398 *Distortion in the Perovskite-type Structures of Lanthanon Mixed Oxides,* $LnMO_3$.

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A qualitative explanation is given of the distortion found in perovskite-type structures of the lanthanon mixed oxides with general formula $LnMO_3$. The changes in lattice symmetry which occur as the distortion increases arise mainly from the non-ideality of the radius ratios of the ions involved. The influence of partial covalent character in M–O linkages on the stabilisation of the structures is demonstrated by reference to the three series $LnAlO_3$, $LnFeO_3$, and $LnGaO_3$. The partial covalent character tends to increase as the lanthanide contraction proceeds along each series. It is most significant if the common M ions have partly filled *d* shells, when the utilisation of inner orbitals may produce an increase in polarisation energy sufficient to extend the range over which the perovskite lattice tolerates distortion. This effect occurs in the $LnFeO_3$ series and should be more pronounced in the $LnCoO_3$ series.

Perovskite-type Structures of Lanthanon Mixed Oxides.—The crystal lattice of an ideal perovskite (AMO_3) has primitive cubic symmetry with all the ions in special positions in the unit cell, *viz.*, $A = \frac{1}{2}\frac{1}{2}\frac{1}{2}$; $M = 000$; $O = \frac{1}{2}00, 0\frac{1}{2}0, 00\frac{1}{2}$. This corresponds to layers of composition $(AO_3)_n$, normal to the cube diagonals of the unit cell, arranged in the cubic order (*abcabc*-) with all octahedral holes formed by oxygen ions occupied by *n*M ions.[1] Since there are no variable parameters in the ideal lattice the non-ideality of the radius ratios and the polarisation of ions is accommodated by ***distortion*** to related lattices of lower symmetry. The limits over which the perovskite lattice can tolerate the non-ideality of ions is often specified by an empirical tolerance factor (t) derived from the geometry of the cubic cell and the radii of the ions (r), *viz.*,

$$t = (r_A + r_O)/\sqrt{2}(r_M + r_O)$$

For most perovskite-type oxides the values of t lie between about 1·1 and 0·8.

The structures of many lanthanon mixed oxides of general formula $LnMO_3$ which are of the perovskite-type have been established in some detail by the work of Geller and his co-workers.[2,3,4] The three series $LnAlO_3$, $LnFeO_3$, and $LnGaO_3$, where Ln represents a series of lanthanons and the M ions exhibit different types of electronic configuration, are of particular interest in the investigation of the factors which govern distortion. I have confirmed Geller and his co-workers' results for compounds belonging to these three series, using *X*-ray powder methods, and have established the structures of $DyAlO_3$ and $DyFeO_3$.[5] A summary of the combined data is given in Table 1. Each series shows a common pattern of distortion away from the ideal cubic lattice through rhombohedral towards orthorhombic symmetry as the lanthanide contraction proceeds. This appears to hold for all $LnMO_3$ perovskites, with the possible exception of the series $LnCoO_3$, which will be discussed later. The electronic configurations of the M ions have no apparent influence on the symmetries assumed by the distorted structures but they do influence the limits over which the perovskite lattice is stable. Thus, the lower limit of t for the $LnAlO_3$ and $LnGaO_3$ series lies in the region of 0·90 and 0·91 but extends beyond 0·85 for the $LnFeO_3$ series.

Factors which influence the Distortion.—It is convenient to discuss the factors which influence the distortion of the perovskite-type lattices of the lanthanon mixed oxides by separating that which arises from the non-ideality of the radius ratios of ions (ionic distortion) from that due to the partial covalent character of M–O linkages (covalent distortion).

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[1] Wells, " Structural Inorganic Chemistry," Oxford Univ. Press, 1950.

[2] Geller, *J. Chem. Phys.*, 1956, **24**, 1236.

[3] Geller *et al.*, *Acta Cryst.*, 1956, **9**, 563, 1019; 1957, **10**, 161, 234.

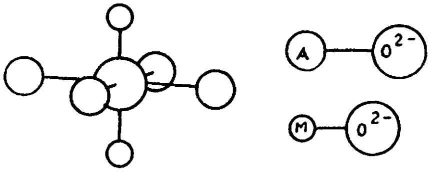
[4] Reimeika, *J. Amer. Chem. Soc.*, 1956, **78**, 4259.

[5] Dalziel and Welch, *Acta Cryst.*, in the press.

Other factors, such as the partial covalent character of Ln–O linkages, will be neglected in the discussion which is therefore approximate. This method of treatment is related to that used by Megaw [6,7] for the $A^{I}M^{V}O_3$ and $A^{II}M^{IV}O_3$ subgroups of the perovskites.

