubic compounds; for rhombohedral compounds $\Theta$ is nearly constant and the measured values of orthorhombic compounds are irregular. In the following discussion this behaviour will be analyzed in terms of a dependence of the magnetic interaction in the configuration $Mn^{3+}-O-Mn^{3+}$ on interionic distances $d$ and on interionic bond angles $\gamma$.

5. Discussion of crystallographic data

5.1. Construction of a model

In cubic perovskites the atomic parameters are fixed by symmetry and we have...
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Fig. 1. Paramagnetic Curie temperatures $\Theta$ of perovskites $A_2(BMn)O_6$, plotted as a function of the average (pseudo)-unit-cell edge $\bar{a}$. The dashed curve indicates Watanabe’s results (from fig. 8 of ref. 3).

\[ d(Mn-O) = \frac{1}{2}a \text{ and } \gamma(Mn^{3+}O-Mn^{3+}) = 180^\circ. \]

In principle a complete structure determination is required to obtain this information where distorted perovskite structures are concerned. In view of the absence of single crystals this is not directly possible for the compounds in question, nor would it be very practical. Therefore we will construct a model that allows an approximate determination of $\gamma$ and $d$ directly from the observed lattice dimensions. The basic assumptions involved follow from the following considerations.

In our series of perovskites $A_2(BMn)O_6$ we find with decreasing size of the A ions (i.e. decreasing tolerance factor $t$) successively cubic, rhombohedral and orthorhombic structures. This sequence is found quite generally $^{10-13}$. Because of its occurrence for a wide variety of B ions in $ABO_3$ compounds Gilleo already stated $^{12}$ that these deformations of the cubic structure are principally induced by steric effects, the electronic configuration of the B ions playing a minor part. Useful information about the nature of the orthorhombic structure can thus be obtained by looking at GdFeO$_3$ and YFeO$_3$, for which compounds accurate structure determinations have been carried out $^{11,14,15}$. In these structures an irregular environment is found around the Gd$^{3+}$ and Y$^{3+}$ ions, whilst the Fe$^{3+}$ ions are in approximately regular octahedra. Moreover the distances $d(Fe-O)$ are very similar in both compounds and nearly equal to those found in FeO$_6$ octahedra in some garnets. Coppens and Eibschütz $^{15}$ concluded that as a first approximation the distance $d(Fe-O)$ is independent of the degree of distortion of the perovskite structure. They calculated the bond angles...
\( \gamma(\text{Fe-O-Fe}) \) in other ferrites directly from the lattice dimensions, assuming that the FeO\(_6\) octahedra in all compounds were exactly alike.

The model of the "stiff" octahedra in ferrites with orthorhombic perovskite structure can be generalized to the other distorted perovskites as well. We then arrive at the following picture. Let us start with a cubic perovskite \( \text{ABO}_3 \) and decrease the size of the A ion. In the first instance the unit cell will shrink uniformly and it remains cubic. However, at some cell edge \( a_m \) the distances \( d(\text{B-O}) \) reach a minimum value \( d_m \); any further decrease of the A ions gives a smaller unit cell only because of rotations of the \( \text{BO}_6 \) octahedra, leading to a distorted perovskite structure. Independently of the pattern of the rotations, the angles \( \gamma_i(\text{B-O-B}) \) are given by the simple relation

\[
\sin \left( \frac{\gamma_i}{2} \right) = \frac{a_i}{2d_m}. \tag{1}
\]

For ferrites the appropriate minimum distance \( d_m \) follows directly from the parameters of the structure of \( \text{GdFeO}_3 \) and \( \text{YFeO}_3 \)\(^{15}\): \( 2d_m(\text{Fe-O}) = 4.02 \text{ Å} \). For some other series of compounds \( \text{ABO}_3 \) with equal B ions \( 2d_m \) can be identified with the lattice dimension of the compound just at the border line between cubic and distorted perovskite. In this way a mere inspection of table I results in the values \( 2d_m(\text{Ti}_{0.5}\text{Mn}_{0.5}\text{O}-) = 3.95 \text{ Å} \) and \( 2d_m(\text{Nb}_{0.8}\text{Mn}_{0.2}\text{O}-) = 3.99 \text{ Å} \). The distance \( 2d_m(\text{Mn-O}) \), which is needed in a discussion of the properties of \( \text{LaMnO}_3 \) and \( \text{BiMnO}_3 \), can be obtained in a roundabout way. The distance \( 2d_m(\text{Ti-O}) \) is 3.90 Å, as follows from the boundary between cubic and distorted perovskite structures in the system \( \text{Sr}_{1-x}\text{Ca}_x\text{TiO}_3 \) (at \( x = 0.1 \))\(^{16}\). As the variation of \( d_m \) with the concentration \( y \) in a system \( \text{ATi}_y\text{Mn}_{1-y}\text{O}_3 \) will as a first approximation be linear, we obtain from the distances for \( y = 1 \) and \( y = 0.5 \), derived above, the value \( 2d_m(\text{Mn-O}) = 4.00 \text{ Å} \). This value of \( d_m \) is equal to the average distance in the octahedra of the structure of \( \text{LaCo}_{0.2}\text{Mn}_{0.8}\text{O}_3 \), as determined by Gilleo\(^{12}\). We will refer to this structure determination in more detail below.

