Acta Cryst. (1957). **10**, 243

Crystallographic Studies of Perovskite-Like Compounds. IV. Rare Earth Scandates, Vanadites, Galliates, Orthochromites*

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(*Received* 22 *August* 1956 *and in revised form* 29 *October* 1956)

Several scandates, vanadites, galliates and orthochromites of several of the rare earth elements and yttrium are isostructural with $GdFeO_3$. The paper includes a summary discussion of the compounds so far studied in this series of papers. Particular emphasis is given the transitions which have been observed and the relations existing among the various compounds and among the three structural types to which they belong.

Transition from the orthorhombic (*Pbnm*) to the rhombohedral ($R\bar{3}m$) structure has been found in $SmAlO_3$; thus the link to the ideal structure is through the rhombohedral. It is predicted that most of the orthorhombic compounds will not transform to the rhombohedral, and probably only one of the rhombohedral to the cubic structure.

Introduction

The work previously reported by us (Geller, 1956; Geller & Wood (I), 1956; Geller & Bala (II), 1956; Gilleo (III), 1957), together with the present work, presents an integrated picture of the structural relationships existing among these compounds. All of the compounds thus far studied in detail fall into one of two groups:† most of them are isostructural with $GdFeO_3$ (Geller, 1956), i.e. they belong to space group D_{2h}^{16}–*Pbnm* with four distorted perovskite units in the true crystallographic cell; three aluminates (Nd^{3+}, Pr^{3+}, La^{3+}) belong to space group D_{3d}^{5}–$R\bar{3}m$ with two formula units per unit cell (II).

Searches for crystallographic transitions in these systems have been made by three methods: P. D. Garn, of these Laboratories, has looked for them using differential thermal analysis; high-temperature X-ray powder photography has been employed; optical investigations have been made. By these means it has definitely been established that the orthorhombic structure may in some cases transform to the rhombohedral and the rhombohedral to the simple cubic (ideal perovskite) structure.

The additional results in this paper pertain mainly to the orthochromites, scandates, galliates and vanadites of some of the trivalent rare earths and of yttrium. A paper by Bertaut & Forrat (1956), published just previous to the writing of this paper, includes results on some of the compounds (orthochromites and vanadites) reported here. The results of our work on these compounds are nevertheless included herein, particularly because there are some important differences in the conclusions of the two studies.

Crystallographic data

Powder photographs were taken of all the compounds with Cr *K* radiation. By comparison with the diffraction data from the orthoferrites (I) and aluminates (II), and by studying the relationships of the diffraction data from the crystals described herein, all of the photographs were indexed on the orthorhombic cell with the lattice constants given in Table 1. Because there was some doubt about the structure of $LaGaO_3$, a single (though multiply twinned) crystal was ground down to a thickness of about 0·2 mm. and photographed with a Buerger precession camera using Mo*K* radiation, which, together with optical examination, established that the crystals are orthorhombic.

Some of the powder photographs were a little more difficult to measure than others: on some there was much overlapping or near overlapping of many lines (e.g. $PrGaO_3$ and $LaGaO_3$); it was difficult to get a really high-grade photograph of one or two of the compounds ($SmCrO_3$, for example). However, the results are consistent and permit us to draw some important conclusions from them.

Crystallographic data on the scandates, vanadites, galliates and orthochromites are given in Table 1. The rare earths we have used include Gd, Sm, Nd, Pr, and La. We have not investigated all of the scandates, vanadites, galliates and orthochromites of these elements. However, by examination of all the papers in the series, it should be possible to predict the lattice constants of missing members to within 0·01 Å: for example, $EuCrO_3$ should have the lattice constants $a = 5{\cdot}34$, $b = 5{\cdot}51$, $c = 7{\cdot}63$ Å.

In the case of the galliates, compounds of Gd, Sm

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* These names are used for convenience and should not imply the presence of discrete complex ions.

† Although stoichiometric $LaMnO_3$ appears to be isostructural with $GdFeO_3$ there is at least one aspect of that crystal which requires making a reservation concerning it (see III).