According to Megaw the symmetry assumed by $A^{I}M^{V}O_3$ and $A^{II}M^{IV}O_3$ perovskites is largely dependent upon the partial covalent character of their M–O linkages, *i.e.*, covalent distortion. In the $LnMO_3$ subgroup of the perovskites covalent distortion should be less important. This follows from the reduced " electrostatic bond strengths " in the M–O linkages and the more symmetrical cationic charge distribution around the oxygen ions in $LnMO_3$ perovskites, as shown in Fig. 1. That the polarisation of the oxygen ions in the nearly cubic structure of $LaAlO_3$ is smaller than in the cubic $A^{II}M^{IV}O_3$ perovskites is demonstrated by the following argument. A cubic perovskite lattice irrespective of polarisation must satisfy the geometrical relationship: $(r_A + r_O)/\sqrt{2} = (r_B + r_O) = a/2$, where (a) is the length of the unit-cell edge. The values of the oxygen-ion radius can then be derived in two ways, *viz.*, $r_O = a/2 - r_B$ or $r_O = (a/\sqrt{2}) - r_A$. Since smaller cations will tend to be less deformed by polarisation than larger anions, the substitution of spherical values for the cationic radii in these equations to obtain numerical values for r_O is justified to an approximation. The values of r_O for $LaAlO_3$ and the cubic $A^{II}M^{IV}O_3$ perovskites,[8] derived in this way, are shown in Table 2. The cationic radii used [9] have been corrected in the case of A and Ln ions for twelve-fold co-ordination. The data in the table show in particular that the oxygen ions in $LaAlO_3$ are nearly spherical and therefore are not polarised. This contrasts markedly with the case of $A^{II}M^{IV}O_3$ perovskites.

FIG. 1. *Asymmetry of cationic charge distribution around oxygen ions in the perovskite lattice and change in electrostatic bond strengths in different subgroups.*



Electrostatic bond strengths

$A^{I}M^{V}O_3$	$A^{II}M^{IV}O_3$	$Ln^{III}M^{III}O_3$
$\frac{1}{12}$	$\frac{1}{6}$	$\frac{1}{4}$
$\frac{5}{6}$	$\frac{2}{3}$	$\frac{1}{2}$

TABLE 1. *Summary of crystallographic data for perovskite-type lanthanon mixed oxides* $LnAlO_3$, $LnFeO_3$, *and* $LnGaO_3$, *where* Ln = La, Nd, Gd, *and* Dy.

Mixed oxide	Space lattice	*Z*	Cell dimensions (Å) *a*	*b*	*c*	*V*	Space group	Transitions
$LaAlO_3$	Rhombohedral	2	5·357 α = 60·10°			54·5	*R*$\bar{3}$*m*	Cubic above 435° c
$NdAlO_3$	Rhombohedral	2	5·286 α = 60·41°			52·7	*R*$\bar{3}$*m*	
$GdAlO_3$	Orthorhombic	4	5·247	5·304	7·447	51·8	*Pbnm*	
$DyAlO_3$	Orthorhombic	4	5·215	5·311	7·407	51·3	*Pbnm*(?)	
$LaFeO_3$	Orthorhombic	4	5·556	5·565	7·862	60·8	*Pbnm*	Rhombohedral above 980°c
$NdFeO_3$	Orthorhombic	4	5·441	5·573	7·753	58·8	*Pbnm*	
$GdFeO_3$	Orthorhombic	4	5·346	5·616	7·668	57·6	*Pbnm*	
$DyFeO_3$	Orthorhombic	4	5·304	5·600	7·621	56·6	*Pbnm*(?)	
$LaGaO_3$	Orthorhombic	4	5·496	5·524	7·787	59·2	*Pbnm*	Rhombohedral above 875° c
$NdGaO_3$	Orthorhombic	4	5·426	5·502	7·706	57·5	*Pbnm*	
" $GdBaO_3$ "	Garnet phase							
" $DyGaO_3$ "	Garnet phase							

Z = number of formula weights per unit cell.
V = volume occupied by one formula weight (Å³).

It is concluded that the least distorted $LnMO_3$ perovskites have structures which are

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[6] Megaw, *Acta Cryst.*, 1952, **5**, 739; 1954, **7**, 187.

[7] Megaw, " Ferroelectricity in Crystals," Methuen, London, 1957.

[8] Megaw, *Proc. Phys. Soc.*, 1946, **58**, 133.

