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.

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

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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

$$(R_{\mathrm{O}}+R_A) = \sqrt{2}\,.\,t(R_{\mathrm{O}}+R_B)\,,$$

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*.

Table 1. *Relation of* $B^{3+}$–$O^{2-}$ *distances with* $Al^{3+}$–$O^{2-}$ *as standard obtained from the various* $A^{3+}$ *ion compounds*

(All values in Ångström units)

| $B^{3+}\backslash A^{3+}$ | Gd | Nd | Pr | La | Y | Average | From Pauling's values | Order from Pauling's values |
|---|---|---|---|---|---|---|---|---|
| Sc | 1·065 | 1·068 | 1·070 | 1·069 | 1·064 | 1·067 | 1·163 | 1 |
| Fe | 1·035 | 1·037 | 1·039 | 1·037 | 1·036 | 1·037 | 1·053 | 5 |
| V | 1·035 | 1·037 | 1·035 | 1·035* | — | 1·035 | 1·084 | 2 |
| Ga | — | 1·029 | 1·029 | 1·028 | — | 1·029 | 1·063 | 4 |
| Cr | 1·025 | 1·028 | 1·026 | 1·025 | 1·024 | 1·026 | 1·074 | 3 |
| Al | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 1·000 | 6 |

* From Yakel's paper (1955).

skite-like structure and whether the ionic sizes should be re-estimated.

From the investigations described in this series of papers, it is concluded that with regard to perovskite-like compounds it is quite necessary to re-estimate the radii of the trivalent *A* and *B* ions. It is true that particular sets of radii which include all ions (like those of Goldschmidt and Pauling) are very good for some quantitative and for more qualitative treatments, but it appears that a better way to determine radii which may be used to discuss a particular type (including pseudotypes) of system is to study many members of the system.* (This has recently been done for intermetallic compounds with the *β*-wolfram structure with rather fruitful results (Geller, 1956*b*).)

It may also be argued that in complex systems the necessity of having a formal table of effective radii is minimized because information obtained from examination of the data may be used to great advantage in making predictions concerning other members of the series. For example, one could already predict from Table 2 of I that the cells of the aluminates should be considerably less distorted than those of the corresponding orthoferrites and that the distortions of the corresponding orthochromites should be between those of the orthoferrites and the aluminates. This is readily seen from a comparison of the volumes as well as the pseudo-cell angles of the yttrium compounds. It was predicted that the pseudo-cell angle of $GdAlO_3$ would be less than 91·6°, for example; it turned out to be (II) 90·6°, and, in fact, there is a considerably larger difference in angle between the $Gd^{3+}$ and $Y^{3+}$ compounds than between the corresponding orthoferrites. A similar result was found for the corresponding orthochromites (see Tables 1 of I and IV.)

It is of importance to note that, even without attempting to establish a set of effective ionic radii, one may arrive at the size relationship among the ions from such data as are set down in Table 1 of IV. We see by inspection that the order of the ions in decreasing size is $Sc^{3+}$, $Fe^{3+}$, $Mn^{3+}$, $V^{3+}$, $Ga^{3+}$, $Cr^{3+}$, $Al^{3+}$.

Consider now the minimum average $B^{3}$–$O^{2-}$ distances. It is probable that the true average $B^{3+}$–$O^{2-}$ distance differs with different $A^{3+}$ ion in the way given by the numbers in Table 1 of IV (see also Tables 4 of I and 5 of II), so that the $B^{3+}$ ion (or, more generally, each ion) affects the size of the other ions.

Use of the minimum averages in the manner shown in Table 1 produces somewhat more illuminating results. In this table we have taken the $Al^{3+}$–$O^{2-}$ distance as standard and compared the other $B^{3+}$–$O^{2-}$ distances with it. The values obtained using Pauling's radii are also shown. Note the rather significant differences between the results of these investigations and those obtained from Pauling's radii:

(1) the $Sc^{3+}$–$O^{2-}$ is only 7% larger than the $Al^{3+}$–$O^{2-}$ distance;
(2) the $Fe^{3+}$ and $V^{3+}$ ions have very nearly the same size;
(3) the difference in order.