Table 1. *Crystallographic data on rare earth scandates, vanadites, galliates, orthochromites*

Compound	Lattice constants			Vol. per unit cell (Å^3)	X-ray density (g.cm.$^{-3}$)	Pseudo-cell dimensions			Minimum average interionic distances (Å)		
	a (Å)	b (Å)	c (Å)			a(=c) (Å)	b (Å)	β (°)	A^{3+}–A^{3+}	A^{3+}–O^{2-}	B^{3+}–O^{2-}
$GdScO_3$	5·487	5·756	7·925	250·3	6·63	3·976	3·963	92·7	3·970	2·807	1·985
$NdScO_3$	5·574	5·771	7·998	257·3	6·13	4·012	3·999	92·0	4·007	2·833	2·003
$PrScO_3$	5·615	5·776	8·027	260·3	5·97	4·029	4·014	91·6	4·023	2·846	2·012
$LaScO_3$	5·678	5·787	8·098	266·1	5·79	4·054	4·049	91·1	4·052	2·865	2·026
$YScO_3$	5·431	5·712	7·894	244·9	4·94	3·941	3·947	92·9	3·941	2·787	1·971
$GdVO_3$	5·345	5·623	7·638	229·6	7·40	3·879	3·819	92·9	3·857	2·728	1·929
$NdVO_3$	5·440	5·589	7·733	235·1	6·87	3·900	3·867	91·6	3·888	2·749	1·944
$PrVO_3$	5·477	5·545	7·759	235·6	6·70	3·892	3·880	90·7	3·891	2·751	1·946
$NdGaO_3$	5·426	5·502	7·706	230·1	7·56	3·864	3·853	91·0	3·860	2·729	1·930
$PrGaO_3$	5·465	5·495	7·729	232·1	7·40	3·875	3·865	90·3	3·871	2·737	1·936
$LaGaO_3$	5·496	5·524	7·787	236·4	7·21	3·896	3·894	90·3	3·895	2·754	1·948
$GdCrO_3$	5·312	5·514	7·611	222·9	7·65	3·828	3·806	92·1	3·820	2·701	1·910
$SmCrO_3$	5·372	5·502	7·650	225·9	7·37	3·884	3·825	91·4	3·837	2·714	1·919
$NdCrO_3$	5·412	5·494	7·695	228·8	7·09	3·856	3·848	90·9	3·853	2·724	1·927
$PrCrO_3$	5·444	5·484	7·710	230·2	6·95	3·864	3·855	90·4	3·861	2·730	1·930
$LaCrO_3$	5·477	5·514	7·755	234·2	6·77	3·886	3·878	90·4	3·883	2·746	1·942
$YCrO_3$	5·247	5·518	7·540	218·3	5·75	3·807	3·770	92·9	3·793	2·682	1·897

Table 2. *High-temperature data on* $SmAlO_3$ *and* $LaGaO_3$

Compound	Temp. (°C.)	Simplest cell		Vol./simplest unit cell	Pseudo-cell dimensions*	
		a	α		a	α
$SmAlO_3$	850	5·316 Å	60° 19′	107·2 Å^3	3·768 Å	90° 16′
$LaGaO_3$	900	5·544 Å	60° 25′	121·6 Å^3	3·933 Å	90° 22′

* The face-centered rhombohedral cell has the cell edge $2a$ and the same angle α.

and Y made by Remeika (1956) do not have the orthorhombic structure of $GdFeO_3$. Variations on Remeika's method and solid–solid reaction did not yield compounds isostructural with $GdFeO_3$. Two different phases were found in these various trials; one of these, the garnet type, is that found by Keith & Roy (1954), whose paper will be discussed later.

Samarium vanadite is isostructural with $GdFeO_3$, but its lattice constants have not been included because the Sm_2O_3 employed was found to contain a substantial Y impurity.

It has now been established that orthorhombic $SmAlO_3$ and $LaGaO_3$ transform to the rhombohedral at 800° C. and 875° C. respectively. The transition temperatures were found by P. D. Garn by differential thermal analysis. Powder photographs taken with a high-temperature camera (designed and built by W. L. Bond) using Cu *K* radiation at temperatures of 850° C. and 900° C. establish the transition of these two compounds from the orthorhombic to the rhombohedral. The lattice constants of the rhombohedral phases are given in Table 2.