[9] Ahrens, *Geochim. Cosmochim. Acta*, 1952, **2**, 155.

dependent primarily upon the effects of ionic distortion on the ideal lattice. As the lanthanide contraction proceeds along a series the distortion increases and the volumes occupied by the formula weights exhibit a regular decrease (Table 1). The significance of

TABLE 2. *Values for the radii of the oxygen ions calculated from the dimensions of cubic perovskites.*

	r_O (Å)			r_O (Å)	
$A^{II}M^{IV}O_3$	from $r_B + r_O$	from $r_A + r_O$	$LnBO_3$	from $r_B + r_O$	from $r_A + r_O$
$SrTiO_3$	1·27	1·54	$LaAlO_3$	1·39	1·44
$SrZrO_3$	1·26	1·67	($NdAlO_3$	1·37	1·41)
$SrSnO_3$	1·30	1·62	($LaFeO_3$	1·32	1·53)
$BaSnO_3$	1·34	1·44			
$BaZrO_3$	1·30	1·50			

the relative decreases in the different series will be considered in more detail later; a decrease in the volume occupied by a formula weight will tend to increase the polarisation of the ions. Hence, covalent distortion will tend to increase as the lanthanide contraction proceeds along each series. Now an estimate of the relative importance of ionic and covalent distortion can be made by the consideration of (*a*) the extent to which increases in ionic distortion can produce the observed changes from cubic through rhombohedral to orthorhombic symmetry in the perovskite lattice, and (*b*) the extent to which covalent distortion is present in the representative series $LnAlO_3$, $LnFeO_3$, and $LnGaO_3$.

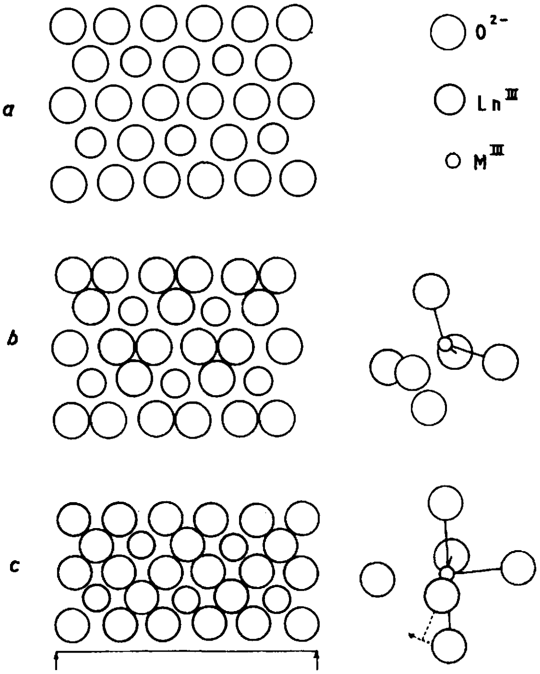

FIG. 2. $(LnO_3)_n$ *Layers with* r_{Ln}/r_O *less than unity, and octahedral sites for* M *ions when layers are arranged in the order abcabc-.*

a. Regular layer of $R\bar{3}m$, $Z = 1$ lattice.

b. Less regular rearrangement (projection on rhombohedral (111) plane and quasi-sp^2 environment of M ions.

c. Layer of *Pmmm*, $Z = 2$ lattice, derived by compression from 2*a* [projection on orthorhombic (101) plane] and quasi-sp^3 environment of M ions.

Ionic Distortion.—In the purely ionic distortion of the perovskite lattice the ions must be represented as rigid spheres, since their deformation would represent covalent distortion. When such ions are formed into $(LnO_3)_n$ layers in the ideal way they are not close-packed if the radius ratio r_{Ln}/r_O is less than unity. Moreover, if the ideal lattice is made from the cubic arrangement of these layers no more than four oxygen ions make contact with each Ln ion. Thus, when r_{Ln}/r_O is less than unity this ideal arrangement is unstable with respect to a less symmetrical one which brings more oxygen ions into contact with each Ln ion and hence increases the coulombic lattice energy.