Having obtained the necessary values of \( d_m \) we can proceed to calculate the interbond angles \( \gamma_i \) directly from the observed pseudo-cell dimensions (formula (1)). The following remarkable regularity is then observed. In a series of rare-earth ferrites\(^{11}\), rare-earth aluminates\(^{10}\), the system (\( \text{Sr}_{1-x}\text{Ca}_x \) \( \text{TiO}_3 \))\(^{16}\) and in our compounds \( \text{A}_2(\text{TiMn})\text{O}_6 \) the boundary between the rhombohedral and the orthorhombic structure is found at angles of 157°, 160°, 159° and 157°, respectively. These angles are practically the same, which supports our basic assumption that steric effects determine the occurrence of the distortions of the perovskite structures involved.

5.2. Influence of the Jahn-Teller effect

Thus far we have neglected the fact that the Mn\(^{3+}\) ion with its electron configuration \( 3d^4 \) in a regular octahedron has a degenerate ground state involving \( e_g \).
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The Jahn-Teller effect states that the Mn$^{3+}$ ion tends to deform its surroundings in order to remove this degeneracy. According to Goodenough\textsuperscript{17}) cooperative Jahn-Teller effects in perovskites induce pseudo-tetragonal or orthorhombic unit cells, the pseudo-cell dimensions obeying the inequality

$$b' < a' \cos \frac{1}{2}\beta' \leq a' \sin \frac{1}{2}\beta'.$$

In compounds that are orthorhombic because of steric effects only, the inequality runs differently:

$$a' \cos \frac{1}{2}\beta' < b' < a' \sin \frac{1}{2}\beta'.$$

As we found the boundary between rhombohedral and orthorhombic perovskites in our compounds at $\gamma = 157^\circ$, just as in other series of perovskites without Jahn-Teller ions, the occurrence of an orthorhombic structure in our compounds is certainly not caused by the cooperative Jahn-Teller effect. On the other hand, the lattice dimensions obey the relation

$$a' \cos \frac{1}{2}\beta' \approx b' < a' \sin \frac{1}{2}\beta',$$

which possibly indicates that the normal orthorhombic structure is slightly adjusted towards the Jahn-Teller structure.

On an atomic scale, the extreme Jahn-Teller structure (with the Mn$^{3+}$ ions only in the $d_{z^2}$ state) calls for tetragonally distorted octahedra, short Mn-O distances in the $b'$-direction, and alternating short and long distances in the $a'$- and $c'$-direction\textsuperscript{17}). A detailed theoretical analysis by Kanamori\textsuperscript{18}), however, showed that even in the structure of MnF$_3$\textsuperscript{19}), which perovskitelike compound shows a strong cooperative Jahn-Teller effect, the occupation of $d_{x^2-y^2}$ orbitals is only slightly less than that of the $d_{z^2}$ orbitals. This could be derived from the Mn-F distances, the distance Mn-F in the $b'$-direction of MnF$_3$ being in between the alternately short and long bonds in the other directions. As our calculation of $\gamma$ is hardly influenced by a change of two equal distances B-O in alternately short and long distances, it follows that the calculation of $\gamma$, with formula (1) will also be correct as a first approximation for Mn$^{3+}$ ions exhibiting a moderate Jahn-Teller effect.