Discussion

The relationship of these compounds to the ideal perovskite (i.e. single formula unit cubic) is elucidated in this series of papers in two ways: by the detailed structure analysis of $GdFeO_3$ (Geller, 1956; I) and of $La(Co_{0.2}Mn_{0.8})O_3$ (Gilleo, 1957); by a study of crystallographic transitions at elevated temperatures which has linked the orthorhombic ($GdFeO_3$ type) to the ideal perovskite through the rhombohedral ($LaAlO_3$ type) structure.

Crystallographic transitions

In the rhombohedral structures (II) the deviations of positions of the O^{2-} ions from the ideal are substantial, but one can see the mechanism by which this structure may go toward the ideal cubic as the temperature is increased. However, the mechanism by which the orthorhombic transforms to the rhombohedral structure is apparently quite complicated. Attempts to clarify this mechanism by studying the geometric transformations of atomic coordinates from the orthorhombic to the primitive rhombohedral lattice have not proved fruitful. From this study one arrives at the conclusion that the transition should be of first order.[*] This was already indicated by Garn's

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[*] In the transition from orthorhombic to rhombohedral the 12 oxygen ions in the former go into two equivalent sets of six equivalent ions in the latter. Four of these come from the eightfold O^{2-} ions and two from the fourfold. These must move at very different rates. In fact, the equivalent sets of four from the eightfold positions must move at very different rates in going to the rhombohedral structure. Consequently the change of symmetry cannot be brought about smoothly.

observations of large endothermic changes for the $SmAlO_3$ and $LaGaO_3$ transitions and no detection of a transition in $LaAlO_3$.

From X-ray and differential thermal analysis we know that the compounds $SmAlO_3$ and $LaGaO_3$ transform to the rhombohedral. A transition temperature of $LaFeO_3$ has also been determined by differential thermal analysis, and it is highly probable that $LaFeO_3$ also goes rhombohedral. The transition temperatures increase in the order $SmAlO_3$, $LaGaO_3$, $LaFeO_3$, despite the fact that the $LaGaO_3$ lattice constants are more distorted from ideal (i.e. $a = b = c/\sqrt{2}$) than are those of $LaFeO_3$. Without having carried out these experiments it might also have erroneously been predicted that the orthorhombic crystals would transform directly to the simple cubic ideal structure.* Obviously, it is important to consider the atomic positions. It may be said that when the positions of the A^{3+} ions are substantially different from ideal (as, for example, in $GdFeO_3$) the lattice constants will also be substantially different from the ideal relationship, and conversely. (The eightfold oxygen ion coordinates in $GdFeO_3$ are not very different from those in $La(Co_{0\cdot2}Mn_{0\cdot8})O_3$ (III), which is one of the least distorted orthorhombic structures, but there is substantial difference in coordinates of the A^{3+} ions.†) However, it appears that when the lattice constants of several of the compounds are close to the ideal dimensions, the nearness to the transition may not be judged from the relative departure of the dimensions from ideal, but only from a knowledge of the atomic coordinates. This knowledge need be only relative to a particular compound. That is, we knew that $LaFeO_3$ did not transform until 980° C. (I); however, from examination of the aluminates (II) it seemed that $SmAlO_3$ should transform at a lower temperature. This is so not because the dimensions of $SmAlO_3$ are so very much closer to ideal, but rather because the intensities of the 'superstructure' lines in the $SmAlO_3$ photographs are relatively lower than in $LaFeO_3$ photographs (i.e. lines with $(h+k)$ odd or l odd relative to lines with $(h+k)$ and l even). The case of $LaGaO_3$ is more striking because the $LaGaO_3$ cell is definitely more distorted from ideal dimensions than is the $LaFeO_3$ cell. However, as indicated earlier, the $LaGaO_3$ transforms to the rhombohedral at 875° C. An examination of $LaGaO_3$ photographs leads to the conclusion that the La^{3+} ions, at least, are closer to the ideal positions in $LaGaO_3$ than in $LaFeO_3$.