The minimum average $O^{2-}$–$O^{2-}$ distances in these compounds are equal to the corresponding $A^{3+}$–$O^{2-}$ distances. Only in the scandates are these distances

Table 2. C.N.(6) *ionic radii in the perovskite-like compounds compared with those of Pauling and Goldschmidt*

| Ion | From perovskite-like compounds | Pauling (*a*) | Goldschmidt (*b*) |
|---|---|---|---|
| $Y^{3+}$ | 0·773 Å (*c*) | 0·93 Å (0·98 Å) | 0·95 Å |
| $In^{3+}$ | 0·714 (*c*) | 0·81 (0·86) | 0·95 |
| $Sc^{3+}$ | 0·686 | 0·81 (0·86) | 0·83 |
| $Fe^{3+}$ | 0·628 | 0·60 (0·65) | 0·67 |
| $Mn^{3+}$ | 0·625 (*d*) | 0·62 (0·67) | — |
| $V^{3+}$ | 0·625 | 0·66 (0·71) | 0·75 |
| $Ga^{3+}$ | 0·613 | 0·62 (0·67) | 0·65 |
| $Ti^{3+}$ | 0·61 (*e*) | 0·69 (0·74) | 0·70 |
| $Cr^{3+}$ | 0·608 | 0·64 (0·69) | 0·70 |
| $Co^{3+}$ | 0·56 (*f*) | — | 0·65 |
| $Al^{3+}$ | 0·558 | 0·50 (0·55) | 0·55 |
| $O^{2-}$ | 1·346 | 1·40 (1·35) | 1·35 |

(*a*) Numbers in parentheses are values referred to $O^{2-}$ radius 1·35 Å.
(*b*) These are values given by Wyckoff (1951).
(c) See discussion.
(*d*) Obtained from $LaMnO_3$ in III.
(*e*) Obtained from $LaTiO_3$ (Kestigian & Ward, 1954).
(*f*) Obtained from $LaCoO_3$ (Askham, Fankuchen & Ward, 1950).

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* At present the calculation of corrections to be applied to Pauling's radii to obtain those derived directly from these compounds would appear to be very complicated.

Table 3. *Relation of* $A^{3+}$–$O^{2-}$ *distances with* $La^{3+}$–$O^{2-}$ *as standard*

(All values in Ångström units)

| | | | | | | | | $A^{3+}$–$O^{2-}$ | | Relative radii $A^{3+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $A^{3+}\backslash B^{3+}$ | Al | Cr | Ga | V* | Fe | Sc | Average | Average | Derived† | |
| Y | 0·9776 | 0·9767 | — | — | 0·9759 | 0·9728 | 0·9758 | 2·699 | 2·627 | 1·281 |
| Gd | 0·9836 | 0·9836 | — | 0·9841 | 0·9817 | 0·9797 | 0·9825 | 2·718 | 2·645 | 1·299 |
| Eu | 0·9847 | — | — | — | 0·9842 | — | 0·9845 | 2·723 | 2·650 | 1·304 |
| Sm | 0·9866 | 0·9883 | — | — | 0·9853 | — | 0·9876 | 2·729 | 2·656 | 1·310 |
| Nd | 0·9892 | 0·9920 | 0·9909 | 0·9917 | 0·9892 | 0·9888 | 0·9904 | 2·739 | 2·666 | 1·320 |
| Pr | 0·9925 | 0·9942 | 0·9938 | 0·9924 | 0·9939 | 0·9934 | 0·9940 | 2·749 | 2·676 | 1·330 |
| La | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 1·0000 | 2·766 | 2·692 | 1·346 |

* Using value obtained for $LaVO_3$ from Yakel's paper (1955).

† Based on ($La^{3+}$–$O^{2-}$) distance in cubic $LaAlO_3$ at 450° C.