Gilleo's structure determination of LaCo$_{0.2}$Mn$_{0.8}$O$_3$\textsuperscript{12}) with Mn-O distances in the $b'$-direction nearly equal to the short distances in the $a'$- and $c'$-directions, would point to an extreme Jahn-Teller structure in this compound. However, this structure determination is far less accurate than that of MnF$_3$. Firstly the large atomic-scattering factor of La greatly obscures the small contributions of the oxygen ions to the intensities and secondly Gilleo's structure analysis was based on X-ray powder diagrams involving only 35 intensities, nearly all of which were superpositions of a large number of single-crystal reflections. For MnF$_3$ more reflections could be measured and moreover no heavy ions complicate the analysis. Therefore we consider the structure determined for MnF$_3$ as far more typical.
5.3. Influence of higher measuring temperatures

Our model now allows the calculation of \( d \) and \( \gamma \) for the compounds at room temperature. In fact we are interested in these quantities in the whole temperature range of the magnetic measurements (300 °K-800 °K). The linear-expansion coefficient of an oxidic perovskite is of the order of \( 10^{-5} \) (°K\(^{-1}\)) (compare for example ref. 13). Thus the total change in average distance from 300 to 800 °K amounts to about \( \frac{1}{2} \% \). On the other hand the minimum distance \( d_m \) is probably rather constant, as the volume at the transition point to cubic symmetry of \( \text{LaAlO}_3 \) \(^{19}\) and those of the relevant compounds in table I are practically equal to \( 8 d_m^3 \), the volume at the boundary at room temperature. Hence it is probably slightly better to calculate the average values of \( \gamma \) at the measuring temperatures from lattice dimensions that are increased by about \( \frac{1}{2} \% \) (or 0.01 Å) above the room-temperature values. In the next section this procedure will be followed. A second influence of the high measuring temperature is that any local Jahn-Teller effects that may be present at room temperature are wiped out, thus decreasing the error introduced by their neglect in the calculation of \( \gamma \) and \( d \).

5.4. Further implications of the model

The model of “stiff” octahedra \( \text{BO}_6 \), which are rotated in respect of their positions in the cubic structure, can be developed in somewhat more detail. It then provides an explanation of the sequence cubic-rhombohedral-orthorhombic perovskite. Further a semiquantitative calculation can be given to explain Geller’s \(^{20}\) observation that the radii of the rare-earth ions derived from the lattice parameters of distorted perovskites differ appreciably from those derived from their oxides \( \text{M}_2\text{O}_3 \) \(^{21}\), the range of values being about three times narrower in the perovskites. The reason is simply that in the distorted perovskites the rare-earth ions are surrounded very irregularly, which increases the repulsive force and hence the apparent size.

A rhombohedral structure with the required symmetry \( \overline{R}3m \) \(^{19}\) can be obtained from the cubic structure by rotating each \( \text{BO}_6 \) octahedron around its principal axes by equal amounts, the directions of the rotations being reversed for neighbouring octahedra. The orthorhombic structure can be derived similarly from the cubic structure by rotating the octahedra around their principal axes, but in a completely different pattern. The rotations around the \( b' \)-axis reverse sign only for octahedra that are neighbours in a \( \{010\} \) plane of the pseudo cell, whereas both other rotations, that are of equal magnitude, are reversed for neighbours in the \( \{010\} \)-direction only. In the first instance both patterns of rotation of \( \text{BO}_6 \) octahedra change the regular 12 coordination of the A ions with oxygen ions at distances \( a/\sqrt{2} \) into a surrounding with 3 short distances \( \{1 - \tan \gamma/\sqrt{2}\} a/\sqrt{2} \), 6 medium distances \( \{1 + \tan^2 \gamma\} a/\sqrt{2} \) and 3 long distances \( \{1 + (\tan \gamma)/\sqrt{2}\} a/\sqrt{2} \). In the rhombohedral structure the A ion will remain at its original position midway between the B ions, because it is still the centre of the oxygen surroundings. In the orthorhombic structure the rotations of \( \text{BO}_6 \) octahedra may be of different magnitude, thus changing the A-O distances, but the original position of the A ions...
is off-centre even with equal rotations around all axes. Consequently the A ions will be shifted and the new surrounding is an approximate 6-coordination with medium-short distances. A simple calculation involving only repulsive energy $U$ due to the 12 A-O distances $d$, approximated as $U = A d^{-q}$, shows that the shift of the A ions stabilizes the orthorhombic structure over the rhombohedral structure only if $\gamma < 175^\circ$. On the other hand, the shift of the A ions decreases the polarization of the oxygen ions and moreover the oxygen-ion packing is more favourable in the rhombohedral structure. Therefore the sequence cubic-rhombohedral-orthorhombic can be explained by the model, but it is not possible to calculate the position of the boundary between the two latter structures.