From comparison of the structures of $GdFeO_3$ and $La(Co_{0\cdot2}Mn_{0\cdot8})O_3$ it appears that the eightfold oxygen ions do not rapidly approach the ideal positions as the cell approaches ideal dimensions. However, in a given series of $A^{3+}B^{3+}O_3^{2-}$ compounds with constant B^{3+} ion, the A^{3+} ions definitely approach the ideal positions as the cell approaches ideal dimensions (i.e. as the A^{3+} ion gets larger) and apparently faster in the galliates than in the orthoferrites. One may say that this approach to the ideal positions is in the right direction for the transition to the rhombohedral structure because the ions in positions $4(c)$ of $Pbnm$ must transform to positions $2(c)$: $\pm(x, x, x)$ of $R\bar{3}m$. The oxygen ions, however, all transform to positions $6(h)$: $\pm(x, x, z; \circlearrowleft)$ of $R\bar{3}m$ and it is not impossible that they are already favorably disposed toward the transition even when the pseudo-cell angle is close to 93°.

The compounds described in this series seem to have roughly the same coefficients of volume expansion. A few examples are given in Table 3. It may be seen that these compounds expand (in volume) about 3% in the first 900° C.

Table 3. *Volumes per formula unit at different temperatures of some of the perovskite-like compounds*

Compound	Vol./formula unit (Å^3)	Temp. (°C.)	Expansion between given temperatures (%)	α_p
$SmAlO_3$	52·2	25	2·7	—
	53·6	850		60° 19′
$PrAlO_3$	53·3	25	2·8	60° 20′
	54·8	950		60° 10′
$LaAlO_3$	54·5	25	2·2	60° 6′
	55·7	650		60°
$LaGaO_3$	59·1	25	2·9	—
	60·8	900		60° 25′

Examination of Fig. 2 of II indicates that there is a slight increase in expansion rate beyond the transition in $LaAlO_3$. But let us suppose that the expansion rate is uniform. At 850° C., the rhombohedral angle α_p for $SmAlO_3$ is 60° 19′, about the same as for $PrAlO_3$ at room temperature. There is a change of about 10′ for 900° C. of temperature increase. Thus, if the melting point of $PrAlO_3$ is greater than 1800° C., we might expect that $PrAlO_3$ would become cubic at that temperature. We would also expect the volume per formula unit of $PrAlO_3$ to be about 56·3 Å^3, which is considerably larger than the volume per formula unit of $LaAlO_3$ when it becomes cubic, i.e. 55·2 Å^3. By this same reasoning, if $SmAlO_3$ became cubic below its melting point (which is doubtful because it would become cubic at about 2700° C.*), its volume at the transition would be greater than that of the $PrAlO_3$ cell.

As the temperature increases the effective sizes of all the atoms increase, but it would seem that the ratio

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* It should be noted that there is more 'line-splitting' in the rhombohedral $SmAlO_3$ and $LaGaO_3$ photographs than in those of the orthorhombic phases. This may be seen adequately by comparing the patterns of the orthorhombic with the rhombohedral aluminates in Table 1 of II.

† The positions of the fourfold oxygen ions are known with least accuracy.

* It should be stressed that the deduction of these temperatures is understood to be speculative.

of the effective radii of the A^{3+} to B^{3+} ions also increases with increasing temperature. The rate of increase of this ratio seems to be about the same for all of these compounds. Thus, considering a series of these compounds with constant B^{3+} ion, if particular compounds transform to cubic, the size of the rare earth ions will be in inverse order to that at room temperature. Again this shows the important effect that the B^{3+} ion has on the apparent size of the A^{3+} ion, e.g. cubicity is not attained by $PrAlO_3$ when the apparent size of the Pr^{3+} ion reaches that of the La^{3+} ion in cubic $LaAlO_3$ at its transition, because at that point in $PrAlO_3$ the Al^{3+} ion is still too large.

It may also be concluded from the foregoing reasoning and examination of the results of the papers of this series that most of the orthorhombic compounds will not transform to the rhombohedral and that it is probable that only the $LaAlO_3$ transforms to the cubic, although there is a possibility that $PrAlO_3$ may also.

Cell-constant relationships

The trends shown by the lattice constants in a series with constant B^{3+} ion are noteworthy. In the series of orthorhombic structures in the direction Y, Gd to La one finds: (1) The lengths of the *a* axes all increase in this direction. (2) The *b* axes show little variation in length, the largest being for the orthoferrites. (3) In all cases except that of the scandates the *b* axes decrease in length in this direction, although there are a few oscillations. In two cases, the galliates and orthochromites, there is an upturn of the *b*-axial length, amounting to 0·03 Å, from the Pr to the La compounds. An error in lattice-constant determination as large as this is hardly to be expected. The *b* axis of $YFeO_3$ is 0·03 Å shorter than the *b* axis of $GdFeO_3$. (4) All of the *c* axes increase in length in this direction.