Table 4. *Data on* $LaInO_3$ *and* $LaYO_3$ *modified from Padurow & Schusterius*

| | Lattice constants | | | | Pseudo-cell dimensions | | | Minimum average distances | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compound | $a$ (Å) | $b$ (Å) | $c$ (Å) | Volume/unit cell (Å$^3$) | $a(=c)$ (Å) | $b$ (Å) | $\beta$ (°) | $A^{3+}$–$A^{3+}$ (Å) | $A^{3+}$–$O^{2-}$ (Å) | $B^{3+}$–$O^{2-}$ (Å) |
| $LaInO_3$ | 5·701 | 5·898 | 8·198 | 275·7 | 4·101 | 4·099 | 91·9 | 4·100 | 2·899 | 2·050 |
| $LaYO_3$ | 5·868 | 6·071 | 8·438 | 300·6 | 4·222 | 4·219 | 91·9 | 4·220 | 2·984 | 2·110 |

as large as 2·80 Å, which, in the $O^{2-}$–$O^{2-}$ directions, would give an effective radius of 1·40 Å. This does not mean necessarily that in the scandates the effective radius of the $O^{2-}$ ion is 1·40 Å in the directions of the nearest $A^{3+}$ and $B^{3+}$ ions.

To obtain some idea of what the average sizes are like, let us take as standard, the distances in cubic $LaAlO_3$ at the transition: $La^{3+}$–$O^{2-}$(=$O^{2-}$–$O^{2-}$) = 2·692 Å; $Al^{3+}$–$O^{2-}$ = 1·904 Å. This would give 1·346 Å for the $O^{2-}$ ion radius and 0·558 Å for the $Al^{3+}$ ionic radius. Using the results shown in Table 1, we may derive radii of $B^{3+}$ ions relative to these. These relative radii are compared with the radii of Pauling and Goldschmidt in Table 2.

Considering now the $A^{3+}$–$O^{2-}$ distances, and using as a standard the $La^{3+}$–$O^{2-}$ distance, we make a survey similar to that for the $B^{3+}$–$O^{2-}$ distances. The results are shown in Table 3. If we take as standard the $La^{3+}$–$O^{2-}$ distance in cubic $LaAlO_3$ we shall probably have derived values which are too low on an absolute basis, but, because we desire merely to obtain some feeling about the size, the choice is a logical one. The relative average ionic radii so derived are given in the last column of Table 3. We may refer to these as effective C.N.(12) radii.

We see that the concept of ionic radii is useful mainly in a qualitative way. For the ideal simple cubic perovskites, the radius ratio may account for the established fact that the equilibrium distances between $A^{3+}$ and $O^{2-}$ ions is substantially affected by the $B^{3+}$ ions, and conversely the $B^{3+}$–$O^{2-}$ equilibrium distances are substantially affected by the $A^{3+}$ ions. The problem of accounting for the distortions from the ideal structure is much more complex, but it has been known for some time that relative effective ionic sizes play a most important role in determining the amount of distortion. This study bears this out in a most direct way, provided that, in thinking of degree of distortion, we consider the actual deviation of the atomic positions from the ideal (as discussed in IV).

Because the $Al^{3+}$ ion is the smallest of the trivalent ions, the aluminates are relatively the least distorted of the compounds. From a study of some of the transitions it may be concluded that the ratio of the sizes of the $Sm^{3+}$ ion to the $Al^{3+}$ ion is somewhat larger than that of $La^{3+}$ to $Ga^{3+}$ and the latter somewhat larger than that of $La^{3+}$ to $Fe^{3+}$.

The most recent set of radii given for rare earth ions are those of Templeton & Dauben (1954), who derived C.N.(6) radii mostly from the oxides. Unfortunately, the *relative* values of these radii differ considerably from those derived here. As in the comparison of the $B^{3+}$ ionic radii with those of Pauling and Goldschmidt, the range of values (Gd to La) is considerably narrower here: i.e. $Gd^{3+}$ has a radius 96·5% that of $La^{3+}$ whereas in the oxides it is 88·4% that of $La^{3+}$.