Such an arrangement occurs when the perovskite lattice assumes rhombohedral symmetry. Megaw [6] has described how the rhombohedral lattice is produced when a force of compression acts parallel to one cube diagonal of the ideal lattice. This brings the $(LnO_3)_n$ layers which are normal to the force closer together, until each Ln ion is in contact with the six oxygen ions of the neighbouring layers. To do this without deforming the oxygen ions the layers which are normal to the force of compression must be opened out. The most regular way of doing this for one $(LnO_3)_n$ layer is shown in Fig. 2*a*. When such layers are arranged in the order *abcabc-* and *n* M ions are placed in the unsymmetrical octahedral sites available, a rhombohedral lattice ($R\bar{3}m$, $Z = 1$) is obtained which is rather more symmetrical than those found for $LnMO_3$ perovskites with rhombohedral distortion. Rhombohedral lattices of lower symmetry can be formed by purely ionic distortion if a less regular arrangement occurs in the layers. Thus, when $(LnO_3)_n$ layers of the kind shown in Fig. 2*b* are arranged, as before, in the order *abcabc-* the rhombohedral unit cell is no longer perfectly centrosymmetrical. It is of interest because the lattice contains octahedral holes, shown in Fig. 2*b*, which would tend to be compatible with sp^2 hybrid character in the M–O linkage. According to Geller and his co-workers the rhombohedral $LnMO_3$ perovskites have two formula weights in their unit cells. Lattices of this kind require a repeating pattern of six layers and a less regular arrangement must occur within the layers. Layers of the kind shown in Fig. 2*b* can be arranged in a six-fold repeating pattern *ab′ca′bc′-*, where the three layers denoted by primes have been turned so that their groups of oxygen ions " point " in the opposite direction from those in the other three layers. This arrangement produces a lattice which contains two kinds of octahedral hole for occupation by M-type ions and is unsatisfactory from this point of view. No more satisfactory arrangement of layers to give a six-fold repeating pattern has been found. However, the lattices of the rhombohedral $LnMO_3$ perovskites are sufficiently close to these lattice models to make it reasonable to conclude that their distortion arises mainly from the non-ideality of the radius ratios of the ions involved. Some confirmation that the distortion is essentially ionic is provided by the observation [3] that the transition from rhombohedral to cubic $LaAlO_3$ is a higher than first-order change. The transition of the related structure of nickel oxide, which is from rhombohedral to cubic symmetry by a higher than first-order change, has also been attributed to the non-ideality of the ionic radii.[10]

Similarly orthorhombic symmetry is produced by ionic distortion as the radius ratio r_{Ln}/r_O departs further from unity. An orthorhombic lattice is formed when a force of compression is allowed to act parallel to a face diagonal of the cubic cell.[6] This force can be resolved into the rhombohedral force of compression and an additional force which acts in the plane of the layers. A layer which has been derived in this way from Fig. 2*a* is shown in Fig. 2*c*. The octahedral holes available for M-type ions when these layers are arranged in the order *abcabc-* would tend to be compatible with sp^3 hybrid character in M–O linkage if they are slightly modified, as shown in Fig. 2*c*. The space-group symmetry of the orthorhombic lattice is *Pmmm*, $Z = 2$. This is the holosymmetrical space-group from which it should be possible to derive *Pbnm*, $Z = 4$, which has been reported by Geller [2] for $GdFeO_3$ and other orthorhombic perovskites, if a repeating pattern of six less regular $(LnO_3)_n$ layers is used. Thus, it appears that the orthorhombic symmetry found in the more distorted $LnMO_3$ perovskite lattices is not inconsistent with the increased non-ideality of the radius ratios of the ions involved. That orthorhombic symmetry occurs commonly, irrespective of the electronic configuration of the M-type ions involved, tends to support the view that ionic distortion is important even in the most distorted $LnMO_3$ perovskites. However, there is evidence that covalent distortion also is present to a significant extent in at least some orthorhombic lattices.

Covalent Distortion.—If the lattices of a series of $LnMO_3$ perovskites with the M ions in common are all essentially ionic in character, the volumes occupied by their formula

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[10] Rooksby, *Acta Cryst.*, 1948, **1**, 226.

weights should decrease as the lanthanide contraction proceeds along the series, but to a smaller extent than would be predicted from the decreases in the volumes of the lanthanon ions alone, because the packing deviates increasingly from close-packing. The relative ionic character in the different series can therefore be tested by a plot of the volumes occupied by one formula weight against those occupied by the respective lanthanon ions in twelve-fold co-ordination. Fig. 3 shows plots of V_{Ln} against V_{LnMO_3} (full lines) and against $V_{LaMO_3}-(V_{La}-V_{Ln})$ (broken lines) for the three series $LnAlO_3$, $LnFeO_3$, and $LnGaO_3$. The deviation between full and broken curves is in the direction expected for ionic distortion only for the $LnAlO_3$ and $LnGaO_3$ series; it is reversed for the $LnFeO_3$ series. This is positive evidence that the increase in polarisation energy, *i.e.*, covalent distortion, in the $LnFeO_3$ series is of a different order of magnitude from that in the other two series and is sufficient to overcome the non-ideality of ionic packing in the more distorted lattices. The larger increase in the polarisation energy, which will tend to stabilise the perovskite lattice, accounts for the lower limit of t in the $LnFeO_3$ series.