Considering series of compounds with constant A^{3+} ion and varying B^{3+} ion, one finds that all the lattice constants and the volumes per formula unit decrease in the following order, Sc, Fe, V, Ga, Cr, Al, with two exceptions: the *b* axial lengths of $GdVO_3$ and $NdVO_3$ are longer than those of the corresponding orthoferrites.

With regard to the pseudo-cell dimensions of the orthorhombic compounds, one sees some striking similiarities as well as differences among the different series. Again, taking the order Y, Gd to La in the orthoferrites, one observes that *a* approaches *b* in length while the β angle approaches 90°. The differences between *a* and *b* lengths and the β angles are:

	Pseudo-cell $\|a-b\|$ (Å)	β (°)
$YFeO_3$	0·041	93·0
$GdFeO_3$	0·043	92·8
$EuFeO_3$	0·041	92·5
$SmFeO_3$	0·029	92·0
$NdFeO_3$	0·018	91·4
$PrFeO_3$	0·007	90·8
$LaFeO_3$	0·001	90·2

As $|a-b|$ of the pseudo-cell approaches zero in the above series, the length of the orthorhombic *a* axis approaches that of the *b* axis, which approaches $c/\sqrt{2}$.

In every case but one the pseudo-cell *a* axis is greater than the pseudo-cell *b* axis. The exception is $YScO_3$ (see Table 1), in which case this may be a result of error in lattice-constant determination. But one sees that the trend in the scandates is not the same as in the orthoferrites. The orthochromites and aluminates, for the most part, show the same trend as the orthoferrites. Because the Cr^{3+} ion is substantially smaller than the Fe^{3+} ion, the pseudo-cells of the orthochromites are nearer cubic dimensions than are those of the orthoferrites. This is even more the case in the aluminates; indeed in that series we find the existence of a group of rhombohedral compounds which we know bear a closer relationship to the ideal cubic structure than does the orthorhombic structure.

Purity of the compounds

Some discussion of purity of compounds was given in II. Ultimate analyses were made on the orthoferrites and are reported by Remeika (1956). Semi-quantitative spectroscopic analyses were made on several of the compounds to assure us of the absence of significant amounts of impurity. Furthermore, the trend of the lattice constants indicates that any impurities present have an insignificant effect. (As was pointed out earlier, we have omitted $SmVO_3$ from Table 1 because we know of the presence of a significant amount of Y impurity in it.) The presence of significant amounts of impurity A^{3+} or B^{3+} ions would have the effect of altering lattice constants, transition temperatures and other physical properties. In some cases it would of course alter structure: for example, the appropriate amount of La^{3+} substituted for Sm^{3+} should push the structure from the orthorhombic to the rhombohedral. The effect on $LaMnO_3$ of substituting some Co^{3+} for Mn^{3+} is shown in III. It has also been shown in I and II (and will be discussed further later) that compounds made by other investigators by different methods (and often without mention of purity), which have the same formula as some of those in this series, really have (when the photographs are indexed properly) very nearly the same lattice constants as those reported in this series.

Previous work

It is well known that in the past thirty years, a large amount of work has gone into the investigation of the perovskite-like compounds. Some of this work has been mentioned in I and II. Whereas we cannot hope to give an exhaustive discussion of the work of others on the same compounds as described in this series, we hope that we shall have covered most of it.

Jonker & van Santen (1950), in a paper devoted mainly to the study of ferromagnetism of compounds containing manganese, also discussed $LaAlO_3$, $LaCrO_3$ and $LaFeO_3$. They call these nearly cubic with 'average unit-cell edges' of 3·78, 3·88 and 3·89 Å respectively. These compare well with our idealized cell edges 3·79, 3·88 and 3·93 Å respectively, except for the $LaFeO_3$ value.