A calculation of the rhombohedral angle $\beta'$ of the pseudo cell of the rhombohedral structure can be carried out as follows. The boundary between rhombohedral and orthorhombic structures is found at about $\gamma = 158^\circ$. The maximum value of $\beta'$ is therefore obtained by using this value in the distances A-O and introducing a rhombohedral distortion. Minimalization of the repulsive energy of the 12 A-O bonds with respect to the rhombohedral angle gives $\beta' = 91.5^\circ$. However, the octahedra BO$_6$ are deformed also and this gives an opposite energy effect. Taking into account the influence of the O-O distances by an energy $U = A d^{-7}$ and using the general formulae of Pauling $^{21}$ to obtain the relative importance of the oxygen-oxygen repulsion with respect to the oxygen-rare-earth-ion repulsion, decreases the calculated value of $\beta'$ to 90.9°. This value is in reasonable agreement with the experimental values of rare-earth aluminates (90.4°) $^{10}$ although the calculated value is a little too large. In our compounds the angle $\beta'$ varies very irregularly, whilst in the aluminates $^{10}$ a regular increase with decreasing lattice parameter is found. This difference must probably be ascribed to the presence of two or three kinds of A ions in our compounds, because $\beta'$ is seen to be smaller the more complicated the occupation of the A sites (table I).

Finally it can be shown that our model provides a simple explanation of Geller's $^{20}$ observation that the radii of the rare-earth ions derived from the lattice parameters of distorted perovskites differ appreciably from those derived from the simple oxides. We first equate the repulsive energy of the 12 O neighbours of the A ions in rhombohedral perovskites to that of a regular 12-coordination at a distance $d_{12}$. The results are given in table II. It is seen that $(a'/\sqrt{2})$ varies much slower than the distance $d_{12}$ of a regular 12-coordination with equal energy. The radii $r_{12}$ can be transformed to radii $r_6$ for regular six-coordination by means of Pauling's formula $^{21}$ \( (r_6/r_{12})^8 = 6/12 \). It is seen (table II) that the radii $r_6$ derived in this way are in very good agreement with the radii derived from the simple oxides. For the other rare-earth ions the calculation cannot be carried out, because no rhombohedral perovskites are found. The environment of the rare-earth ions in the orthorhombic perovskites is probably very similar to that in the rhombohedral perovskites, but certainly very irregular. Therefore the same influence changes the radii of the rare-earth ions here.

<table>
<thead>
<tr>
<th>perovskite</th>
<th>$a'$(Å)</th>
<th>$\tan \frac{\gamma}{2}$ (calc.)</th>
<th>$a'/d_{12} \sqrt{2}$ (calc.)</th>
<th>ion</th>
<th>$r_{12}$(Å) (calc.)</th>
<th>$r_6$(Å) (calc.) (Geller $^{20}$)</th>
<th>$r_6$(Å) (calc.) (ref. 21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaAlO$_3$</td>
<td>3.789</td>
<td>0.083</td>
<td>1.007</td>
<td>La$^{3+}$</td>
<td>1.316</td>
<td>1.346</td>
<td>1.060</td>
</tr>
<tr>
<td>CeAlO$_3$</td>
<td>3.766</td>
<td>0.137</td>
<td>1.021</td>
<td>Ce$^{3+}$</td>
<td>1.262</td>
<td>-</td>
<td>1.010</td>
</tr>
<tr>
<td>PrAlO$_3$</td>
<td>3.762</td>
<td>0.145</td>
<td>1.024</td>
<td>Pr$^{3+}$</td>
<td>1.251</td>
<td>1.330</td>
<td>1.000</td>
</tr>
<tr>
<td>NdAlO$_3$</td>
<td>3.749</td>
<td>0.166</td>
<td>1.033</td>
<td>Nd$^{3+}$</td>
<td>1.220</td>
<td>1.320</td>
<td>0.972</td>
</tr>
<tr>
<td>O$_2^-$</td>
<td></td>
<td></td>
<td></td>
<td>O$_2^-$</td>
<td>1.346</td>
<td>1.346</td>
<td>1.380</td>
</tr>
</tbody>
</table>
6. Discussion of the magnetic data