One of the most interesting recent papers on perovskite-like compounds is that of Padurow & Schusterius (1955), in which the compounds $LaInO_3$* and $LaYO_3$ are reported. These authors have indexed their photographs on a monoclinic cell. Included also are the patterns for $CaTiO_3$ and $CaZrO_3$, which are said to have the same structure as the $LaInO_3$ and $LaYO_3$. Except for a few very weak reflections it is possible to index these patterns in the same orthorhombic structure as the compounds in this series. Padurow & Schusterius have chosen an orthorhombic cell with twice the $a$ and $c$ cell edges (their $c$ would be our $b$, their $b$ our $c$) as we would like to think they have. We wish only to pursue the discussion relative to the $LaInO_3$ and $LaYO_3$. If we suppose that these are iso-

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* See also Keith & Roy (1954).

structural with $GdFeO_3$ we would obtain the results given in Table 4. If we follow the procedure as outlined above and shown in Tables 2 and 3, we find that the ratios of the $In^{3+}$–$O^{2-}$ and $Y^{3+}$–$O^{2-}$ distances to the $Al^{3+}$–$O^{2-}$ distance in $LaAlO_3$ are 1·082 and 1·113 respectively. With 1·904 Å as the standard $Al^{3+}$–$O^{2-}$ distance, and using 1·346 Å for $O^{2-}$, we obtain 0·714 and 0·773 Å for the relative radii of $In^{3+}$ and $Y^{3+}$ in these compounds. The values of C.N.(6) ionic radii given by Pauling (1945) are 0·81 and 0·93 Å respectively. Pauling gives the value 0·81 Å for $Sc^{3+}$ also, but in these compounds, the $In^{3+}$ ion is larger than the $Sc^{3+}$ ion (this would be so even if we took the cell given by Padurow & Schusterius).

The structures of $In_2O_3$ and $Y_2O_3$ are presumably the same as those for the rare earth oxides (cubic modification). Templeton & Dauben (1954) have calculated the average rare earth ion–oxygen ion distances in these compounds. They use the value $0{\cdot}21441a$ (where $a$ is the cell constant), as obtained from the work of Pauling & Shappell (1930). To obtain radii comparable with those of Templeton & Dauben, 1·38 Å was used as the $O^{2-}$ radius. In this way the average C.N.(6) radii of $In^{3+}$ and $Y^{3+}$ relative to those of Templeton & Dauben are 0·779 and 0·893 Å respectively.

The bonding in the rare earth oxides, both in the $La_2O_3$ and $Tl_2O_3$ types, is rather complicated, but the rare earth ions have essentially C.N.(6) in these compounds. The volumes per formula unit of $Y_2O_3$, $LaYO_3$ and $La_2O_3$ are 74·44, 75·14 and 81·87 Å$^3$ respectively. Note that the volume of $LaYO_3$ is only 1% larger than that of $Y_2O_3$, even though in $LaYO_3$ the $La^{3+}$ ion has C.N.(12). From this comparison alone, it is unlikely that the $La^{3+}$ ion 'shrinks', and of course it is evident that it gets effectively much larger when it is in the perovskite-like structure. Apparently, the average $Y^{3+}$–$O^{2-}$ distances are shorter in $LaYO_3$ than in $Y_2O_3$. This may be interpreted as a shrinking of the effective size of either the $Y^{3+}$ ion or the $O^{2-}$ ion, or both. Actually in $LaYO_3$ it is most likely that the $Y^{3+}$ ion size decreases although the distance of closest approach of two $O^{2-}$ ions gets quite small in many of the compounds.

## Conclusions

Sets of relative radii have been obtained for the ions in rare earth perovskite-like compounds. There are significant differences between these and sets of radii not so derived, and there does not appear to be a way at present of predicting such differences. This, therefore, supports the thesis that it is worth while studying series of compounds in this way for the purpose of obtaining direct knowledge of effective ionic (or atomic) sizes.

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