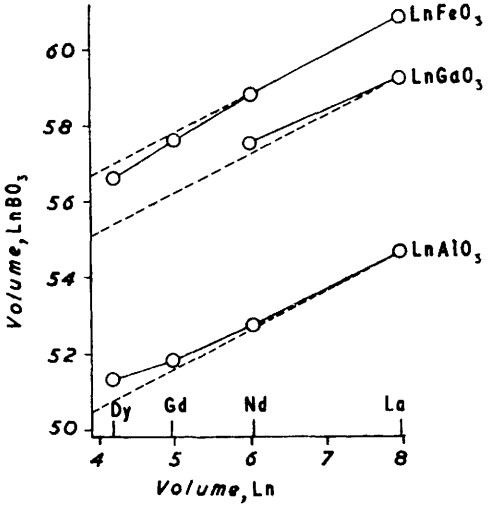

FIG. 3. *Relationships between the volumes of formula weights of* $LnMO_3$ *perovskites and the volumes of their lanthanon ions (full lines) compared with* $V_{LaMO_3}-(V_{La}-V_{Ln})$ *(broken lines) in* Å^3.

Significant partial covalent character in M–O linkages would also account for the observation that transitions from orthorhombic to rhombohedral symmetry may be first-order changes.[3]

The reason for the differences between the polarisation energies in series of $LnMO_3$ perovskites can be understood when the atomic orbitals of the M ions, which can be utilised in the formation of partial-covalent M–O linkages, are considered. The tervalent ions of aluminium, iron, and gallium, which have an inert-gas, a half-filled *d* shell, and an eighteen-electron configuration respectively, have been chosen as representative M ions from this point of view. If the polarisation energy in a perovskite lattice is small the M ions are subjected to a relatively weak electrostatic crystal-field effect.[11] In this case all types of M ion, irrespective of their electronic configurations, will tend to utilise their outer atomic orbitals and M–O linkages with relatively weak partial covalent character will be formed. It is reasonable to suppose that the outer sp^2 and sp^3 hybrid orbitals will be utilised successively as the lanthanide contraction proceeds along any series. Already, it has been seen that sp^2 and sp^3 hybrid character in M–O linkages would tend to be nearly compatible with rhombohedral and orthorhombic distortion respectively. The utilisation of these outer hybrid orbitals therefore should not produce appreciable changes in the symmetry of perovskite lattices which are subjected primarily to ionic distortion, as described above. However, if outer orbitals only are involved in the formation of M–O linkages Goodenough

[11] Gillespie and Nyholm, *Quart. Rev.*, 1957, **11**, 339.

and Loeb[12] consider that partial covalent character should increase in the order Al < Fe < Ga. This is not in accordance with the trends shown in Fig. 3 although it provides a reason for the observed tendency of gallium ions to favour tetrahedral co-ordination with oxygen ions in the ready formation of garnet phases. The discordance is removed if it is assumed that in the $LnFeO_3$ series the larger increase in polarisation energy arises by the interaction of the ferric ions with a relatively strong electrostatic crystal field. Then the inner orbitals of the ferric ions can be utilised in the formation of Fe–O linkages with significant partial covalent character. The configuration of the ferric ion will alter from its spin-free state ($d_\epsilon^3 d_\gamma^2$) towards the spin-paired state ($d_\epsilon^5 d_\gamma^0$) as the lanthanide contraction proceeds and the d_γ orbitals can then be utilised, probably for the formation of $d_\gamma^2 sp^3$ hybrid orbitals. The utilisation of inner orbitals by tervalent first-row transition metal ions should be most pronounced in the case of cobalt.[13] In the series $LnCoO_3$ it would be expected that, as the polarisation energy increases along the series, there should be a large tendency to form symmetrical octahedral Co–O linkages with appreciable covalent character. This effect might even be sufficient to act as a restorative force and reduce the distortion of the perovskite lattice as the lanthanide contraction proceeds. It is significant therefore that the distortion in the $LnCoO_3$ series is anomalous; the rhombohedral distortion in $LaCoO_3$ is reported[14] to decrease as the lanthanide contraction proceeds until at $SmCoO_3$ the perovskite lattice is nearly cubic.[15]

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[12] Goodenough and Loeb, *Phys. Rev.*, 1955, **98**, 391.
[13] Griffith and Orgel, *Quart. Rev.*, 1957, **11**, 381.
[14] Wold, Post, and Banks, *J. Amer. Chem. Soc.*, 1957, **79**, 6365.
[15] Wold and Ward, *J. Amer. Chem. Soc.*, 1954, **76**, 6060.