Náray-Szabó's (1947) work in connection with the orthoferrites and aluminates was discussed in I and II. He also investigated $LaCrO_3$ and $LaGaO_3$ and considered both of these to be cubic with cell edges 3·88 and 3·89 kX. (probably). These compare very well with our idealized cell values of 3·88 and 3·895 Å, but it is very improbable that the compounds examined by Náray-Szabó were cubic if they had the composition stated.

Yakel's (1955) work on $LaFeO_3$ and $LaMnO_3$ were discussed to some extent in I and III respectively. Yakel has also examined a $SmCrO_3$ which he claims is unrelated to perovskite. As seen in Table 1, our $SmCrO_3$ fits into the series of orthochromites very nicely. We have not, however, attempted to make the compound by solid–solid reaction. Yakel reports that $LaCrO_3$ is either monoclinic with $a = c = 7{\cdot}777$, $b = 7{\cdot}750$ Å, $\beta = 90^\circ 15'$ or orthorhombic with $a = 11{\cdot}022$, $b = 7{\cdot}750$, $c = 10{\cdot}975$ Å, but states also that but for a few weak reflections the a and c axes could be halved, giving $a = 5{\cdot}511$, $c = 5{\cdot}488$ Å. These are in very good agreement with our values. Finally, Yakel finds $LaVO_3$ cubic with a cell edge 7·842 Å. We would guess that this structure is orthorhombic with very nearly cubic dimensions, i.e. with $a \cong b \cong c/\sqrt{2} = 7{\cdot}842/\sqrt{2} = 5{\cdot}546$ Å. (It is very likely that a is slightly smaller than b, as in $LaFeO_3$.) It is seen that this fits the vanadite series (Table 1) rather well. The work of Wold & Ward (1954) on $LaCrO_3$ and $LaVO_3$ is mentioned in Yakel's paper. Wold & Ward reported these compounds as cubic with cell edges 3·90 and 3·91 Å respectively.

Keith & Roy (1954) prepared a large number of ceramics with the formulae of many of the compounds reported in this series of papers. There are several differences between the conclusions of these authors and those in this series of papers. The most important difference is the conclusion by Keith & Roy that there is justification for calling $YCrO_3$ a new type structure, the implication being that this is a more complicated structure than that of $LaFeO_3$, for example. Their powder pattern (Table 4 of their paper) for $YCrO_3$ compares favorably with that of our $YCrO_3$ (Table 1 of I), which has the same structure as $GdFeO_3$. The same is true for all the other compounds in the table except for $LaInO_3$, which we have not investigated (but see V). The pattern given for $3Y_2O_3.5Al_2O_3$ in that table is very much like our pattern for $YAlO_3$ (Table 1 of I).* There are some lines in the patterns of Keith & Roy which do not appear in ours, but our experience has led us to believe that there is more chance of impurity lines because of incomplete reaction in patterns from ceramics than from the crystals made by Remeika's method.

Recently a paper published by Bertaut & Forrat (1956) included some of the compounds described in this series of papers. The arrangement of the rare earth ions (involved in our series of papers) in order of increasing size as found by us is Gd^{3+}, Eu^{3+}, Sm^{3+}, Nd^{3+}, Pr^{3+}, La^{3+}, in agreement with that long established for the lanthanides. However, the order that would be obtained from the results of Bertaut & Forrat for the vanadites is Sm^{3+}, Pr^{3+}, Nd^{3+}, Gd^{3}, La^{3+}. The most important discrepancy is that involving $GdVO_3$.

In the orthochromite series, Bertaut & Forrat find the volume of the $PrCrO_3$ cell larger than that of $LaCrO_3$, which implies that Pr^{3+} is larger than La^{3+}. It appears that their a value for $PrCrO_3$ is too large: it should lie between the values for $NdCrO_3$ and $LaCrO_3$. Furthermore, it is quite improbable that $a = b$ in $LaCrO_3$ and $PrCrO_3$; it is also highly improbable that $a = b$ in $LaFeO_3$. In the films of our compounds, such reflection pairs as (240), (420) and (241), (421) are completely resolved (see Table 1 of I). A difference in size of lattice constants a and b in $LaFeO_3$ has also been ascertained by single-crystal Weissenberg photography. Also, we have found a compound $GdCrO_3$ which is isostructural with $GdFeO_3$.