6.1. Analysis of the data

The discussion of the crystallographic data in the preceding section makes it clear, that the measured Curie temperatures $\Theta$ in the cubic perovskites directly give the distance dependence of the $180^\circ$ ($\text{Mn}^{3+}$-$\text{O}$-$\text{Mn}^{3+}$) magnetic interaction $\Theta_1$ ($\Theta_1 = \frac{3}{2} \Theta$). It is seen (black squares in fig. 1) that this interaction is ferromagnetic and increases with decreasing interionic distances. On the other hand the distances Mn-O in the rhombohedral and orthorhombic perovskites are, according to our model, constant and independent of the lattice parameters. Thus the differences in $\Theta$-values for these compounds are due to differences in interionic angles $\gamma$. The average angles $\bar{\gamma}$ for the different compounds were calculated with the aid of the model and the magnetic interaction $\Theta$ was plotted as a function of $\bar{\gamma}$ (fig. 2). It is seen that $\Theta$ decreases slowly if $\gamma$ begins to deviate from $180^\circ$, but at values of $\gamma \approx 150^\circ$ a much faster decrease is observed, leading to negative values of $\Theta$ at smaller angles $\gamma$. The value of $\Theta$ for Ca$_2$(NbMn)O$_6$ now fits very satisfactorily in with the picture of the $\Theta$-values of compounds A$_2$(MnTi)O$_6$ (fig. 2), whereas in fig. 1 a large deviation was present (the $\gamma$ vs $\Theta$ curve for compounds A$_2$(NbMn)O$_6$ has not been indicated in fig. 2, but it probably runs congruently and ends at $\Theta = 90^\circ$K at $\gamma = 180^\circ$).

6.2. Application to LaMnO$_3$ and BiMnO$_3$

The interpretation of our experimental data in terms of a distance and angle dependence is supported by the results of its application to the data of the compounds BiMnO$_3$ and LaMnO$_3$, as reported in the literature.
MAGNETIC INTERACTIONS BETWEEN Mn$^{3+}$ IONS IN PEROVSKITES

From sec. 5.1 we know that in these compounds we have $2d_m(Mn-O) = 4\cdot00 \text{ Å}$. At such a distance the strength of the ferromagnetic interaction $\Theta_1$, of the configuration Mn$^{3+}$-O-Mn$^{3+}$ with $\gamma = 180^\circ$ is only $72 \text{ (K)} \times 2/3 = 48 \text{ °K}$ (see fig. 1). To get the angle dependence of this interaction we therefore have to multiply the $\Theta$ scale of fig. 2 by a factor 48/128 or 0·38. The $\Theta_1$-values in the compounds in question then follow directly from a calculation of the interbond angles $\gamma_i$ with eq. (1). The Néel point of LaMnO$_3$ is given by the formula

$$T_N = \sum_{i=1}^{3} |\Theta_1|_i$$

and the extrapolated paramagnetic Curie temperature $\Theta$ by

$$\Theta = \sum_{i=1}^{3} (\Theta_1)_i.$$  

It is seen (table III) that the agreement is very satisfactory, except for the paramagnetic Curie temperature of the high-temperature structure of LaMnO$_3$.

In the latter structure no Jahn-Teller effect is present. We have assumed that no significant change in volume occurs at the transition towards this structure, but that only the pseudo-cell edges become much more alike. Such a behaviour is to be expected from the observed behaviour of the lattice parameters in series of mixed compounds between LaMnO$_3$ and other perovskites, the latter without a Jahn-Teller ion $^2$).

**TABLE III**

Crystallographic and magnetic data of LaMnO$_3$ and BiMnO$_3$. The observed magnetic data (from refs 2, 3, 5, 8 and 24) are compared with values derived from the distance and bond-angle dependence of the magnetic interaction in mixed perovskites $A_2(BMn)O_6$ (figs 1 and 2)

<table>
<thead>
<tr>
<th>compound</th>
<th>LaMnO$_3$</th>
<th>BiMnO$_3$ $^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature</td>
<td>300 °K</td>
<td>900 °K</td>
</tr>
<tr>
<td>pseudo-cell</td>
<td>a$' = c'$</td>
<td>3.99</td>
</tr>
<tr>
<td>dimensions</td>
<td>b$'$</td>
<td>3.845</td>
</tr>
<tr>
<td>(Å) and angles (°)</td>
<td>β$'$</td>
<td>92.1</td>
</tr>
<tr>
<td></td>
<td>a$' = \gamma'$</td>
<td>90 $^{24}$)</td>
</tr>
<tr>
<td>interbond angles (calc.) (°)</td>
<td>172, 172, 148</td>
<td>162</td>
</tr>
<tr>
<td>corresp. $\Theta_1$-values (calc.) (°K)</td>
<td>45, 45, -25</td>
<td>40</td>
</tr>
<tr>
<td>Néel temperature (calc.) (°K)</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>(obs.) (°K)</td>
<td>100 $^{8}$, 140 $^3$)</td>
<td></td>
</tr>
<tr>
<td>Curie temperature (calc.) (°K)</td>
<td>65</td>
<td>120</td>
</tr>
<tr>
<td>(obs.) (°K)</td>
<td>20-50 $^2$, 65 $^3$)</td>
<td>180-200 $^{2,8}$</td>
</tr>
</tbody>
</table>
6.3. Theoretical considerations

An extensive theoretical treatment of the magnetic interactions in transition-metal oxides has been given among others by Goodenough \(^\text{17}\). His treatment leads to the following general rules for ions in regular octahedra. The \((180^\circ)\) total superexchange between two \(d^5\) ions, having filled \(e_g\) orbitals pointing to the oxygen ion midway, is strongly antiferromagnetic; the superexchange between two \(d^3\) ions, having empty \(e_g\) orbitals pointing to the oxygen ions midway, is moderately antiferromagnetic and the superexchange between a \(d^3\) and a \(d^5\) ion, so between empty and filled \(e_g\) orbitals, is moderately ferromagnetic. If the octahedra for \(d^4\) ions were to remain completely regular, the interaction between the ions would be weakly antiferromagnetic (the arithmetic mean for electron occupancy of \(d_{z^2}\) and \(d_{x^2-y^2}\) states being used). If, however, static local Jahn-Teller distortions are present, with extreme ordering of the electrons, there are some ferromagnetic and some antiferromagnetic interactions present which, after averaging, result in effective ferromagnetic behaviour (the configurations quasi \(d^3\) - quasi \(d^5\) ion being stabilized). Finally one can assume that the Jahn-Teller deformations are not static, but only quasi-static; the electronic configurations redistribute themselves immediately according to the positions of the nuclei, which are fluctuating because of temperature motion. The result is then a ferromagnetic \(3d^4\)-anion-\(3d^4\) coupling.

Goodenough \(^\text{17}\) explains the observed ferromagnetic interactions in manganites with the latter mechanism. If applied to configurations \(\text{Mn}^{3+}\)-\(\text{O}\)-\(\text{Mn}^{3+}\) with \(\gamma = 90^\circ\), this mechanism leads to antiferromagnetic interactions. Therefore Goodenough states that somewhere in between, say \(135^\circ < \gamma_c < 150^\circ\), the \(\text{Mn}^{3+}\)-\(\text{O}\)-\(\text{Mn}^{3+}\) interaction must change from ferromagnetic to antiferromagnetic. This is confirmed by our experimental values (fig. 2); only \(\gamma_c\) lies at the borderline of the region indicated. However, our interpretation of the data of \(\text{LaMnO}_3\) differs from that given by Goodenough \(^\text{17}\). From the strong Jahn-Teller effect in \(\text{LaMnO}_3\) Goodenough in this case concluded to the presence of the second mechanism: a static Jahn-Teller distortion, leading to extreme ordering of the electrons and hence to some ferromagnetic and some antiferromagnetic interactions. However, as Kanamori’s \(^\text{18}\) analysis of \(\text{MnF}_3\) showed that the electron ordering in that compound was by no means extreme, we think that the same will hold in the case of \(\text{LaMnO}_3\). Then the deviation of the angles from \(180^\circ\) constitutes the primary effect of the occurrence of antiferromagnetic interactions, whilst a Jahn-Teller electronic ordering provides only a slight strengthening of the antiferromagnetic interaction.

The high value of the paramagnetic Curie temperature \(\Theta\) in the high-temperature structure of \(\text{LaMnO}_3\) \((T \approx 800 \text{ °K})\) is probably connected with the observed large electronic conductivity. The conductivity may be ascribed to the presence of Mn ions with deviating valency and then the Zener double-ex-
change mechanism \(^{25}\)) provides another ferromagnetic coupling between the Mn\(^{3+}\) ions, thus increasing \(\Theta\).

\[ Eindhoven, \ August \ 1966 \]

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