The lattice constants of $GdFeO_3$, $SmFeO_3$ and $NdFeO_3$ reported by Bertaut & Forrat check ours very well and the agreement between their lattice constants of $PrFeO_3$ and $LaFeO_3$ and ours is satisfactory.

We would hesitate to separate these orthorhombic compounds into three groups as Bertaut & Forrat have done, because this only tends to complicate what now appears to be a rather simple system of closely related compounds.

From the paper of Bertaut & Forrat one might have the impression that in the orthorhombic compounds the A^{3+} ion positions have a zero x component. It has been shown that the position of Gd^{3+} in $GdFeO_3$, which is almost the most distorted of the structures, has a substantial x component. In III it was shown that in one of the least distorted structures, $La(Co_{0\cdot2}Mn_{0\cdot8})O_3$, the La^{3+} ion position has a non-zero x component, and presumably the positions of the A^{3+} ions in all of the orthorhombic compounds have a non-zero x component.

Conclusions

The compounds of formula ABO_3 with trivalent rare-earth A ions and trivalent B ions are mostly isostructural with $GdFeO_3$. The detailed structure analysis of $La(Co_{0\cdot2}Mn_{0\cdot8})O_3$ (III) confirms the $GdFeO_3$ structure and also shows that the oxygen ion positions do not change toward the ideal structure, as one might at first expect from examination of lattice constants;

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* Goldschmidt (1926) was correct in calling $YAlO_3$ perovskite-like.

rather, the oxygen ions are in positions which are probably more favorably disposed toward transition to the rhombohedral structure. This is corroborated by high-temperature studies which have linked the orthorhombic structure to the ideal through the rhombohedral structure. However, only a very few of the orthorhombic compounds may be expected actually to transform to the rhombohedral at any temperature. Also, very few of the rhombohedral crystals may be expected to transform to the cubic at any temperature.

Sufficient crystallographic data have now been obtained to permit an estimate to be made of the relative ionic radii in these compounds. This is done in the paper (V) (Geller, 1957) which follows.

The success of this study is in large measure a consequence of the method for preparing single crystals of these compounds evolved by J. P. Remeika (1956), who supplied all of the specimens used in this investigation with the exception of the vanadites prepared by E. Corenzwit by solid–solid reaction.

This work has profited greatly from discussions with M. A. Gilleo.

The author also wishes to thank P. D. Garn for the differential thermal analyses, V. B. Bala for his assistance with the experimental work, Miss D. P. Booth for carrying out the *d*-spacing calculations on the IBM machines, F. Barbieri for grinding the $LaGaO_3$ crystal for X-ray photography and W. Hartman for the spectroscopic analyses of several of the compounds.

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Crystallographic Studies of Perovskite-Like Compounds. V. Relative Ionic Sizes

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(*Received* 22 *August* 1956 *and in revised form* 8 *December* 1956)

Sets of relative radii are derived for the ions in the crystals investigated in the first four papers in this series. These sets of radii are compared with those of Goldschmidt, Pauling, and Templeton & Dauben.

Introduction

In the first four papers of this series,* crystallographic data have been presented for a large number of perovskite-like compounds (ABO_3) involving trivalent A and B ions. It is now possible to obtain from these data some idea of the relative sizes of the ions in these compounds. It may well be that these sizes are important with respect to the perovskite-like compounds only, but the possibility that they may be useful in other applications cannot now be excluded.

Discussion

In the last three decades, much discussion has been given perovskite-like compounds with respect to the tolerance factor (Goldschmidt, 1926*a*, *b*) which is defined as

$$(R_O+R_A) = \sqrt{2}.t(R_O+R_B)\ ,$$

where the R's are theoretical ionic radii. Wood (1951) has shown some of the difficulties which ensue with the use of particular sets of radii in the tolerance factor. Wood has also illustrated, by use of a structure-field, that certain of the compounds known to have perovskite-like structures have tolerance factors which fall well out of the range given by Goldschmidt. In the particular way in which Wood calculated the tolerance factors, most of the compounds considered to have perovskite-like structures fall within the required range. It thus would seem worth while to check the compounds which do not lie within the required range to determine whether they do indeed have a perov-

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* I: Geller & Wood, 1956; II: Geller & Bala, 1956; III: Gilleo, 1957; IV: Geller, 1957; see also Geller, 1956*a*.